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SECTION IV
ORGANIC CHEMISTRY

VOL. VI

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SECTION IV — ORGANIC CHEMISTRY

CONTENTS

NEUERE ERGEBNISSE DER ERFORSCHUNG DER ZUSAMMENSETZUNG DER EIWEISS-STOFFE

Von Emil Abderhalden, Halle a./S.

Es sind vornehmlich zwei Probleme, die zur Zeit bei der Erforschung des Aufbaus der Proteine im Vordergrund des Interesses stehen. Einmal interessiert uns die Frage, ob wir schon alle Bausteine, d. h. alle Aminosaeuren kennen. Die Arbeiten von Osborne und Abderhalden haben gezeigt, dass die von Emil Fischer eingefuehrte Estermethode zur Isolierung der Monoaminosaeuren so grosse Verluste ergibt, dass bei einer Beruecksichtigung dieser fuer weitere Bausteine kaum noch Platz bleibt. Die Moeglichkeit, dass fuer bestimmte Proteine noch besondere Bausteine gefunden werden, bleibt jedoch offen. Der Befund, dass es gelingt, bei Hunden durch ein Gemisch von Aminosaeuren zu den Eiweissbedarf zu decken, spricht auch dafuer, dass uns zur Zeit keine biologisch unentbehrlichen Bausteine des Eiweisses unbekannt sind.

Ferner interessiert uns die Struktur der Proteine. Hier muss die partielle Hydrolyse, d. h. der stufenweise Abbau der Eiweissstoffe neue Einblicke geben. Es ist gelungen, eine ganze Anzahl von Polypeptiden beim stufenweisen Abbau von Proteinen zu erhalten. Sie sind alle mit den entsprechenden synthetisch dargestellten Verbindungen identifiziert worden. Es unterliegt somit keinem Zweifel mehr, dass in den Proteinen wenigstens ein Teil der Aminosaeuren saeureamidartig verknuepft ist. Zur Identifizierung isolierter Polypeptide besitzen wir verschiedene Methoden. Einmal koennen wir die Eigenschaften, vor allem das Drehungsvermoegen vergleichen. Ferner laesst sich durch Kuppelung mit Saeurechloriden entscheiden, welcher Baustein des Polypeptids die Aminogruppe traegt. Endlich koennen wir den Abbau eines solchen Produktes mit Huelfe von Fermenten studieren und das erhaltene Resultat mit Befunden vergleichen, die an synthetisch dargestellten Polypeptiden erhoben worden sind.

LOESUNG DES PROBLEMS DER SYNTHETISCHEN DARSTELLUNG DER NAHRUNGSSTOFFE

Von Emil Abderhalden, Halle a./S.

Der Versuch die in der Natur verkommenden und in letzter Linie auf die Pflanze zurueckfuehrbaren, kompliziert gebauten Nahrungsstoffe im Laboratorium synthetisch darzustellen, konnte bisher nur teilweise in Angriff genommen werden, weil unsere Kenntnisse ueber den Aufbau vieler Nahrungsstoffe noch sehr lueckenhaft sind. Das ganze Problem schien erst nach Jahren loesbar. Nun ist es durch das physiologische Experiment geglueckt, das Problem der kuenstlichen Darstellung der Nahrungsstoffe auf eine ganz neue Basis zu stellen. Es ist gelungen, Hunde mehrere Wochen ausschliesslich mit Salzen, Wasser, Sauerstoff, Traubenzucker, Fettsaeuren, Glycerin, Aminosaeuren zu ernaehren, ja das Koerpergewicht nahm erheblich zu. Da wir nun alle genannten organischen Stoffe synthetisch bereiten koennen, ist das Problem der kuenstlichen Gewinnung der Nahrungsstoffe als geloest zu betrachten. Es waere zwecklos in Laboratorium kompliziert zusammengesetzte Nahrungsstoffe zu bereiten, weil im Magendarmkanal doch bevor die Resorption einsetzt eine Spaltung in die einfachsten Bausteine erfolgt.

NEUERE FORTSCHRITTE AUF DEM GEBIETE DER POLYPEPTIDFORSCHUNG

VON EMIL ABDERHALDEN, HALLE a./S.

Nachdem ueber hundert Polypeptide nach den Methoden von Emil Fischer dargestellt worden sind, konzentriert sich jetzt das Interesse auf strukturisomere Polypeptide. Es ist die Frage zu entscheiden, in welchen Eigenschaften Polypeptide, die aus den gleichen Bausteinen aufgebaut sind, sich unterscheiden. Es sind alle Polypeptide aufgebaut worden, die die Aminosaeuren Glykokoll, d-Alanin und l-Leucin enthalten. Es ergaben sich folgende strukturisomere Verbindungen:

Glycyl-d-alanyl-l-leucin.
Glycyl-l-leucyl-d-alanin.
d-Alanyl-glycyl-l-leucin.
d-Alanyl-l-leucyl-glycin.
l-Leucyl-glycyl-d-alanin.
l-Leucyl-d-alanyl-glycin.

Sie zeigen alle ein verschiedenes Drehungsvermoegen und verschiedene Eigenschaften. Bedenkt man, dass am Aufbau der Proteine *ca* 16 verschiedene Aminosaeuren beteiligt sind, dann erkannt man ohne weiteres, dass allein schon durch die verschiedene Reihenfolge der einzelnen Bausteine eine gewaltige Zahl von strukturisomeren Proteinen moeglich sind. Das Studium des Verhaltens dieser Polypeptide gegenueber Fermenten verschiedener Herkunft wird die Moeglichkeit eroeffnen, derartige Polypeptide beim Abbau der Proteine abzufangen.

THE RENNIN COAGULATION OF MILK FROM A COLLOID-CHEMICAL STANDPOINT

By Jerome Alexander, M. Sc.

The object of this paper is to show that the rennin coagulation of milk is readily explainable upon the simple principles of colloid chemistry, and that this explanation is probably the correct one.

To make even a brief review of the principal literature on the subject of the rennin coagulation of milk would unduly extend the length of this paper; a résumé of the most important work is compressed into eleven pages of a monograph on the Chemistry of Milk, by Kastle and Roberts, published in Bulletin No. 56, U. S. Public Health and Marine Hospital Service, pp. 348 et seq.

It has been recently shown[1] that the casein in milk is an unstable, irreversible, or suspension colloid, which is stabilized or protected by the milk albumen. The significance of this colloidal protection may be seen at a glance from the following table, which gives the average composition of cow's milk and mother's milk (according to Koenig) and shows their behavior with rennin and acid:

Kind of Milk	Per cent Casein	Per cent Lactalbumen	Behavior with Acid and Rennin
Cow's Milk	3.02	0.53	Readily coagulates.
Woman's Milk . . .	1.03	1.26	Does not readily coagulate.
Ass's Milk	0.67	1.55	

When protective colloids (Schutz-Kolloide) such as gelatin or gum arabic are added to cow's milk, its casein is rendered more

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[1] J. Alexander: Zeitschr. f. Chem. u. Ind. der Kolloide, *4*, 86 (1909); ibid., *5*, 101 (1909); ibid., *6*, 197 (1910); Journal Soc. Chem. Industry, *28*, 280 (1909); Jour. Am. Chem. Soc., *32*, 680 (1910). Alexander and Bullowa: Arch. Pediat., *27*, 18 (1910); Jour. Am. Med. Assoc., *45*, 1196 (1910).

stable, and it becomes quite insensitive to acid and to rennin, thus resembling woman's milk. The coagulation of the casein of cow's milk and its non-coagulation after additional colloidal protection may be clearly demonstrated in the ultramicroscope.

My explanation of the mechanism of rennin coagulation is this: the enzyme acts upon and alters the lactalbumen, thus destroying its protective action, and probably at the same time producing or setting free substances which act as coagulants to the sensitized or unstabilized casein. In support of this explanation, I may mention a few experiments which were made with lactalbumen and casein, kindly prepared from cow's milk by Prof. William Gies. The method of preparation was as follows:

Equal volumes of cow's milk and saturated ammonium sulphate solution were mixed, and sodium chlorid added to saturation. The resulting precipitate of casein containing globulin (caseinogen and lactoglobulin), after being dialyzed, constituted the casein used in one experiment. The filtrate from the casein was saturated with ammonium sulphate and the precipitated lactalbumen dialyzed free from salts, and used in the following experiments:

Experiment No. 1.—Lactalbumen + $NaCl$ + $AgNO_3$ gave an almost clear colloidal solution of $AgCl$, which in the ultramicroscope exhibited very numerous and very active ultramicrons. This shows that lactalbumen acts as a protective colloid.

Experiment No. 2.—Lactalbumen was digested with pepsin and then $NaCl$ and $AgNO_3$ added. The resulting solution was much more opalescent than Experiment 1, and in the ultramicroscope exhibited large coagulated masses of ultramicrons. This shows that digested lactalbumen is not a protective colloid, but either permits or causes coagulation.

Corresponding experiments conducted with sodium phosphate and calcium chlorid gave similar results, while in the presence of pepsin solution these two reagents gave a coagulated precipitate.

Experiment No. 3.—Casein prepared as above described was much more readily coagulated by acid than the casein in cow's milk. This shows that a decrease in the protection of cow's casein renders it more sensitive to coagulation.

I have not yet investigated the products resulting from the action of rennin upon lactalbumen, but they probably consist of albumoses and peptones which, as Zunz has shown,[1] possess marked coagulative properties.

It is furthermore extremely probable that the disintegration of the lactalbumen sets free combined or absorbed calcium salts, which also exert a coagulative or "salting out" effect upon the unstable casein. This effect is all the more marked because the casein contains calcium. In fact, according to Ringer[2] fresh milk is coagulated upon warming with small quantities of calcium salts.

Thus, if we regard the rennin coagulation of milk as a case of the destruction of colloidal protection with the probable simultaneous production of coagulating substances, its mysterious features vanish, together with such uncertain terms as "caseinogen" and "paracasein," and we recognize the curd as a casein gel containing absorbed substances in varying proportion.

I take this occasion to express my thanks to Dr. Jesse G. M. Bullowa, who assisted me with the experiments and the discussion of their results.

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[1] See Zsigmond, Colloids and the Ultramicroscope, 83; E. Zunz, Bull. Soc. Roy. des sciences med. et nat., June 11, 1906.

[2] Ringer, J. of Physiol., *2*, 464–477 (1890).

AN ELECTRIC STILL ADAPTED FOR DIFFICULT DISTILLATIONS

Presented by Permission of the Director of the U. S. Bureau of Mines, Irving C. Allen

U. S. Bureau of Mines, Pittsburgh, Pa.

The process of separating two or more volatile liquids possessing different boiling points by distillation was one of the first processes employed in the early days of chemistry. With uncomplex mixtures it is comparatively simple. In early attempts at distillation the volatile substances were heated in earthen bottles over wood or charcoal fires; to-day they are heated in metal or glass retorts over gas flames.

The modern glass distilling flask heated with a Bunsen flame is too well known to need description here, but connected with its use are many difficulties that often are not fully appreciated. The continual wavering of the flame, even when it is most carefully screened from air currents, and the variations of the gas pressure subject the retort to an uneven and intermittent heating. Such heating causes irregularity in the rate of distillation, and for this reason duplicate distillations do not yield distillates that are alike in quantity and quality. Also, strains in the glass are produced by this uneven heating, and the glass often cracks. With inflammable liquids this is a serious danger. With easily decomposable materials local superheating causes decomposition. Again, the upper parts of the flask are not directly heated, and these chill the vapors and cause them to drip back, thus retarding greatly the progress of the distillation.

In the distillation of petroleum, for instance, one has to do with a material composed of a great number of bodies, or rather a number of series of bodies that range from the lightest petroleum ethers to solid paraffins and asphaltums and form a group the adjacent members of which so closely resemble one another in their physical and chemical properties that absolute differentiation is wellnigh impossible with the present methods of procedure. Close adjustment and control of temperature is the prime requisite in effecting the separation of these important series.

Dissatisfaction with the ordinary method of distillation led the authors to develop a still heated externally by electricity; this apparatus has given such satisfactory results that a description will be of value, it is believed, to those having to do with laboratory stills and similar heating devices.

DESCRIPTION OF STILL

The Heater

The heater here described was first furnished to the writers by Dr. David T. Day of the United States Geological Survey, and has been used by him in the petroleum laboratory of the Survey at Washington, D. C. The pattern now used by the writers has been developed from his spherical pattern, and consists essentially of two pear-shaped halves of heat-resisting materials inclosing and closely fitting the retort or distilling flask. The halves hold on their inner or concave surfaces a metal resistance wire, wound back and forth (Pl. II) for conducting an electric current. The electrically heated wire warms the flask and its contents, and boiling proceeds quietly, uniformly, and most satisfactorily.

Pl. I shows the still in its developed form as used in the petroleum laboratory of the Bureau of Mines.

Protection of Still Neck

The heaters are wired, that is, the retorts are actually heated, throughout the entire length of the neck; they thus differ from the Day heaters, which are heated only to the base of the neck and have the neck jacketed. The retorts are heated throughout that there may be no cooling or dephlegmatory action in the still neck. If a naked neck is exposed to the variable air currents of the laboratory, chilling effects are bound to result, consequently there will be variable condensation in the neck and resultant, variations in the distillates.

The obtaining of uniform products in the distillation of petroleums depends not so much on rigid adherence to the exact dimensions of the retort,[1] and the length and declination of the condenser, though these are important, as on obtaining absolute control of the heating itself. The condenser should be no longer than is necessary for a perfect cooling; a total length of 60 cm. should suffice.

With the lighter fractions of petroleums, such as naphthas and gasolines, or with mixtures of alcohols, ethers, or volatile substances in general, a fractionation with a proper dephlegmator gives a better separation than a fractionation without such a dephlegmator; particularly if a long evaporator neck [2] is used and is kept at a definite temperature by means of a water jacket or by means of an electrically heated jacket, as described on the following pages.

With the heavier oils, however, the continuous heating that is necessary when a dephlegmator is used causes a degradation in the quality of the distillates. In distilling such bodies as petroleums consisting of a solution of gasolines, kerosenes, lubricants, waxes, and solid asphaltums, a dephlegmator makes a clean-cut separation of the naphthas, but delays the distillation of the kerosenes and absolutely prevents the fractionation of the heavier lubricants.

Therefore, to insure uniformity of results, to remove all oils that boil below their point of decomposition, and to compare various oils under like methods of treatment, control of the temperature in the still and the still neck must be maintained in some manner.

The thermal influences of variable air currents on the still, particularly if it is not jacketed (the gas-heated retorts in most laboratories are usually without jackets), play an important rôle, but are in a measure overcome by incasing the entire retort with the heater.

Moreover, the lag of the distillates in the condenser, particularly noticeable in the case of heavier fractions, must be minimized

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[1] Redwood, Boverton, Engler's Fractionating System: Petroleum and its Products, *2*, 534–536 (1906). Holde, Untersuchung der Mineralole und Fette, 20–22 (1909).

[2] Young, Sydney, Fractional Distillations, 166–168 (1903).

by setting the cooler in a nearly vertical position and heating the cooling water as the distillates become viscous and move more sluggishly.

It is therefore considered advisable to maintain control of the thermal conditions in the retort and the still neck by warming the neck with the retort itself. Such warming is necessary with the heavier oils in order that the last portion of the vapors may be driven over and not be allowed to lag in the hot retort under conditions that cause superheating and consequent decomposition.

A simple jacketing of the still neck without special heating gives good results in the case of the lighter fractions—the naphthas and the lighter burning oils—but does not suffice for the heavy lubricating fractions. This fact is made evident by comparing the temperature curves in Fig. 3 with those in Fig. 10.

As there is little or no lag of the vapors in the still neck—this being of the same temperature throughout and the vapors being driven onward by the continuous and steady generation of more vapors from below—they cannot be materially superheated while passing through the neck. Their clean odor, the absence of color, and the non-appearance of carbonaceous deposits at the base of the still neck, at least until the higher temperatures are reached, lead to this conclusion.

CONSTRUCTION OF THE STILL

The Heater

The body of the heater is composed of 100 parts by weight of powdered magnesia, 100 parts by weight of powdered silica, 40 parts by weight of finely shredded asbestos, and 10 parts by weight of powdered sodium silicate, thoroughly mixed together, dry, and made into a paste with a 10% aqueous solution of magnesium chlorid. The use of this paste was suggested by Mr. A. V. Bleininger, formerly ceramics chemist of the United States Geological Survey. The paste may be molded into any form desired, and after setting over night it becomes hard and firm enough to endure gentle handling.

To prevent cracking and warping during the subsequent drying, the heater is warmed in an oven at about 50° C. for 48 hours, after which it is heated at 200° C. for several hours to expel the last traces of moisture. The heater is then hard and sufficiently strong for most laboratory purposes. It will endure heating, without corrosion of the wire and without injury to the insulating material, to the temperature at which the glass of the retort begins to soften, the highest temperature to which the heaters in the Pittsburgh laboratory have as yet been subjected.

This heater may be made in any desired form, for heating ovens, water baths, hot plates, viscosimeter jackets, etc., and is most admirably adapted for incasing a still neck or dephlegmator to maintain any desired temperature within, from room temperature up to the temperatures at which heavy oils decompose and carbonize.

Wiring the Heater

The manner of wiring the heater for a distilling flask is most important. Wrapping the wires equidistant from one another from the bottom of the flask up to the top of the neck develops too great a heat in the neck and in consequence causes superheating of the heavier oil vapors (Fig. 5).

Wrapping the wires from the bottom of the flask up to the base of the neck results in a dephlegmatory action in the neck that cannot be controlled (Fig. 4).

After repeated trials, shown graphically in Figs. 4 to 9, the method of wiring shown in Fig. 10 has been developed. This method gives a nearly uniform temperature from the bottom of the boiling liquid to the side tube carrying off the vapors—a temperature which is always under the control of the operator.

Mold for Heater

The forms for a distilling flask may conveniently be made as follows:

Turn from a block of wood a model the size and form of the distilling flask, with the bulb and neck in one piece, and saw the model into halves from top to bottom. Hollow out the bulb and neck to form a shallow dipper, making the cavity about 1 cm. deep, and leaving the rim about 3 mm. thick. Drill holes the size of a small wire brad 1 cm. apart and 3 mm. below the edge of the rim of the dipper and along the handle or neck as far as it is desired to have the heating wire. Insert brads through these holes from the inside and allow the points to project about 3 mm., thus forming a comb of brad points around the outside of the dipper near the edge (Pl. II, *a*).

Then, after greasing well the convex surface of the mold to prevent the paste from sticking, wrap the heating wire back and forth, the wires being 1 cm. distant from one another, across the convex surface of the dipper between these points, in the manner shown in Pl. II, *a*, and Fig. 10, tying the wire in place with asbestos cord and making its two ends fast to binding posts projecting at convenient positions. Lay the wired form, convex side up, on a smooth board covered with a sheet of paper and apply freshly prepared paste to the desired thickness, about 2 cm.

Allow the paste to harden over night. Remove the brads from the inside of the mold. The heater will then be released and ready for the final drying described above. Do not pass a current through the wire until the heater has been thoroughly dried, else rapid corrosion of the wire will result.

A ⅛-liter heater requires about 500 gm. of material and 3.5 meters of wire; a ¼-liter heater about 1000 gm. of material and 5.5 meters of wire, and a 1-liter heater about 2000 gm. of material and 11 meters of wire.

The completed heater is shown at *b* in Pl. II.

Wire

Any high-resistance wire may be used. In the laboratory of the Bureau of Mines, a No. 24 (B. & S.) nickel-chrome wire (the alloy contains about 60% nickel, 18% chromium, and 22% iron) insulated with asbestos is used. This wire has a resistance of about 4.66 ohms per meter at 20° C.[1]

TEMPERATURE CONTROL

The current, and therefore the temperature, are most admirably controlled by a simple water rheostat. Such a rheostat hardly needs a description, as its principle is so well known. The one

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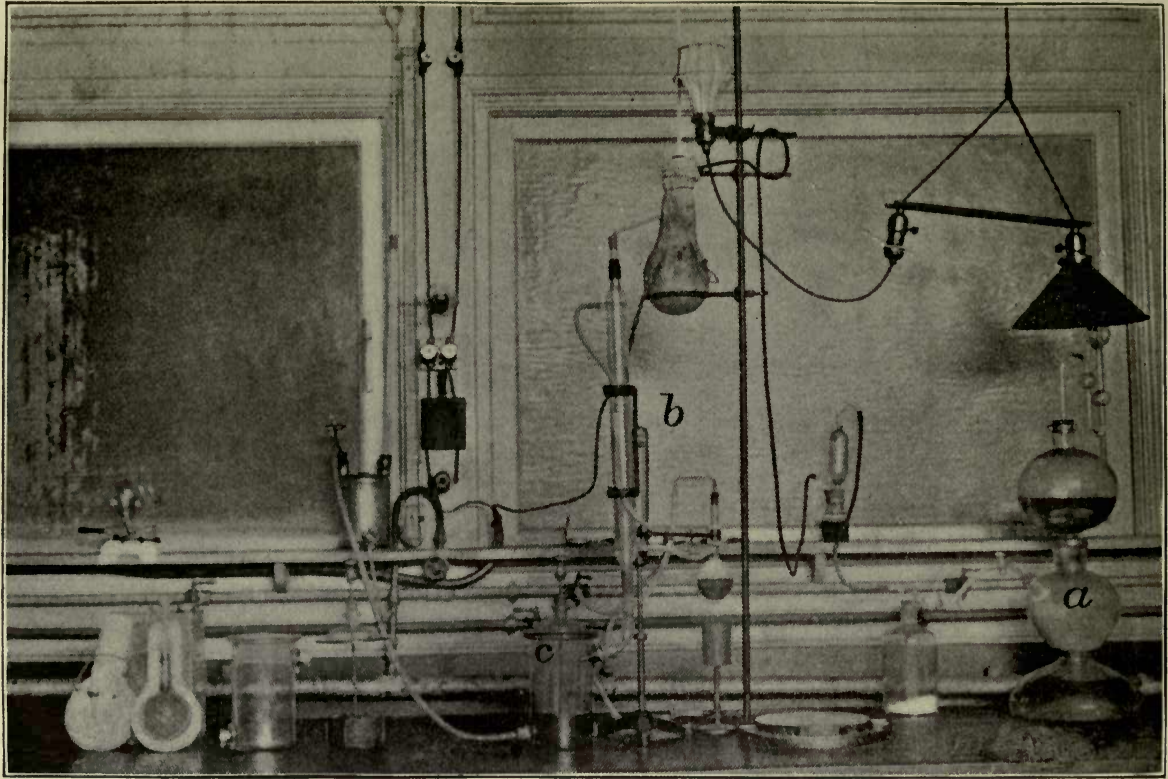
[1] This wire may be obtained from the Driver-Harris Wire Co., Newark, N. J.



Electric Still and Accessories.
(*a*) Apparatus for Generating CO_2. (*b*) Liebig Condenser with Water Heater. (*c*) Bruehl Receiver.

used consists simply of a 10-liter stone jar containing slightly saline water, a metal (preferably a carbon) plate at the bottom of the jar, and a triangular carbon plate that dips into the water and is suspended from a windlass. The plate at the bottom of the jar is connected with one side of the electric circuit in series with the heater, and the triangular plate is connected with the other side of the circuit (Fig. 1). By turning the windlass the upper plate may be lowered into the water and the current increased. The slightest turn, the lowering of the plate 1 mm. into the water, effects a change in the temperature of the heater. With a steady current, any temperature between the temperature of the room and the coking temperature of asphaltum is readily maintained throughout any reasonable time of distillation. Similarly, a digestion at any desired temperature may be carried on throughout a period of several hours.

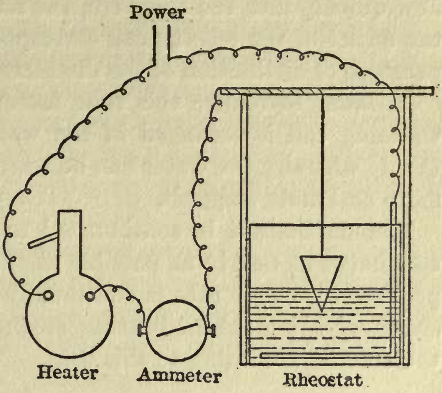


Fig. 1. — Arrangement of Electric Circuit for Heater.

Either alternating or direct current may be used, though the former is less destructive to the rheostat plates. In either case, however, the current must be carefully regulated by means of an ammeter during the entire distillation.

The current required ranges from a very low amperage, at the beginning of distillation, to 3 or 3.5 amperes at 220 volts, as the temperature approaches 325° C.

METHOD OF DISTILLING

Position of Condenser—Use of Warming Coil

The manner of petroleum distillation adopted in the Pittsburgh laboratory differs from the Engler method[1] in that the con-

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[1] Redwood, Boverton, Petroleum and its Products, *2*, 534–536 (1906). Holde, Untersuchung der Mineralole und Fette, 20–22 (1909).

denser is placed in a nearly vertical position instead of at the usual angle of 75° with the vertical. This is done in order that the distillates condensing in the cooler may flow into the receivers in the shortest possible time. Care must be exercised to prevent the direct falling of the drops to the lower end of the condenser, or the spattering will cause loss. When the condensed vapors flow quickly into the receivers, the reading of the thermometer at the outlet of the retort neck corresponds more nearly to the temperature of distillation of the distillate as collected in the receivers.

In order to reduce this time factor or lag in the condenser, a warming coil is arranged in the water system of the condenser (Pl. I) whereby the water can be warmed as the distillates become more and more sluggish.

The distillation is continuous[1] and not intermittent[2] and is conducted as nearly as possible at the rate of 1 drop of distillate per second. This rate is continually controlled by observing the swing of a pendulum beating seconds, and carefully regulating the current according to this drip.

Arrangement of Receivers

By arranging a Bruehl receiver with 10 or more receiving tubes, a fractionation of any ordinary petroleum may be carried on under atmospheric pressure up to the desired temperature, say 325° C., that is, nearly up to that temperature at which the petroleum begins to decompose, thus removing the naphthas and burning oils. Then, by simply replacing the receivers by empty ones (the temperature must be dropped to 125° C. in order to subject the oil to vacuum distillation), up to near the decomposing point of the petroleum residues, thereby removing the lubricating oils. The distillate cuts are made at each increment of 25° C. With an asphaltum oil this procedure gives 15 or 20 fractions and leaves a dry, brittle asphaltum residue without causing undue decomposing of the distillates or carbonization of the residue. It is to be noted that before the distillation of the lubricating oils under

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[1] Ubbelohde, L., Fixation de la limite d'ebullition du pétrole: Moniteur du pétrole Roumain, 279–283 (March 10, 1908).

[2] Redwood, Boverton, Petroleum and its Products, *2*, 534–536 (1906). Holde, Untersuchung der Mineralole und Fette, 20–22 (1909).

vacuum begins, the receivers containing the naphthas and burning oils should be removed, else a considerable percentage of these fractions will be volatilized and lost. Also in distilling light oils the receivers should be packed in ice to prevent volatilization of the lighter portions of the oils during the distillation.

Minor Details

In order that a high vacuum may be maintained successfully, it is advisable to lute all joints with a thin paste of glycerin and litharge, which rapidly hardens and forms a strong air-tight seal. Very effective litharge, canary yellow in color, is readily prepared by heating finely pulverized (200-mesh) commercial litharge or, better, chemically pure lead carbonate, in an electric furnace at 600° C. for 45 minutes.

Great care must be exercised in obs ervingthe barometric and the vacuum pressures during the distillations, the vacuum should be maintained as near a constant as possible, and corrections should be made for the boiling point[1] if one would duplicate his work.

By making use of a good "evaporator neck" either ice cooled or electrically heated, according to the temperature desired, an elaborate refractionation of any desired distillate may be accomplished, and any petroleum may be readily separated not only into its technologic components, but also into bodies having fairly definite boiling points.

The rapid removal of the distillate oils from the asphaltum residue is thought to be advisable because the latter is of variable and unstable composition, and continuous heating degrades the quality of the distillates and injures the properties of the asphaltum itself.

All distillations are made by weight, the flask and receivers being weighed empty and with contents. This procedure is more convenient and more accurate than measuring by volume.

Accuracy of Distillations

The heaters described are used either for the lightest gasolines or for semi-solid bitumens. As an example of the readiness with which difficult distillations can be conducted with the above still,

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[1] Young, Fractional Distillation, 14–16 (1903).

there has been distilled without difficulty an emulsified crude petroleum, an analysis of which gave the following results:

	Per cent
Water	33.0
Distillable oils, atmospheric pressure	9.4
Distillable oils, vacuum pressure of 18 mm. mercury	25.8
Asphaltum, brittle at room temperatures	29.4
Sand, etc.	1.0
Total distillation losses	1.4
	100.0

Again, a petroleum fractionation made in duplicate by means of this still gave the following results:

	I	II
	Per cent	Per cent
Air fractions (747 mm. pressure):		
175° to 200° C.	0.9	0.9
200° to 225° C.	14.5	14.1
225° to 250° C.	9.0	9.4
250° to 275° C.	7.6	7.5
275° to 300° C.	7.6	7.6
300° to 325° C.	8.2	8.1
Total	47.8	47.6
Vacuum fractions (31 mm. pressure):		
200° to 225° C.	2.9	3.0
225° to 250° C.	4.2	4.0
250° to 275° C.	4.3	4.6
275° to 300° C.	5.3	4.8
300° to 325° C.	6.3	7.0
Total	23.0	23.4
Residue	28.0	27.8
Distilling loss	1.2	1.2
Total residue and losses	29.2	29.0
	100.0	100.0

Prevention of "Bumping"

In the internally heated apparatus described by Beckmann[1] in his account of his boiling-point determinations there is mention of "bumping" when he was boiling anilin (boiling point 184° C. at 760 mm.). In the above externally heated still there is used in this laboratory, as in many other laboratories, a "boiling stone" of porous porcelain (or of a pumice stone for the lighter oils) weighing about 0.5 gm., and no trouble from bumping is experienced even with heavy oils that boil at temperatures as high as 325° C. under a vacuum of 20 mm. mercury pressure.

Richards and Matthews, in describing their internally heated still, remark:[2]

"In brief, this note (description) shows that while distillation by means of a wire heated electrically effects a somewhat better separation than the ordinary method and causes much less superheating in the liquid, the gain in efficiency of separation is not always as great as had been at first inferred from the great constancy of boiling point observed in a special series of cases."

This result is to be expected, as conditions are similar to those of the ordinary method: Sharp local internal heating with the small wire coil, as compared with sharp local external heating with the Bunsen burner.

In the internally heated systems of Beckmann, Richards and Matthews, and Biglow,[3] only nonelectrolytic materials can be heated. As the authors state regarding them:

"The short circuiting through the liquid causes slight decomposition and this method is not applicable to liquids of this (the electrolytic) type."

The internal coil must be wholly immersed in the liquid, else there will be injury to the wire by overheating, with consequent decomposition of the oil, so that distillation to dryness of even low boiling liquids is not practicable.

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[1] Beckmann, E., Zeitschr. anorg. Chem., No. 51, 100 (1906). Zeitschr. physik. Chem., No. 63, 177–215 (1908); No. 64, 506 (1908).

[2] Richards, T. W., and Matthews, J. H., Proc. Am. Acad. Arts and Sci., 521–524 (June, 1908). Zeitschr. physik. Chem., No. 64, 120 (1908). Jour. Am. Chem. Soc., No. 30, 1282–1284 (1908); 1200–1202 (Nov., 1909).

[3] Biglow, S. L., Am. Chem. Jour., No. 22, 280–287 (1899).

The internal coil partially prevents "bumping," but a fresh "boiling stone" accomplishes a like result. The boiling stone must be porous and must be fresh. If ebullition once ceases, the boiling stone seems to become less effective. Hence it is advisable, when practicable, to put a fresh unused boiling stone in the cooled liquid before again heating the liquid to boiling.

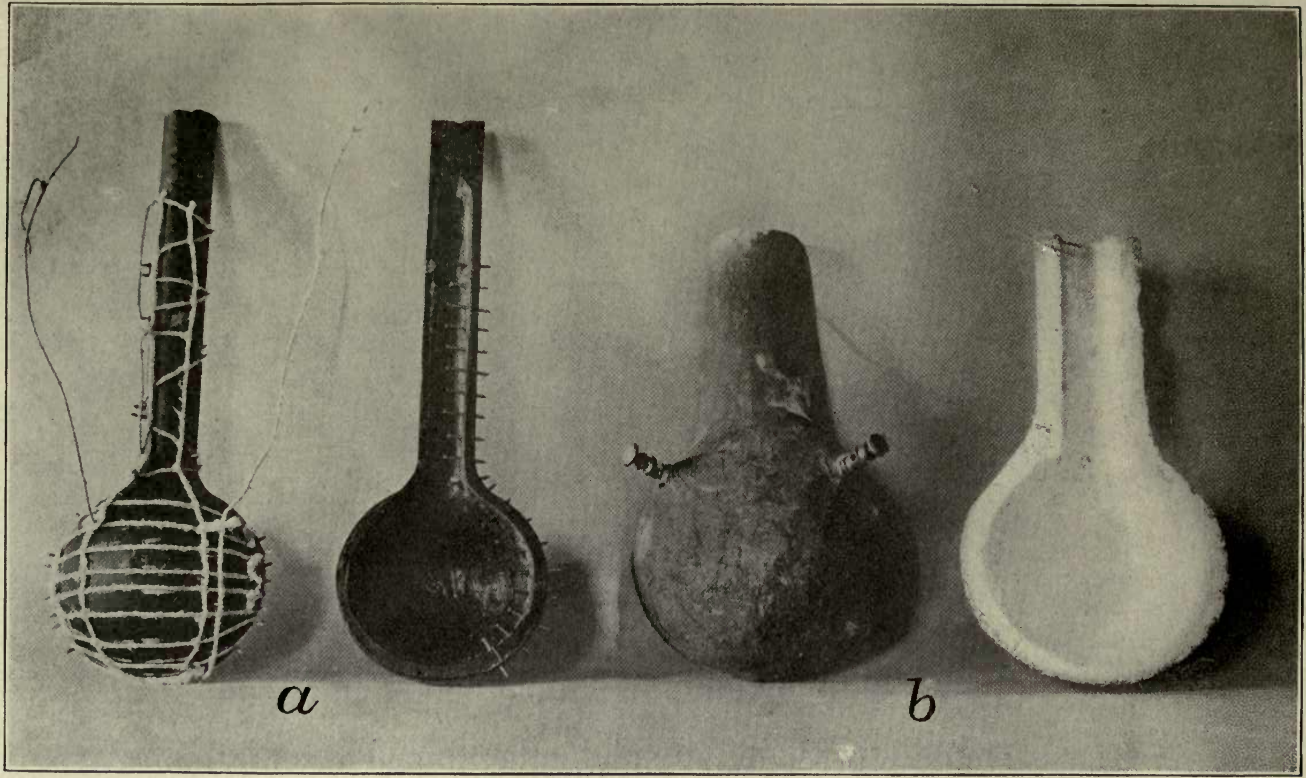
The bumping is caused, the authors believe, primarily by uneven and irregular heating. Once bubbling has started, if it does not cease by reason of varying and disturbing external heat conditions, always to be considered in connection with an exposed or a gas-heated flask, or by reason of a diminution of the vacuum when one is used, the boiling will continue quietly. With the residual heavy tars and asphaltums, the internal coils are a source of annoyance in cleaning the apparatus.

When oils contain emulsified water, it is advisable during the early stages of the distillation with all forms of stills to slowly pass a dry inert gas, such as CO_2, through the still contents, by means of a capillary tube extending nearly to the bottom of the distilling flask, until the water is entirely removed. In such case it is difficult to insert the two internal conductors, a capillary tube and a thermometer through one stopper in the narrow neck of the ordinary distilling flask. To fuse the conductors through the bottom of the flask, though possible, is difficult and hardly practicable for general laboratory usage.

In short, the externally heated still described above is adapted to most, if not all, classes of laboratory work. In modified form it may be used for a great variety of heating devices. The authors recommend it to those interested.

RELATION OF MANNER OF WIRING TO TEMPERATURES OBTAINED

The temperature curves shown in Figs. 1 to 10 were platted from simultaneous readings, at five-minute intervals during a distillation at the rate of 1 drop per second, of three thermometers placed with their bulbs: (1) Immersed in the boiling liquid; (2) at the base of the neck; and (3) at the point of exit of the vapors. The curves demonstrate the necessity of proper wiring.



Electric Heater and Mold.
(*a*) Mold, After and Before Wiring. (*b*) Completed Heater.

Figs. 2 and 3 show that when a still is heated with a Bunsen-burner gas flame, as in the ordinary method of distillation, the temperature of the vapors at the point of exit is some 40° C. cooler than the temperature of the boiling liquid.

Fig. 4, in which the distilling flask is electrically heated and wired to the base only of the neck, shows a similar condition, the vapors at the point of exit being about 30° C. cooler than the temperature of the boiling liquid.

Fig. 5, in which the flask and neck are incased completely and uniformly within the heating wires, shows a condition entirely different from that previously shown; the temperature of the vapors at the point of exit is some 70° C. hotter than the temperature of the boiling liquid.

Figs. 6 and 7, by a modification of the wiring of the neck, show a temperature of the vapors at the point of exit about 30° C. and 15° C., respectively, higher than the temperature of the boiling liquid.

Figs. 8 and 9, with a further modification in the manner of wiring, show the temperature curves approaching and crossing one another.

Fig. 10, in which the form of wiring is the most nearly perfect yet devised, shows that the temperatures of the vapors at the point of exit during the early part of the distillation are only about 3° C. higher than the temperature of the boiling liquid; these curves intersect during the middle part of the distillation and re-intersect near the end of the distillation. This manner of wiring probably cannot be improved, for the characteristics of the different oils themselves would mask any differences due to further slight modification in wiring.

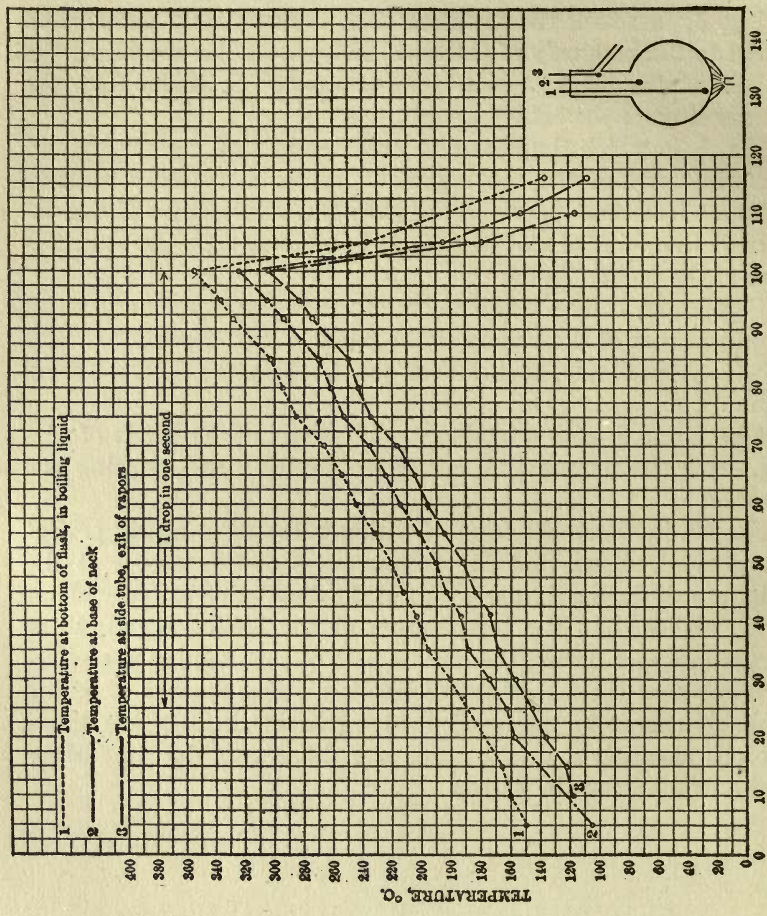


FIGURE 2.—Temperatures in still heated by Bunsen burner.

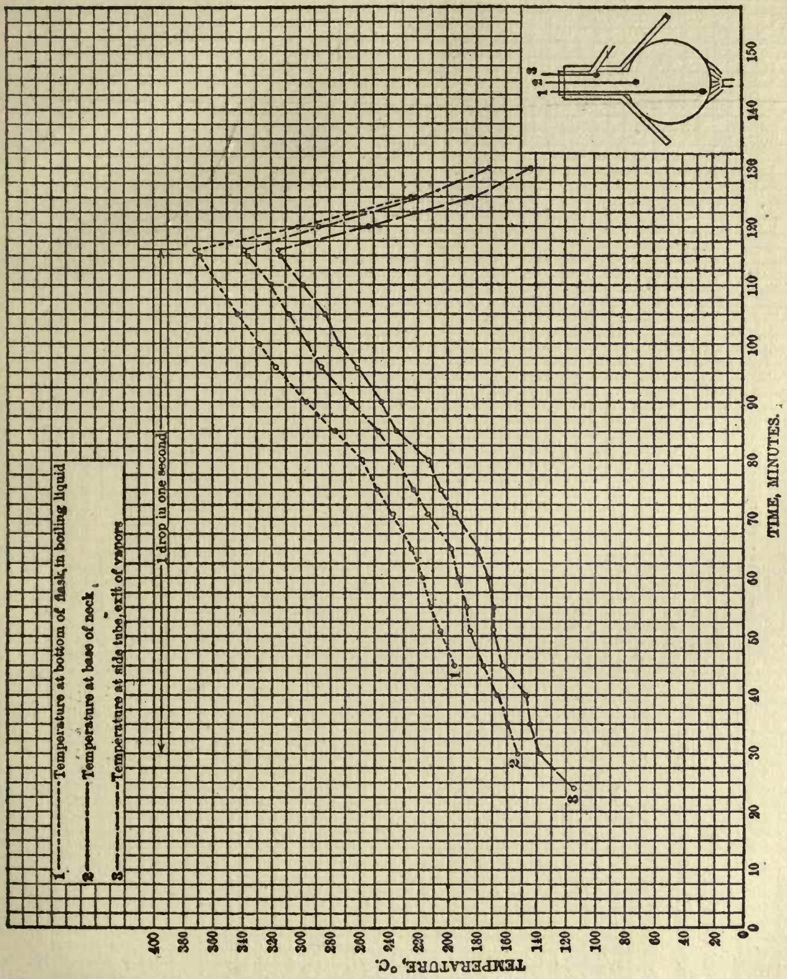


FIGURE 3.—Temperatures in still heated by Bunsen burner, still neck jacketed.

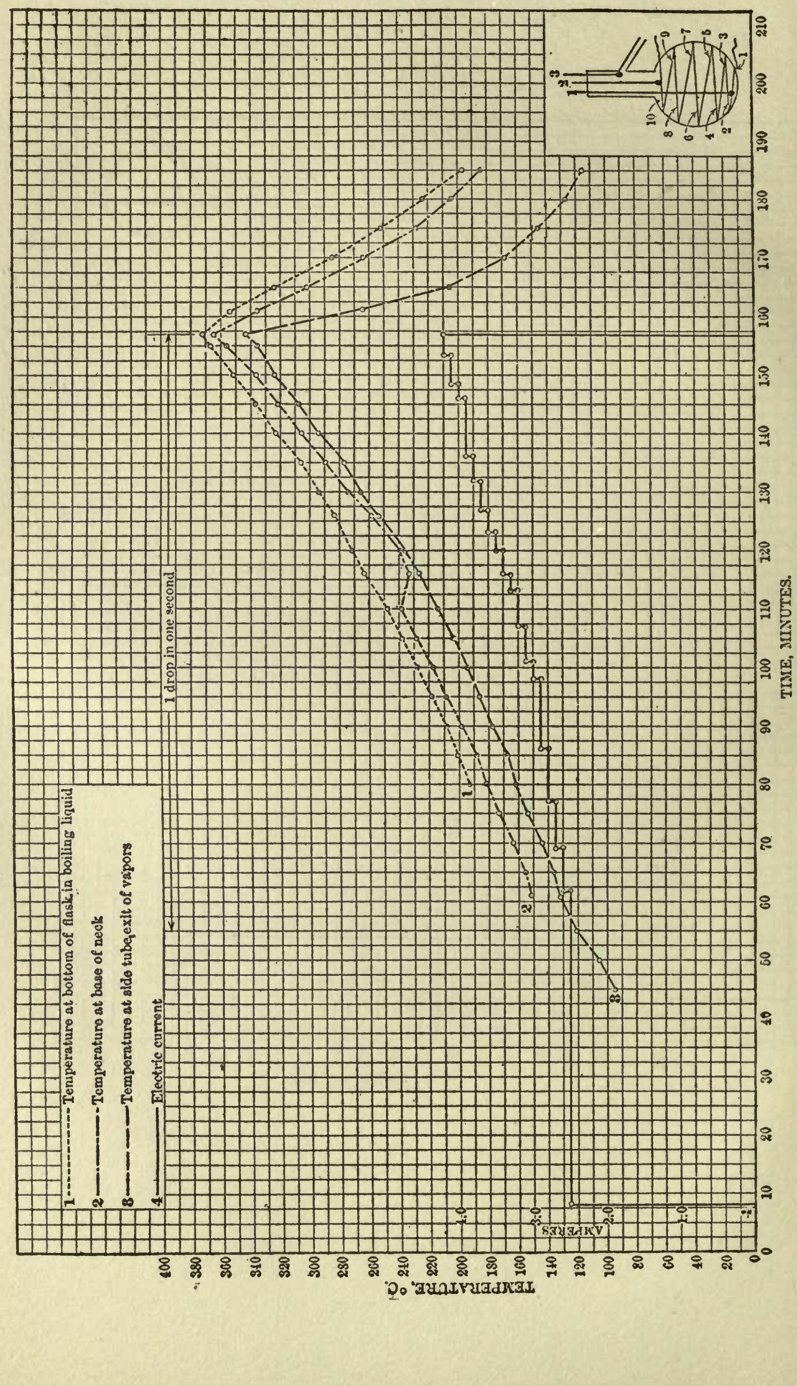


FIGURE 4.—Temperatures in electrically heated still, with still neck not heated.

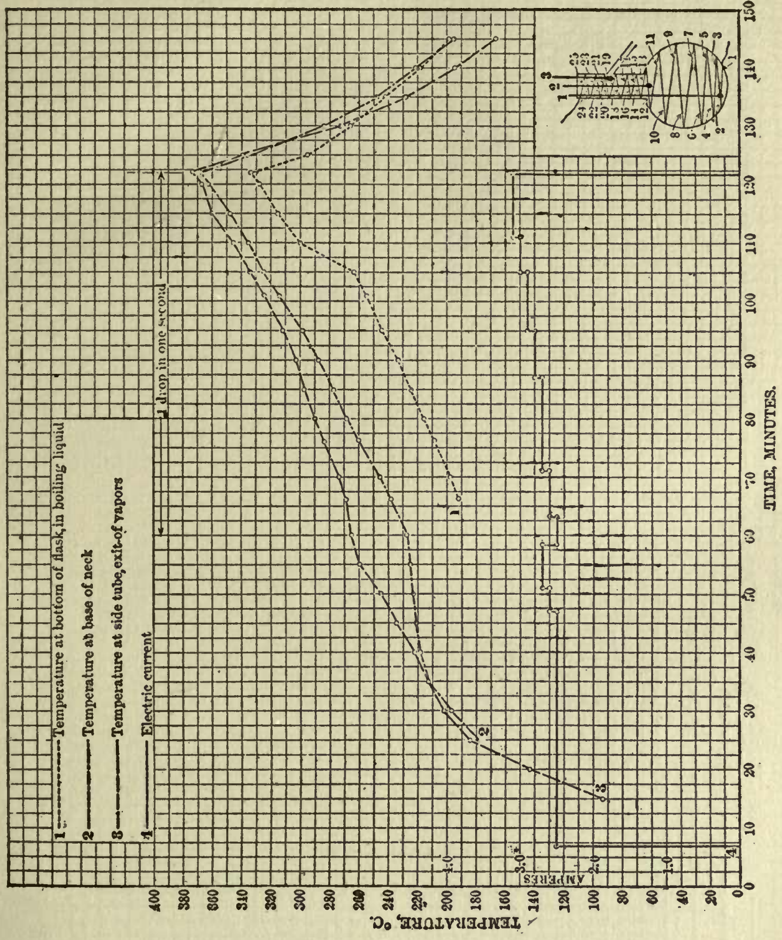


FIGURE 5.—Temperatures in electrically heated still, with still neck heated.

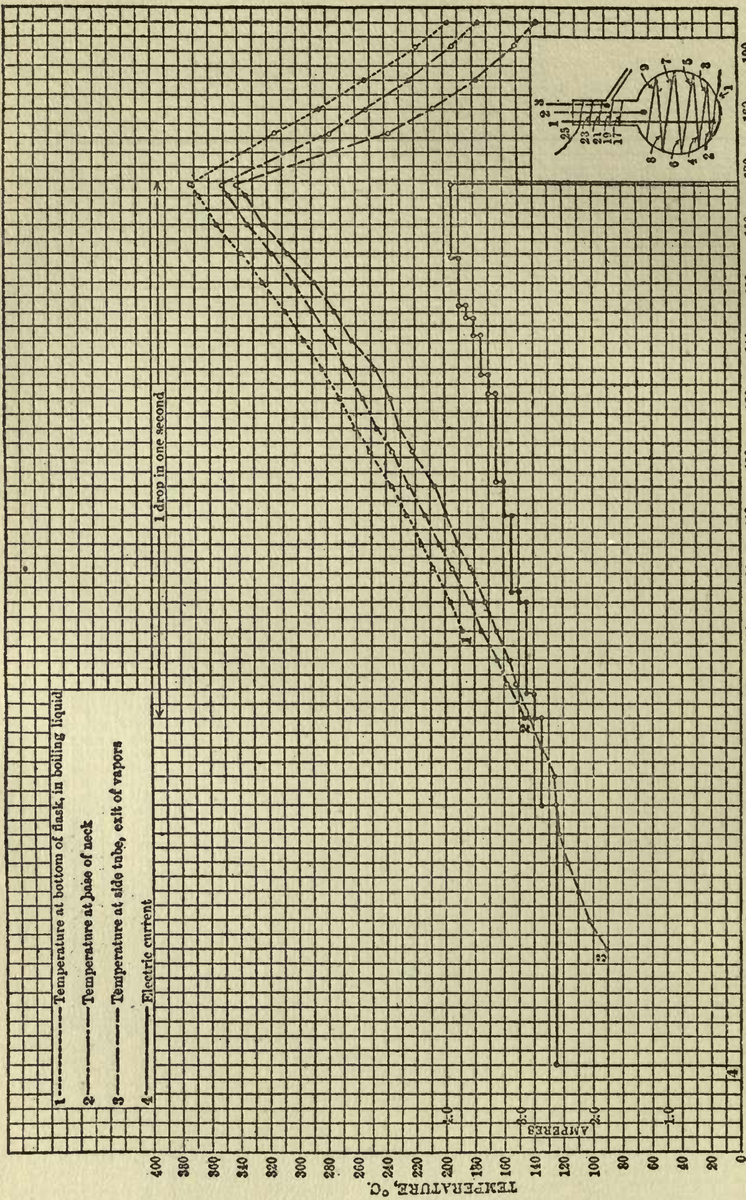


FIGURE 6.—Temperatures in electrically heated still, with another wiring of heater.

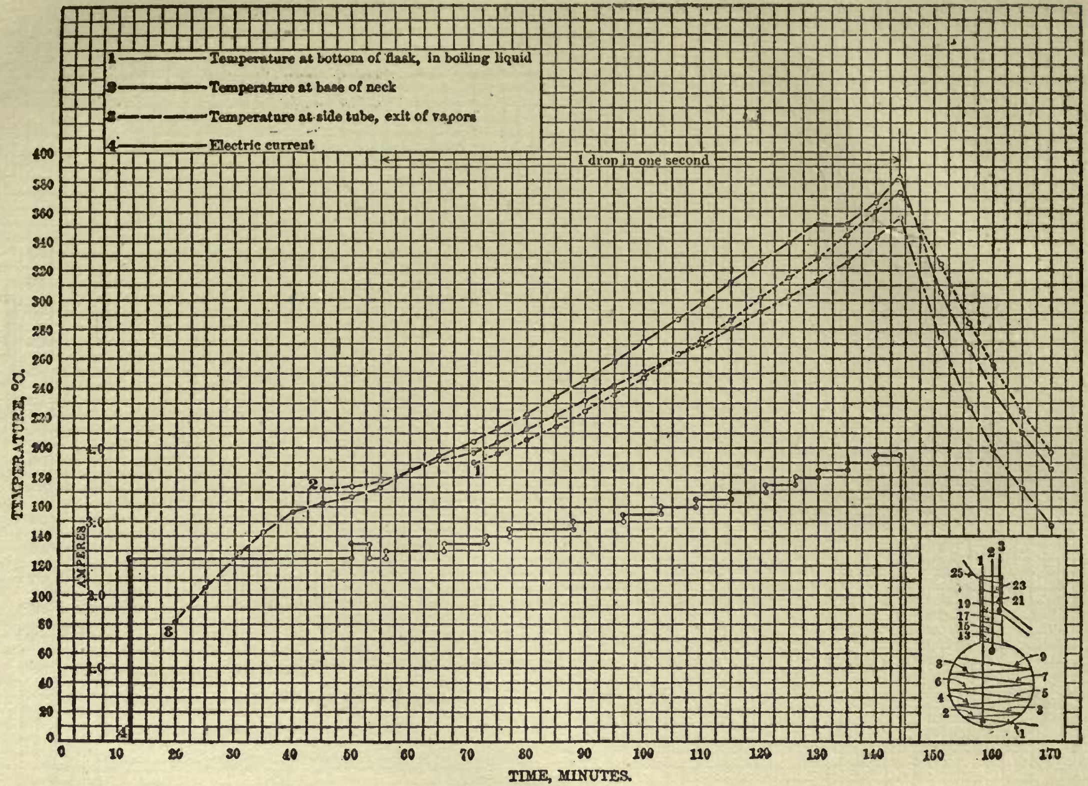


FIGURE 7.—Temperatures in electrically heated still, with another wiring of heater.

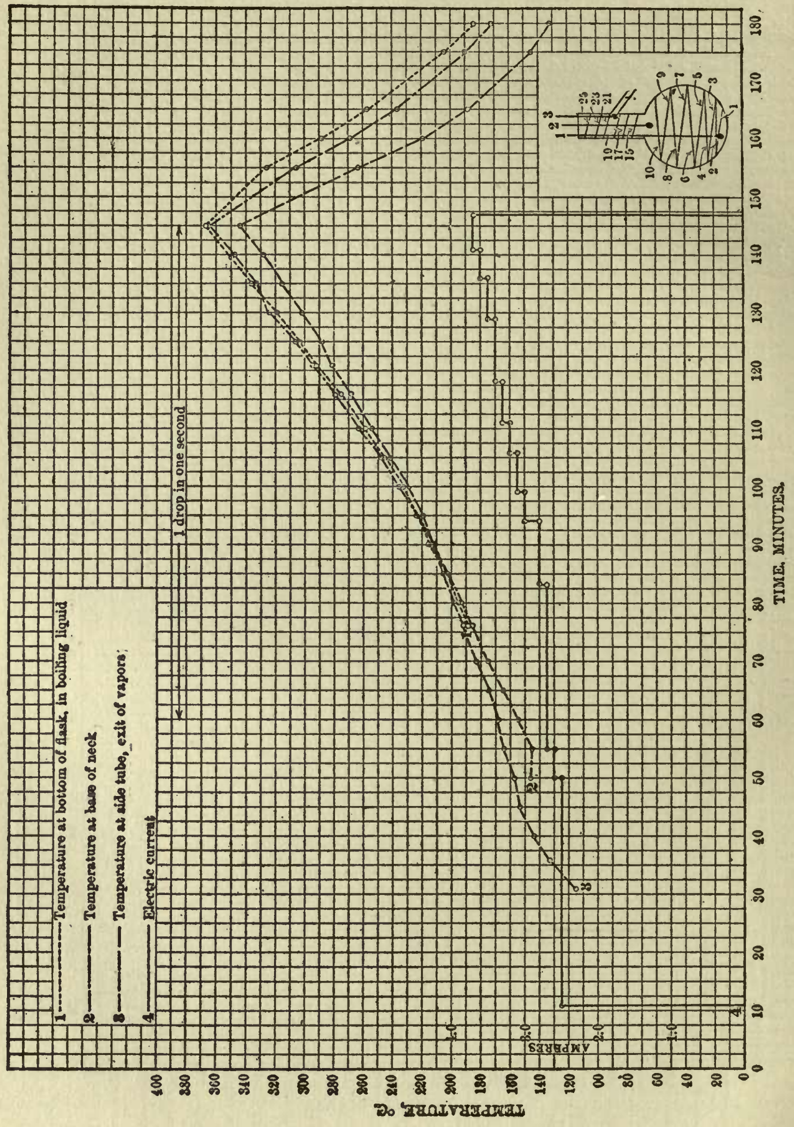


FIGURE 8.—Temperatures in electrically heated still, with another wiring of heater.

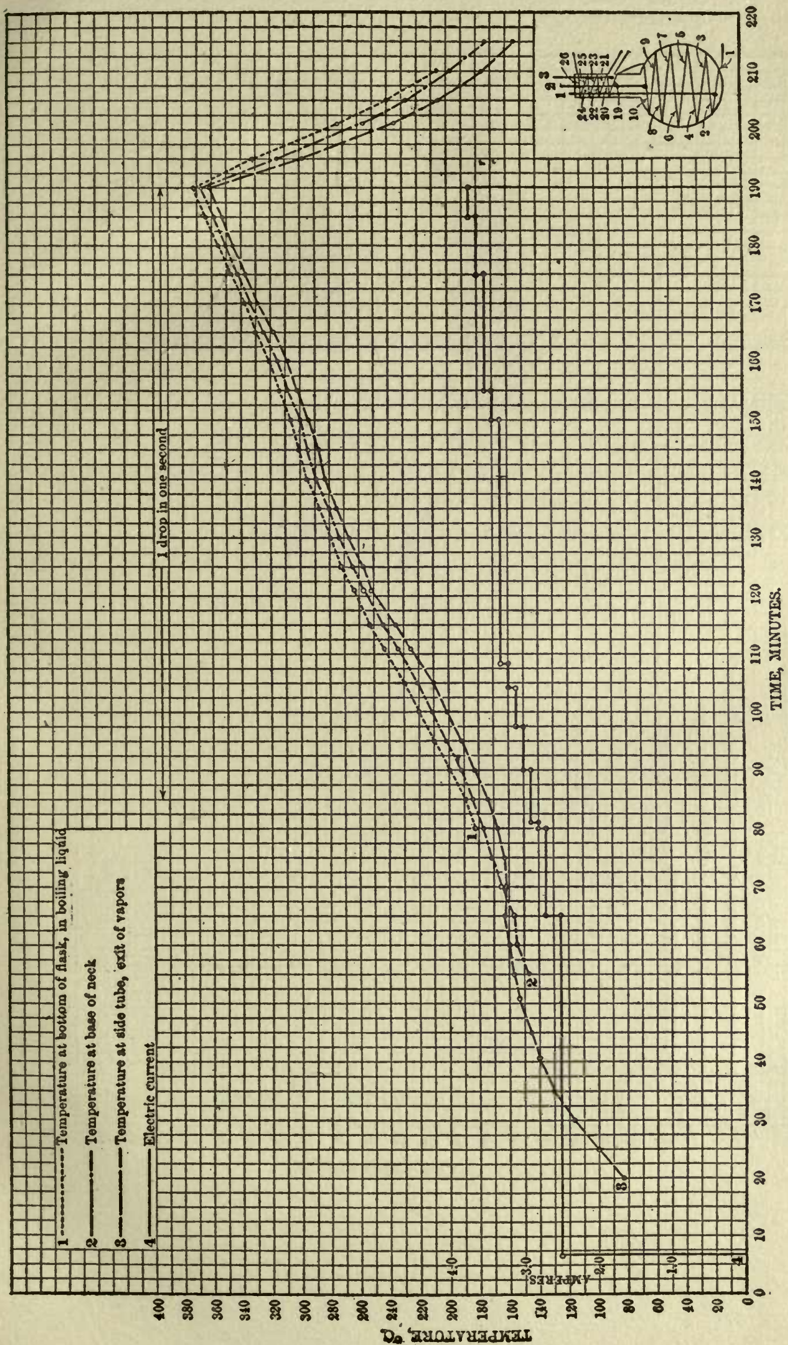


FIGURE 9.—Temperatures in electrically heated still, with another wiring of heater.

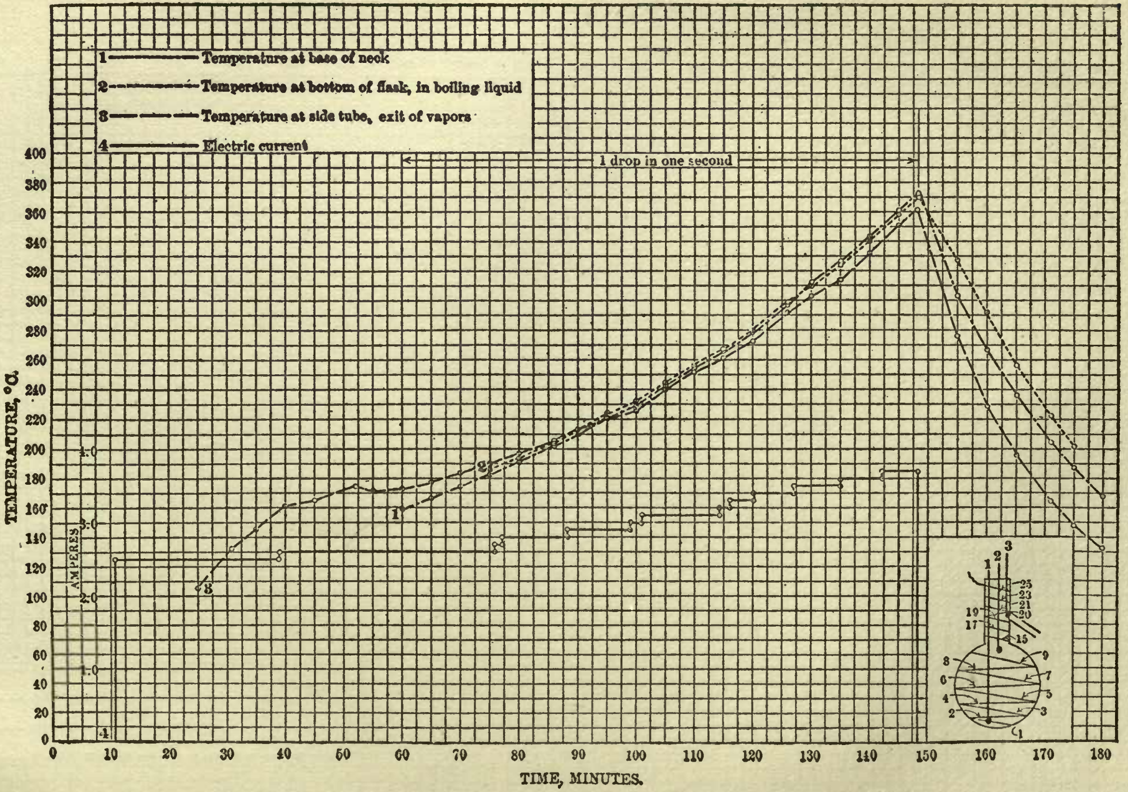


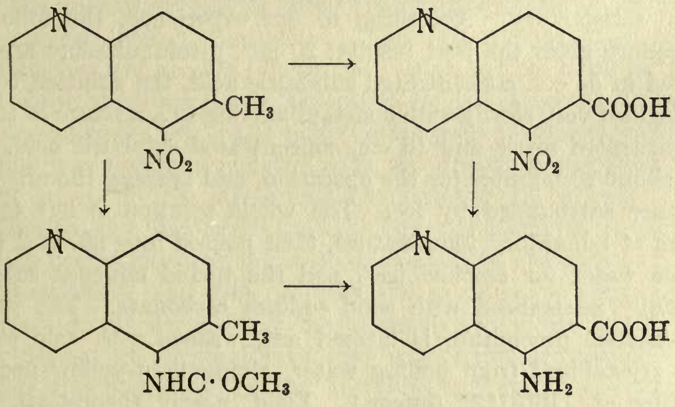
FIGURE 10.—Temperatures in eletriccally heated still, with perfected wiring of heater.

THE PREPARATION AND PROPERTIES OF 5-AMINOQUINOLINE-6-CARBOXYLIC ACID AND CERTAIN RELATED COMPOUNDS

By Marston Taylor Bogert and Harry Linn Fisher
New York

The purpose of this investigation was to prepare an aminoquinoline carboxylic acid of anthranilic type from which, in turn, new heterocyclic systems might be derived and studied.

The point of departure was p-toluquinoline which, on nitration and reduction, yields the ana-amino-p-toluquinoline (5-amino-6-methylquinoline), as shown by Noelting and Trautmann.[1] It was hoped that the desired acid could be obtained either (*a*) by oxidation of the nitro toluquinoline to the nitro acid, with subsequent reduction of the nitro group, or (*b*) by direct oxidation of the acetamino toluquinoline:



Unfortunately, attempts to oxidize either the nitro or the acetamino toluquinoline with nitric acid, with potassium permanganate, alone or in presence of magnesium sulphate, or with chromic

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[1] Ber., *23*, 3655 (1890).

acid in dilute sulphuric acid solution, all failed. Niementowski[1] found that 7-methyl benzoylene urea was either unattacked by chromic acid in glacial acetic acid solution or was burned to oxalic acid and carbon dioxide, although he finally succeeded in oxidizing the methyl group to a carboxyl by the use of potassium permanganate in presence of dilute sulphuric acid or, still more readily, in alkaline solution.

Success was finally attained by boiling the nitro toluquinoline with alcoholic caustic alkali, the methyl group being thereby oxidized and the nitro group compensatingly reduced, thus giving directly the amino acid sought, a method which has been successfully employed for the production of anthranilic acid from o-nitrotoluene.[2]

EXPERIMENTAL

5-Nitro-6-Methylquinoline (*ana-Nitro-p-toluquinoline*).—Noelting and Trautmann[3] have prepared this both by the direct nitration of p-toluquinoline and by the application of the Skraup reaction to 2-nitro-4-aminotoluene.

We have tried both methods, and find the former much the more satisfactory. According to our experience, the following procedure gives the best results: 20 gm. p-toluquinoline are dissolved in 54 c.c. concentrated sulphuric acid, the solution cooled and added very slowly with constant stirring to a mixture of 10 c.c. concentrated nitric and 16 c.c. concentrated sulphuric acid, taking about 20 minutes for the operation, and keeping the nitrating mixture surrounded by ice. The whole solution is left for 24 hours at laboratory temperature, then poured into about 2 liters of ice water (or cracked ice), and the turbid aqueous solution carefully neutralized with solid sodium carbonate. The yellow voluminous precipitate is filtered out, washed with cold water, and crystallized from boiling water, giving light-yellow needles, melting at 116°–117° (uncor.). Yield, nearly theoretical. On long boiling with water, the compound seems to resinify somewhat. If the nitrating mixture is heated, there is apt to be some charring, with consequent reduction in the yield of pure product.

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[1] Ber., *29*, 1357 (1896).

[2] D. R. P., 114839; Winther, *1*, 562.

[3] Loc. cit.

Numerous attempts were made to oxidize this nitro-methylquinoline to the corresponding nitroquinoline acid, by long boiling with dilute nitric acid, or by heating with it under pressure, by the use of potassium permanganate alone or in the presence of magnesium sulphate, but all proved fruitless. The compound either remained unattacked or was completely burned, and our efforts to regulate the reaction so as to yield the desired acid were unsuccessful. When the substance was heated with chromic acid and dilute sulphuric acid for 27 hours at 100°, it was practically unaffected. With a similar oxidizing mixture in a sealed tube for 18 hours at 160°, it was completely burned. Boiled with sodium hydroxide, in alcoholic solution, it gave the desired aminoquinoline carboxylic acid, as described beyond.

5-Amino-6-methylquinoline (*ana-Amino-p-toluquinoline*) was prepared from the nitro compound by reduction with iron and acetic acid, as described by Noelting and Trautmann.[1] Yield, 92%. These investigators give its melting point as 145°. Our product melted at 135° (cor.), and this melting point was not altered by further re-crystallization. The same melting point was obtained when the substance was prepared by the hydrolysis of its carefully purified acetyl derivative. The latter crystallizes from water in colorless needles, m. p. 160°, as stated by Noelting and Trautmann; it is but slowly saponified by hot aqueous solutions of the caustic alkalies, but is easily hydrolyzed by mineral acids.

Experiments were conducted with the object of oxidizing the methyl group of this acetamino toluquinoline to carboxyl, but all failed to give the desired acid. The oxidations were carried out with potassium permanganate, alone and in presence of magnesium sulphate, and with chromic acid in dilute sulphuric acid solution. As in the case of the attempts to oxidize the nitrotoluquinoline, the original substance was either unattacked (except for the hydrolysis of the acetyl group) or it was totally destroyed; there seemed no intermediate halting point.

5-Aminoquinoline-6-carboxylic Acid.—The method finally worked out for the preparation of this acid is as follows: 50 gm. of the nitrotoluquinoline are dissolved in 125 c.c. 95% alcohol in a liter flask provided with a reflux condenser and heated at 100°;

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[1] Ber., *23*, 3657 (1890).

35 gm. powdered potassium hydroxide are added gradually to this boiling solution during 4 hours, and the boiling is then continued for 4 hours longer. The mixture is distilled with steam, to remove alcohol and a small amount of volatile basic substances formed in the reaction, and is then filtered. The brownish solid remaining on the filter contains a certain amount of the material mentioned below as obtained from the filtrate. The deep red filtrate is brought nearly to the neutral point with strong acetic acid and then treated carefully, drop by drop, with dilute acetic acid. At first there comes down a brown flocculent precipitate, apparently identical with the minor constituent of the first residue referred to above.[1] When all this brown flocculent material has been precipitated and removed, further acidification brings down the amino acid as an orange or reddish-brown precipitate, either granular or amorphous. The amorphous form, on standing for half an hour, generally becomes granular. Yield, 30%.

It takes some practice to tell just when the brown flocculent material is all precipitated and the amino acid is beginning to come down. If hydrochloric is used instead of acetic acid, the process is further complicated by the precipitation of a mixture of the amino acid and its hydrochloride. These mixtures give sharp and definite melting points, running all the way from that of the acid itself (218.5°) to that of the pure hydrochloride (264.7°), depending upon the proportion of each present. The hydrochloride is quite difficultly soluble in hydrochloric acid, and after acetic acid has thrown down as much of the amino acid as it will, addition of excess of concentrated hydrochloric acid to the filtrate may be used to precipitate the rest of the amino acid as hydrochloride.

The crude amino acid was purified by repeated solution in caustic alkali and precipitation with acetic acid. It crystallizes slowly from dilute acetic acid, and melts with decomposition at 218.5° (cor.). From concentrated solutions it separates as a bright-yellow mass, but from dilute solutions it comes down slowly as a reddish-brown solid, darkening on drying. From water it crystallizes in red nodules. It dissolves easily in alkalies, pyridine, quinoline, glycerol, mineral acids, formic or acetic acid, or in acetic anhydride; less readily in water, methyl or ethyl alcohols,

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[1] The composition of these residues has not yet been satisfactorily worked out.

or in acetone; very slightly in benzene or toluene; and is apparently insoluble in ether, petroleum ether, chloroform, carbon tetrachloride, carbon bisulphide or turpentine. Most of these solutions are reddish.

For analysis, the acid was purified as stated, dried to constant weight, and proven to be ash-free.

Found: C, 63.98; H, 4.78; N, 14.96 and 15.01. Calculated for $C_{10}H_8O_2N_2$: C, 63.75; H, 4.28; N, 14.89.

A neutral aqueous solution of the acid gave amorphous precipitates with aqueous solutions of the following salts: barium chloride, light brown, moderately soluble; calcium chloride, light brown, moderately soluble; cadmium iodide, light brown, abundant; copper sulphate, brown; nickel chloride, light green; indium chloride, light brown, moderately soluble; mercuric chloride, light brown, abundant; silver nitrate, yellowish green.

Heated with soda lime, the acid yields 5-aminoquinoline. When used as a coupler for benzidine diazonium salts, a deep magenta solution resulted; and with diazo sulphanilic acid, in alkaline solution, a similar color.

Hydrochloride.—Red needles, or an orange powder, melting at 264.7° (cor.) with decomposition, difficultly soluble in hydrochloric acid, but dissolving easily in water to a beautiful red solution.

Found: N, 12.75. Calculated for $C_{10}H_8O_2N_2 \cdot HCl$: N, 12.48.

On standing, it very slowly loses its hydrochloric acid, and the melting point recedes towards that of the free amino acid. Thus, after two months' standing, it melted at 245° and contained 54.05% carbon, the carbon percentage in the pure hydrochloride being 53.46.

In our first experiments for the preparation of the amino acid, the boiling of the nitro toluquinoline with alcoholic sodium hydroxide was invariably followed by a treatment with ammonia and hydrogen sulphide, but, as a careful study of the reaction showed that this treatment did not increase the yield of amino acid, it was omitted in all subsequent preparations.

An examination of the distillate obtained by blowing steam through the mixture after boiling the nitro toluquinoline with alcoholic sodium hydroxide disclosed the presence of small amounts of ammonium carbonate and of acetic *aldehyde*, together with a trace of a pleasant smelling basic substance not isolated in sufficient amount to be identified.

Methyl Ester.—An attempt to prepare this ester by suspending the amino acid in *methyl alcohol* and saturating the solution with hydrochloric acid gas gave only the hydrochloride of the acid.

The amino acid was then treated with the calculated amounts of sodium bicarbonate and dimethyl sulphate, in presence of sufficient water, the mixture stirred for several minutes and then left over night at room temperature. The deep red liquid gradually deposited red needles, which crystallized from water in beautiful lustrous bright red needles, carrying water of crystallization.

The amount of water present in these crystals was determined by drying them to constant weight at 110°–115°.

Found: H_2O, 13.97 and 14.59. Calculated for $C_{11}H_{10}O_2N_2 \cdot 2H_2O$: H_2O, 15.12.

The first of the above analyses was run on a sample which had been standing for several days in a desiccator, while the second sample had merely been drying in the open for about 12 hours. The hydrated ester loses some of its water very easily and, on the other hand, the anhydrous ester is quite hygroscopic.

The anhydrous ester forms an amorphous scarlet powder, melting with decomposition at 245° (cor.). Yield, 35%.

Found: N, 13.93. Calculated for $C_{11}H_{10}O_2N_2$: N, 13.87.

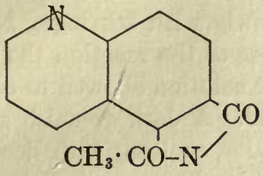
The ester is more or less soluble in water, methyl or ethyl alcohols, acetic or hydrochloric acids; insoluble in sodium carbonate solution; and is readily saponified by warm dilute sodium hydroxide solution.

5-Acetaminoquinoline-6-carboxylic Acid.—The amino acid dissolved in hot acetic anhydride to a red solution, from which on cooling there separated yellowish needles of the lactame of the acetamino acid. When these needles were warmed with dilute sodium hydroxide solution and the solution then carefully acidified with dilute acetic acid and allowed to stand, the turbidity which formed at first gradually cleared and fine yellow needles of the acetamino acid separated, often united in rosettes. These were filtered out, washed with water, dried to constant weight at 110°, and analyzed.

Found: N, 12.18. Calculated for $C_{12}H_{10}O_3N_2$: N, 12.17.

The compound is soluble in alcohol, dilute acetic acid or in the mineral acids, and melts with decomposition at 237° (cor.).

5-Acetaminoquinoline-6-carboxylic Acid Lactame.—5-Aminoquinoline-6-carboxylic acid was added slowly to boiling acetic anhydride and the clear red solution concentrated one third.



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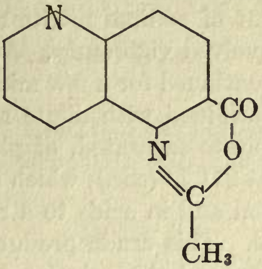

On cooling, long yellowish brown needles separated, which were recrystallized first from acetic anhydride and then from ligroin, giving nearly colorless branched needles, melting at 190° (uncor.), which tend to become slightly yellow on standing, but show no great tendency to absorb moisture from the air and pass into the acetamino acid again. The compound is more or less soluble in benzene, toluene, acetic anhydride, ligroin, chloroform, or carbon tetrachloride.

Found: N, 13.48. Calculated for $C_{12}H_8O_2N_2$: N, 13.21.

With primary amines it yields naphthoisotriazines, as will be described in a subsequent paper.

5 - Benzalaminoquinoline - 6 - carboxylic Acid, $C_6H_5 \cdot CH:N \cdot C_9H_5N \cdot COOH$.—When the amino acid was boiled with excess of benzaldehyde, it rapidly dissolved and water was driven off. On cooling, rosettes of needles separated, which were filtered out, washed with ether, then with petroleum ether, dried at 110° to constant weight, and analyzed.

Found: N, 10.14. Calculated for $C_{17}H_{12}O_2N_2$: N, 10.15.

The compound melts with decomposition at 221.4° (cor.). It dissolves in alcohol or chloroform; only slightly in ether; and is practically insoluble in water, petroleum ether, or benzene. It is easily soluble in aqueous caustic alkalies, and is re-precipitated in white flocs on acidification with dilute acetic acid.

An attempt was made to prepare a metoxazine compound from this by the method recently described by Ekeley and Dean,[1] but it was unsuccessful.

5-Hydroxyquinoline-6-carboxylic Acid.—The hydrochloride of the amino acid was dissolved in the calculated amount of warm dilute hydrochloric acid, and an aqueous solution of the calculated amount of sodium nitrite added slowly with stirring. Nitrogen was evolved vigorously. At the close of the reaction the heating was continued for a few minutes, the solution allowed to cool, and then acidified with dilute acetic acid. A dark greenish granular precipitate separated, of pleasant odor, melting with decomposition at 211.7° (cor.), which dissolved in alkalies to a dark greenish solution and in acids to a reddish green one. Yield, nearly theoretical. This crude product was dissolved in sodium hydroxide solution and this solution boneblacked twice. On acidifying the final filtrate from the boneblack, rosettes of brown needles gradually separated, of the same melting point as before (211.7°) and dissolving in alkalies or in acids to a light yellowish green solution.

The compound dissolves in concentrated or in dilute hydrochloric acid, in glacial acetic acid, in alkaline hydroxides or carbonates, pyridine, quinoline or glycerol; less readily in methyl, ethyl or amyl alcohol, benzene, toluene or carbon bisulphide; and is apparently insoluble in ether, chloroform, carbon tetrachloride or acetone.

Found: N, 7.57. Calculated for $C_{10}H_7O_3N$: N, 7.40.

It gives amorphous precipitates with aqueous solutions of the following salts: barium chloride, brownish green, moderately soluble; zinc chloride, dark green; cadmium iodide, dark green; copper sulphate, brownish green; mercuric chloride, brownish green; silver nitrate, olive green.

Efforts to esterify this acid with dry hydrochloric acid gas in absolute methyl alcohol solution, or with dimethyl sulphate, proved unavailing, while the action of nitrous acid upon the corresponding ester of the amino acid gave chiefly the free hydroxy acid.

The free acid, used as a coupler for diazotized benzidine, gave a dark purple solution, and with diazo sulphanilic acid, in alkaline solution, a red solution.

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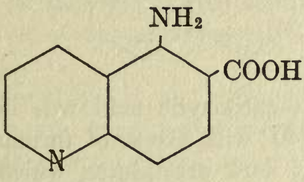
[1] Jour. Am. Chem. Soc., *34*, 161 (1912).

[*Contribution from the Chemical Laboratories of Columbia University, No.* 211]

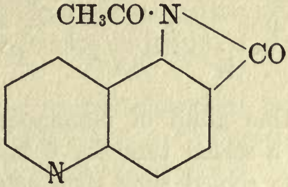
THE SYNTHESIS OF 1, 3, 7-NAPHTHOISOTRIAZINES; DERIVATIVES OF A NEW HETEROCYCLIC SYSTEM

By Marston Taylor Bogert and Harry Linn Fisher

In another paper[1] the authors have described the preparation and properties of 5-aminoquinoline-6-carboxylic acid, its acetyl derivative, and the lactame of the latter:

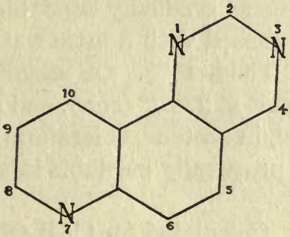


5-Aminoquinoline-
6-carboxylic acid



Lactame of 5-acetaminoquinoline-
6-carboxylic acid

From these substances, by reactions entirely analogous to those used by us in the synthesis of quinazolines,[2] and later papers in same from this laboratory, we have prepared compounds containing the nucleus which, in conformity with the system of nomenclature adopted in Richter's Lexikon, we have designated the



1, 3, 7-naphthoisotriazine nucleus. So far as we have been able to discover, by a careful search of the literature, these are the first

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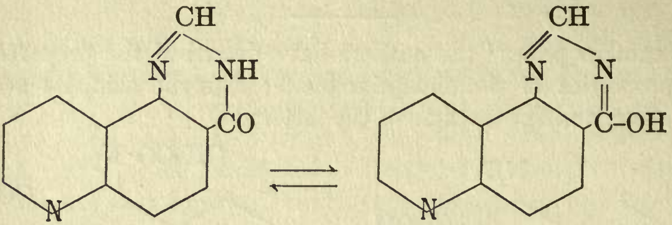
[1] These Proceedings, (1912).
[2] Vide Jour. Am. Chem. Soc., *32*, 784 (1910).

compounds to be described containing this nucleus, although, as all organic chemists will appreciate, it is an exceedingly difficult task to look up all possible derivatives, and we may be wrong in this assumption.

EXPERIMENTAL

4-Keto-2, 3-dihydro-1, 3, 7-naphthoisotriazine (4-Hydroxy-1, 3, 7-naphthoisotriazine).[1]



One gram of 5-aminoquinoline-6-carboxylic acid was heated in a sealed tube for 6 hours at 140° with excess of formamide. The cooled tube then contained a dark precipitate, which was boiled with sodium hydroxide solution, the solution filtered, and the filtrate saturated with carbon dioxide. The turbid solution thus obtained, on standing for two weeks, deposited dark crystals, which were purified by re-dissolving them in sodium hydroxide solution, filtering, diluting the filtrate, making faintly acid with acetic acid, filtering from a small amount of flocculent precipitate, and allowing the filtrate to stand for a few days. Glistening pinkish prisms gradually crystallized out. These were separated, carefully washed with a little water, and dried at 110° to constant weight. Yield, 10%. On standing, the crystals turn light brown. They melt at 298.7° (cor.), and are soluble in methyl, ethyl, or amyl alcohol, in acetone, chloroform, benzene, or in aqueous alkalies, but are practically insoluble in ether or carbon tetrachloride.

Found: N, 21.43. Calculated for $C_{11}H_7ON_3$: N, 21.31.

Efforts to obtain the same compound by substituting for the aminoquinoline acid its methyl ester in the above reaction, proved

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[1] For the sake of uniformity, the various derivatives of this structure will be designated as ketodihydro naphthoisotriazines and formulated accordingly.

fruitless; but we obtained it in poor yield by heating together the amino acid and formamide in an open vessel for an hour and a half at 115°-125°.

2-Methyl Derivative, $CH_3(C_{11}H_6ON_3)$.—The lactame of 5-acetaminoquinoline-6-carboxylic acid (hereinafter referred to simply as "the lactame"), when boiled with ammonium hydroxide solution, gradually dissolved to a red solution and, as the excess of ammonia was driven off, fine yellow needles separated in abundance. Re-crystallized from alcohol, the compound melted with decomposition at a point above 300°, and showed marked tribo-electric properties. It is soluble in alcohol, slightly soluble in acetone or pyridine, and practically insoluble in ether, chloroform, carbon tetrachloride, benzene, carbon disulphide, petroleum ether, or ammonium hydroxide solution. In aqueous caustic alkalies it dissolves and is re-precipitated from such solutions by carbon dioxide.

For analysis, it was purified by several re-crystallizations from alcohol, and by repeated solution in caustic alkali and re-precipitation by carbon dioxide, and then dried to constant weight at 110°.

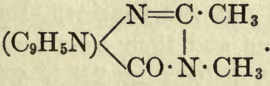
Found: C, 68.08; H, 4.44; N, 20.26, 20.49, and 20.06. Calculated for $C_{12}H_9ON_3$: C, 68.22; H, 4.30; N, 19.91.

When added to a diazotized benzidine solution, it gives a brown precipitate. An attempt to form a phthalone from it by condensation with phthalic anhydride was unsuccessful.

2-Styryl Derivative, $C_6H_5\cdot CH{:}CH(C_{11}H_6ON_3)$.—One gram of the compound just described was ground to a paste with a gram of benzaldehyde and 3 drops of acetic anhydride, and the mass heated for 3 hours at 180°. The melt when cold was pulverized and extracted thoroughly with boiling alcohol. This removed all contaminants and left the styryl derivative as a yellow crystalline powder, melting with decomposition above 300°. It was dried at 110° to constant weight and analyzed.

Found: N, 14.12. Calculated for $C_{19}H_{13}ON_3$: N, 14.05.

2, 3-Dimethyl Derivative,



$$(C_9H_5N)\left<\begin{matrix} N{=}C\cdot CH_3 \\ | \\ CO\cdot N\cdot CH_3 \end{matrix}\right.$$

.—Two grams of the lactame were treated with 20 c.c. water containing slightly more than the calculated amount of methylamine, and the temperature raised to the boiling point. The lactame gradually dissolved, and on cooling long yellowish needles separated. Recrystallized thrice from water, the substance melted at 178° (uncor.). It is tribo-electric and very easily soluble in alcohol.

Found: C, 69.65 and 69.11; H, 5.45 and 5.48; N, 18.74. Calculated for $C_{13}H_{11}ON_3$: C, 69.33; H, 4.89; N, 18.66.

The *2-Methyl-3-ethyl Derivative* was prepared in much the same way as the foregoing, using ethylamine instead of methylamine. It forms light yellow needles, melting at 152.5° (uncor.), and is easily soluble in water or alcohol.

For analysis, it was crystallized thrice from water and dried to constant weight at 110°.

Found: N, 17.80. Calculated for $C_{14}H_{13}ON_3$: N, 17.57.

The *2-Methyl-3-n-propyl Derivative,* prepared in a similar manner, forms yellowish needles, melting at 121°–122° (uncor.), readily soluble in water or alcohol.

For analysis, it was crystallized twice from water and dried to constant weight at 110°.

Found: N, 16.61. Calculated for $C_{15}H_{15}ON_3$: N, 16.60.

2-Methyl-3-phenyl Derivative.—One gram of the lactame and 10 c.c. aniline were boiled together for about 5 minutes, and the clear solution on cooling deposited dark crystals. These were removed, washed thoroughly with ether, and purified by crystallization from alcohol and then from acetone. Rosettes of grayish needles were thus obtained, melting at 263°–263.5° (cor.); soluble in alcohol, chloroform, carbon tetrachloride or acetone, but only slightly soluble in ether.

Found: N, 14.56. Calculated for $C_{18}H_{13}ON_3$: N, 14.63.

2-Methyl-3-p-anisyl Derivative.—This was obtained similarly, by heating for 1¾ hours at 150° an intimate mixture of the lactame and p-anisidine in equimolecular proportion. Steam was evolved, but the mixture did not fuse at this temperature. When cold, the mass was pulverized and extracted with boiling toluene, which dissolved out the triazine. Purified by re-crystallization, first from toluene and then from alcohol, it appeared in yellow glistening plates, melting at 246.9°–247.9° (cor.), soluble also in acetone or benzene, but practically insoluble in water or ether.

Found: N, 13.26. Calculated for $C_{19}H_{15}O_2N_3$: N, 13.24.

The *2-Methyl-3-amino Derivative* was prepared in an analogous manner, by adding 1 gm. of the lactame to the calculated amount of hydrazine hydrate in 50% aqueous solution. The crude product was purified by boiling with dilute ammonium hydroxide solution, to convert unchanged lactame to triazine, which was dissolved out by a dilute sodium hydroxide solution, the insoluble residue being then dissolved in hot dilute acetic acid and re-precipitated by ammonia. A colorless flocculent solid was obtained, melting at 256.7° (cor.), tribo-electric, very slightly soluble in water, and apparently insoluble in the ordinary neutral organic solvents.

Found: N, 24.57. Calculated for $C_{12}H_{10}ON_4$: N, 24.78.

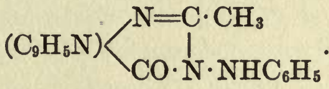
An attempt to secure a condensation of di-quinazolonyl type, by using a large excess of hydrazine hydrate in proportion to the amount of lactame, resulted only in the formation of the above amino derivative.

The *2-Methyl-3-acetamino Derivative* was prepared from the above by the action of acetic anhydride. It crystallizes from water in colorless flocculent form, melting at 268.5°–269.5° (cor.), and is soluble also in alcohol.

Found: N, 21.13. Calculated for $C_{14}H_{12}O_2N_4$: N, 20.89.

The *2-Methyl-3-benzalamino Derivative* was prepared by boiling the amino derivative with excess of benzaldehyde, filtering out the yellow crystals which separated on cooling, and purifying them by repeated crystallization from alcohol. The compound forms colorless fluffy branched needles, melting at 222.6° (cor.), resolidifying at 250°–260°, and then darkening at about 300°.

Found: N, 18.03. Calculated for $C_{19}H_{14}ON_4$: N, 17.83.

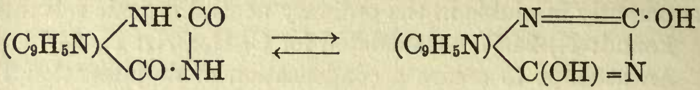
2-Methyl-3-anilino Derivative,  $(C_9H_5N)\left\langle\begin{array}{l} N{=}C\cdot CH_3 \\ \quad\;| \\ CO\cdot N\cdot NHC_6H_5 \end{array}\right.$.—The interaction of pure phenylhydrazine and the lactame was so violent when the mixture was heated to the reaction point that decomposition ensued with violent ebullition. It was, therefore, necessary to dilute the phenylhydrazine with alcohol to secure a smooth reaction.

One gram of the lactame was added to a solution of 1.25 c.c. phenylhydrazine in 25 c.c. alcohol, and the mixture boiled gently for an hour. The lactame slowly dissolved, and a crystalline product soon separated from the solution, causing violent bumping. When the mixture had cooled sufficiently, the crystals were filtered out, washed thoroughly with cold alcohol, dried to constant weight at 110°, and analyzed.

Found: N, 18.72. Calculated for $C_{18}H_{14}ON_4$: N, 18.55.

The compound forms pale brownish needles, melting at 249.5°–250.5° (cor.).

2, 4-Diketo-1, 2, 3, 4-tetrahydro-1, 3, 7-naphthoisotriazine (*2, 4-Dihydroxy-1, 3, 7-naphthoisotriazine*).—



$$(C_9H_5N)\left\langle\begin{array}{l} NH\cdot CO \\ \quad\;\; | \\ CO\cdot NH \end{array}\right. \rightleftarrows (C_9H_5N)\left\langle\begin{array}{l} N\!=\!=\!=\!=C\cdot OH \\ \qquad\qquad | \\ C(OH)=N \end{array}\right.$$

Equal weights of 5-aminoquinoline-6-carboxylic acid and urea were fused together. Water and ammonia were evolved during the fusion and, on cooling, a brown hard mass was obtained. This was pulverized and extracted with cold dilute sodium hydroxide solution, which dissolved out the dihydroxy triazine. From this solution the triazine was precipitated by carbon dioxide, or acetic acid, as a yellowish or brownish powder, melting above 300°, and difficultly soluble in water or in alcohol.

Found: N, 19.54. Calculated for $C_{11}H_7O_2N_3$: N, 19.72.

With diazotized benzidine, the compound gives a dark red solution; and with diazo sulphanilic acid, in alkaline solution, a deep red one.

ORGANIC LABORATORY, Columbia University,
New York.

UEBER CHINONCARBONSAEUREESTER

VON KARL BRUNNER

Innsbruck, Austria

Aus dem chemischen Institute der k. k. Universität in Innsbruck. Vortrag für die IV. Sektion (Organische Chemie) des VIII. Internationalen Kongresses für angewandte Chemie in Washington und New York. September, 1912.

Die Carbonsäure des Benzochinons ist nicht bekannt, auch deren Ester konnten bisher noch nicht hergestellt werden, wiewohl die Gewinnung dieser Verbindungen durch den Einfluss von Oxydationsmitteln, welche Hydrochinon sehr leicht in Chinon überführen, von verschiedenen Chemikern bei der Hydrochinoncarbonsäure wiederholt angestrebt wurde. Auch heute noch gilt daher die schon vor 26 Jahren von A. Hantzsch und K. Loewy zu Beginn ihrer Abhandlung "Ueber neue Chinonderivate aus Succinylobernsteinsäureäther"[1] niedergeschriebene Bemerkung: "Beim Ueberblick über das Gebiet der sonst so gut studierten Chinone bemerken wir zur Zeit noch eine Lücke: es sind nämlich Carbonsäuren des Benzochinons und seiner Homologen bisher noch nicht bekannt, oder wenigstens noch nicht mit Sicherheit als solche erkannt worden."

Allerdings hatte kurz vor dem Erscheinen der eben erwähnten Abhandlung, wenn man eine schon im Jahrgange 1875 der Berichte der Deutschen Chemischen Gesellschaft erwähnte Vermutung von P. v. Rakowski und W. Leppert,[2] Chinoncarbonsäure in den Händen gehabt zu haben, als unbewiesen, ganz übergeht, J. U. Nef im chemischen Laboratorium der Akademie der Wissenschaften in München aus Diamidodurylsäure eine Chinoncarbonsäure, nämlich das Durylsäurechinon dargestellt, das er mit Recht den ersten Repräsentanten eines carboxylierten Chinons nannte,[3]

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[1] Berichte d. Deutschen Chemischen Gesellschaft, Jahrg. 19 (1886), S. 27.
[2] Berichte d. Deutschen Chemischen Gesellschaft, Jahrg. 8 (1875), S. 790.
[3] Berichte d. Deutschen Chemischen Gesellschaft, Jahrg. 18 (1885), S. 3499.

und bald darnach aus dem Diamidopyromellithsäureester einen Chinontetracarbonsäureester[1] erhalten.

Ein drittes Chinonsäurederivat, den Dioxychinondicarbonsäureäther erhielten A. Hantzsch und K. Loewy[2] aus dem Paradioxyterephtalsäureester. Endlich gewannen Joh. Thiele und Fritz Günther[3] vom Dicyanhydrochinon ausgehend, das Anhydrid einer Chinondicarbonsäure.

Wenn nun in den erwähnten Verbindungen tatsächlich schon vier Repräsentanten carboxylierter Chinonderivate vorliegen, so sind dies doch nur mehrfach substituierte, vom Chinondicarbonsäureanhydrid abgesehen, sogar sechsfach substituierte Benzolderivate.

Auf diesen Umstand wies schon J. U. Nef hin, der sich am eingehendsten mit den Chinoncarbonsäuren befasste, indem er hervorhob, dass die Chinonbildung nur bei sechsfach substituierten Benzolderivaten bewerkstelligt werden konnte,[4] hingegen bei der Paradioxybenzoesäure und deren Aethylester nicht gelang.[5]

Obwohl nun diese Erfahrung und vergebliche Versuche mit Toluhydrochinoncarbonsäure, die ich selbst seinerzeit[6] ausführte und die später auf meine Veranlassung V. Juch[7] mit der Hydrochinoncarbonsäure und deren Aethylester nochmals aufnahm, wenig Aussicht boten, die freie Benzochinoncarbonsäure oder auch nur deren Ester herstellen zu können, habe ich dennoch neuerdings, verleitet durch die Vermutung, dass es vielleicht bei Ausschluss von Wasser gelinge, Versuche zur Darstellung dieser Chinonverbindungen begonnen.

Nach mehreren Vorversuchen, bei denen ich das von Joh. Thiele und Fr. Günther mit so gutem Erfolge beim Dicyanhydrochinon angewendete Verfahren[8] der Einwirkung von Salpetersäuredämpfen auf die trockenen Substanzen benützte und, als dieses versagte, leicht reducierbare Metalloxyde auf die Lösung des Hydrochinoncarbonsäuremethylesters in Aether oder in Benzol,

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[1] Annalen der Chemie, Bd. 237 (1887), S. 28.
[2] Berichte d. Deutschen Chemischen Gesellschaft, Jahrg. 19 (1886), S. 28.
[3] Annalen der Chemie, Bd. 349 (1906), S. 66.
[4] Annalen der Chemie, Bd. 237 (1887), S. 2.
[5] Ibid., S. 35.
[6] Monatshefte für Chemie, Bd. 2 (1881), S. 464.
[7] Monatshefte für Chemie, Bd. 26 (1905), S. 840.
[8] Annalen der Chemie, Bd. 349 (1906), S. 50.

bei Zimmertemperatur oder beim Kochpunkte dieser Lösungsmittel einwirken liess, erkannte ich, dass sich hiedurch krystallisierte Chinonderivate herstellen lassen.

Und zwar lieferte dieser Ester beim Kochen der Benzollösung mit gelben Quecksilberoxyd, dem zur Bindung des bei der Reaktion entstehenden Wassers Chlorcaleium zugesetzt wurde, ein gut krystallisierendes schwarzbraunes Chinhydron. Beim Kochen der ätherischen Lösung mit Silberoxyd und entwässerter Pottasche entstand nebst dem Chinhydron ein heller gefärbtes Chinon. Längeres Kochen verminderte die Ausbeute und verursachte die Bildung von Salzen, die beim Filtrieren mit dem Silberschlamm zurückblieben und bei der nachträglichen Zersetzung mit Salzsäure nur amorphe und nicht chinonartige Produkte lieferten. Am besten konnte das gelbe chinonartige Produkt durch nur fünf Minuten dauerndes Schütteln der warmen Benzollösung des Esters mit Silberoxyd und entwässerter Pottasche hergestellt werden.

Ich blieb daher zur Darstellung des chinonartigen Produktes bei folgendem Verfahren, das sich im wesentlichen mit dem von R. Willstätter und A. Pfannenstiel[1] zur Darstellung von Orthobenzochinon aus Brenzkatechin empfohlenen deckt.

In eine auf 40° bis 50° erwärmte Lösung von 5 gr. Hydrochinoncarbonsäuremethylester in 40 gr. Benzol wird ein Gemenge von 8 gr. entwässerter Pottasche und 15 gr. frisch gefälltem Silberoxyd, das mit kalten Wasser, Aceton und Aether gewaschen, endlich über Schwefelsäure im Vacuum von Aether befreit worden war, eingetragen und fünf Minuten hindurch geschüttelt. Die nach dem Filtrieren und Auswaschen mit warmen Benzol erhaltene gelbrot gefärbte Lösung wird durch Destillation unter vermindertem Druck von Benzol befreit. Es bleibt ein zunächst zähflüssiger Rückstand, der nach mehrstündigem Stehen im Vacuum über Schwefelsäure an einem kühlen Orte zu gelben Krystallen erstarrt, deren Menge durchschnittlich 4 gr. das ist 80 Procent beträgt.

Zur Reinigung wird der Rückstand aus siedendem Aether oder Schwefelkohlenstoff und Akkühlen der Lösung in einer Kältemischung umkrystallisiert. Das durch Abgiessen vom Lösungsmittel befreite Produkt bildet gelbrote, wetzsteinförmig zugespitzte,

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[1] Berichte d. Deutschen Chemischen Gesellschaft, Jahrg. 37 (1904), S. 4745.

flache Krystalle von schwachem, Chinon ähnlichem Geruch, die bei 53.5–54° C. schmelzen. Die Substanz löst sich reichlich in Benzol, Alkohol, Chloroform, weniger leicht in Aether, Schwefelkohlenstoff, schwer in Petroleumäther. In Wasser ist sie in der Kälte nicht, in der Wärme aber löslich, diese Lösung ist jedoch dunkel braun gefärbt und scheidet beim Erkalten statt des krystallisierten Produktes nur einzelne dunkel braune Flocken ab; sie enthält somit nur mehr Zersetzungsprodukte der ursprünglichen Verbindung.

Da die Verbindung bei der Elementaranalyse und bei der Bestimmung der Gefrierpunktserniedrigung ihrer Lösung in Benzol Resultate ergab, die in guter Uebereinstimmung mit den für die Formel $C_8H_6O_4$ berechneten standen, so entspricht ihre Zusammensetzung der des Methylesters der Benzochinoncarbonsäure.

Die Verbindung zeigt das für ein Chinon charakterische Verhalten.

Eine wässerige Lösung von schwefliger Säure färbt sie dunkelbraun und bewirkt beim Erwärmen eine farblose Lösung, aus der sich beim Erkalten farblose Krystalle ausscheiden, deren Verhalten zu Lösungsmitteln und Schmelzpunkt mit dem Hydrochinoncarbonsäuremethylester übereinstimmt.

Kocht man die ätherische Lösung dieses Chinonesters mit der äquimolekularen Menge an Hydrochinoncarbonsäureester, so geht nach einiger Zeit die ursprüngliche gelbe Farbe der Lösung in eine braune über und scheiden sich beim Erkalten dunkelrote metallisch glänzende Krystalle aus, die bei 85–86° schmelzen und in Aether viel schwerer löslich sind als die Komponenten. Die Elementaranalyse bestätigte die für ein Chinhydron berechnete Zusammensetzung.

Dasselbe Produkt bildet sich direkt aus dem Hydrochinoncarbonsäuremethylester beim Kochen seiner Lösung in Benzol mit gelben Quecksilberoxyd. Die Bildung dieses Chinhydrons ist bemerkenswert, weil bei den bisher bekannten Chinoncarbonsäuren ein solches nicht erhalten wurde.[1]

Wie Benzochinon in alkoholischer Lösung mit Anilin das von A. W. Hofmann zuerst dargestellte Chinonanilid[2] bildet, so gibt

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[1] J. U. Nef. Annalen der Chemie, Bd. 237, S. 12 u. S. 16.

[2] Zeitschrift f. Chemie u. Pharm., Jahrg. 6 (1863), S. 424.

auch diese Verbindung ein entsprechend zusammengesetztes Anilid, das sich nach der Vereinigung der ätherischen Lösungen von Chinoncarbonsäuremethylester und Anilin, wobei eine auffällig intensive Rotfärbung eintritt, im Laufe einiger Stunden in Form von dunkelroten seidenglänzenden Krystallen abscheidet, die aus kochendem Benzol oder Alkohol umkrystallisiert, bei 202–203° schmelzen. Ihre Zusammensetzung entspricht der Formel $C_{20}H_{16}O_4N_2$. Weniger leicht als der Methylester der Chinoncarbonsäure lässt sich der Aethylester darstellen, da er nahe bei Zimmertemperatur schmilzt und namentlich im flüssigen Zustande bald eine Zusetzung erleidet.

Ich konnte ihn unter Befolgung des für die Darstellung des Methylesters angegebenen Verfahrens aus dem Hydrochinoncarbonsäureäthylester als gelbroten krystallisierten Rückstand auch mit 80 procentiger Ausbeute erhalten. Die zunächst gewonnenen Krystalle schmolzen nach dem Abpressen im kühlen Raume zwischen Papier schon bei 15° C. Wurden sie bald nach der Darstellung durch Lösen in kochendem Petroleumäther und Abkühlung der Lösung in einer Kältemischung umkrystallisiert, so zeigten die vom Lösungsmittel getrennten und einige Stunden im kalten Raume auf Filtrierpapier im Vacuumexsiccator gelegenen Krystalle den Schmelzpunkt bei 22° C.

Die bald nach der Darstellung analysierte Substanz gab gut mit der Formel $C_9H_8O_4$ übereinstimmende Resultate, sie stellt somit den Aethylester der Benzochinoncarbonsäure dar.

Die Krystalle bilden gelbrote Blättchen von intensiven Geruch nach Chinon, färben die Haut braungelb und werden selbst bei niederer Temperatur aufbewahrt, allmählich flüssig, wobei eine Zersetzung eintritt, da ihre vorher vollständige Löslichkeit in warmen Petroleumäther immer mehr abnimmt.

Mit Anilin gibt der Chinoncarbonsäureäthylester beim Vermischen ätherischer Lösungen beider sofort eine intensiv rot gefärbte Lösung, aus der sich nach mehrstündigem Stehen braunschwarze Krystalle eines Anilides ausscheiden, das nach dem Umkrystallisieren aus kochendem Weingeist blauschillernde Krystallnadeln von dunkelroter nach dem Trocknen fast schwarzer Farbe darstellt, die bei 178–179° C. schmelzen.

Durch diese Experimentaluntersuchung ist der Nachweis erbracht worden, dass Ester der Benzochinoncarbonsäure herstellbare und sogar gut krystallisierende Verbindungen sind.

Es ist jedoch bisher noch nicht gelungen, die freie Benzochinoncarbonsäure darzustellen. Versuche, sie aus den eben beschriebenen Estern durch Verseifung, herzustellen, waren vorläufig erfolglos.

ISOMERIC NAPHTHENIC ACIDS

By F. W. Bushong and I. W. Humphrey
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PRELIMINARY PAPER

The earliest investigations of the acid constituents of petroleum were those of Hell and Medinger,[1] who examined the acids obtained from soaps salted out of the alkaline sludges obtained in the refining of the illuminating-oil distillates from Wallachian petroleum. They isolated acids belonging to the series $C_nH_{2n-2}O_2$, and demonstrated that they differed in their properties from the unsaturated acids derived from the series of fatty acids. They more closely resembled the fatty acids themselves, but on account of their very weak acid character these authors were led to doubt whether they contained the carboxyl group, and to suggest the possibility of a keto-alcohol or ether-alcohol structure. Later a lacto-alcohol structure was proposed by Zaloziecki.[2]

Through the classical researches of Markownikow[3] and his co-workers it has been shown that the chief constituents of Caucasian petroleum are saturated cyclic hydrocarbons, called naphthenes. A number of acids were isolated from Caucasian petroleum, among which was one identical with an acid of Hell and Medinger. Markownikow considered these the monocarboxylic derivatives of the naphthenes. The correctness of this view was demonstrated by Aschan.[4] He converted octonaphthenic acid, $C_8H_{14}O_2$, into its amide, and this into the nitrile, $C_7H_{13}CN$, and also into the amine, $C_7H_{13}NH_2$. He also succeeded in reducing this acid, by the aid of hydriodic acid and phosphorus, to an octonaphthene identical with that found in petroleum.

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[1] Berichte d. d. chem. Ges., *7*, 1216 (1874) ; *10*, 541 (1877).
[2] Berichte d. d. chem. Ges., *24*, 1808 (1891).
[3] Ann. de Chim. et de Phys., (6), *2*, 372 (1884); Jr. prakt. Chem., (2), *49*, 88 (1894).
[4] Chemie der alicyclischen Verbindungen, 508 (1905). Berichte d. d. chem. Ges., *24*, 2710 (1891).

Attempts were then made both by Markownikow and by Aschan to synthesize naphthenic acids by the hydrogenation of benzoic acid, and the three toluic acids, but the hexahydro-derivatives which they prepared were quite different in their properties from the natural naphthenic acids, and up to the present time the cyclohexane carboxylic acids have not been found in petroleum. Markownikow[1] has, however, converted the naphthenic acid of the composition $C_6H_{11}COOH$ into the amine $C_6H_{11}NH_2$, which appears to be identical with the synthetically prepared methyl-1-amino-2-cyclopentane. It is evident, therefore, that the lower-boiling naphthenic acids are cyclopentane derivatives. Since Markownikow considered the acid described by him to be isomeric with the methyl-pentamethylene carboxylic acid (2.1) synthesized by Colman and Perkin,[2] the relation of the side-groups to the pentamethylene ring remains in doubt.

EXPERIMENTAL PART

The material under examination was the commercial naphthenic acid obtained from Baku, Russia. It was found to contain approximately 50% water and more than 5% of hydrocarbons of such density and boiling point as to reveal that they were derived from the illuminating oil distillates. A considerable quantity of soap formed a gelatinous layer in the container.

Forty liters of this material were subjected to fractional esterification, as follows: Several 3-liter balloon flasks were fitted out as in the laboratory method for making ether. In each flask 2 liters of the naphthenic acid were treated with 200 c.c. of ethyl alcohol and 400 c.c. of sulphuric acid. Distillation was carried on until, by the evaporation of water, the boiling point was raised to 140°. 200 c.c. more alcohol were then slowly admitted through a dropping funnel, and the esterification was continued without further rise in temperature. From the distillate collected during this process 1.5 liters of a mixture of the most volatile esters and hydrocarbons were separated. From the united contents of the

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[1] Liebig's Annalen der Chemie, *307*, 367 (1899).

[2] Berichte d. d. chem. Ges., *21*, 739 (1888). See also Zelinsky, Berichte d. d. chem. Ges., *25*, 2690 (1902).

retorts nearly 23 liters of an upper layer consisting of free naphthenic acids and their esters were separated.

The distillate containing the most volatile esters was then saponified with alcoholic potash, after which the unsaponifiable hydrocarbons were removed by steam distillation. The soap when acidified with sulphuric acid yielded half a liter of free naphthenic acids. These were treated with 400 c.c. of methyl alcohol and 50 c.c. sulphuric acid and converted into methyl esters. These methyl esters were subjected to 12 successive fractional distillations. Up to the sixth distillation a Wurtz dephlegmator was employed. In the remaining distillations advantage was taken of suggestions made in a private communication by V. F. Herr,[1] chief of the laboratory of the Baku Section of the Imperial Russian Technological Society. The upper bulb of a three-bulb LeBel-Henninger dephlegmator was filled with lead bullets. Although no special comparison of the efficiency of the dephlegmator with and without the bullets was made, the results obtained were highly satisfactory. The amount of lead attacked was so slight as to be negligible. The constants of the ester fractions are shown in the table on page 60.

Fraction No. 2 contains hexanaphthene carboxylic ester, $C_6H_{11}COOCH_3$, which according to the theory should contain 67.55% C and 9.93% H, and its molar weight should be 142.1. The last traces of water are extremely difficult to remove, as both Markownikow and Aschan have already pointed out, and we have found this to be especially true in the lower fractions of a series, since the water is carried over with these earliest fractions. The presence of a small amount of water would tend to increase the content of H and to lower the molar weight, determined by the lowering of the freezing point of benzene. Aschan [2] found the boiling point of this ester to be 165.5°–167.5°, and the specific gravity to be 0.90547 at 18.4°. Markownikow [3] gives the boiling point as 164°–166° at 750 mm. pressure, and d 20°/20° = 0.9065. Frangopol [4] separated a fraction prepared from Rouma-

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[1] See also "Ein neuer Dephlegmator für Naphtha-Fraktionierung," Chemiker-Zeitung, 1908, Nr. 13.

[2] Berichte d. d. chem. Ges., *23*, 870 (1890).

[3] Liebig's Annalen der Chemie, *307*, 370 (1899).

[4] Revue du Pétrole, *4*, 134 (1911).

nian petroleum boiling at 163°–166° which had the density 0.9063 at 20°, and the refractive index 1.4418 at 25°.

NAPHTHENIC METHYL ESTERS (after 12 distillations)

No.	Boiling point.	Sp. gr. 23°/15°	Ref. index at 23°	Mol. wt. in C_6H_6	Opt. rot. 20cm. tube	Analysis	
						C	H
	degrees				degrees	per cent	per cent
0	140–148	. . .	1.4048	. . .	. . .	. . .	. . .
00	148–160	. . .	1.4120	. . .	. . .	. . .	. . .
1	160–165	. . .	1.4162	137.1	−0.92	65.64	10.70
2	165–170	.907	1.4201	139.5	−0.94	67.25	10.61
3	170–175	.9158	1.4243	144.7	−0.65	68.14	10.64
4	175–179	.9195	1.4268	145.8	−0.36	68.25	10.55
5	179–183	.9213	1.4283	147.0	−0.29	68.76	10.47
6	183–186	.9230	1.4298	151.6	−0.21	68.71	10.44
7	186–189	.9245	1.4311	154.9	−0.13	69.29	10.45
8	189–192	.9262	1.4323	154.1	−0.04	69.32	10.50
9	192–194	.9252	1.4331	156.4	−0.02	69.35	10.59
10	194–196	.9255	1.4336	155.8	−0.02	69.77	10.63
11	196–198	.9235	1.4340	159.7	0.00	69.99	10.59
12	198–200	.9235	1.4341	158.5	+0.04	70.18	10.65
13	200–202	.9230	1.4345	161.7	+0.06	70.16	10.72
14	202–204	.9230	1.4350	162.9	+0.10	70.45	10.73
15	204–206	.9232	1.4359	164.4	+0.19	70.51	10.71
16	206–208	.9248	1.4367	165.9	+0.17	70.60	10.86
17	208–210	.9258	1.4372	170.1	+0.24	70.68	10.79
17	208–210	. . .	. . .	. . .	. . .	70.71	10.76
18	210–212	.9261	1.4383	170.6	+0.36	70.83	10.68
19	212–214	.9262	1.4389	170.0	+0.40	70.93	10.67
20	214–216	.9269	1.4395	172.6	+0.32	71.17	10.94
21	216–218	.9269	1.4400	171.9	+0.39	71.38	10.83
22	218–220	.9276	1.4410	173.3	+0.40	71.36	10.72
23	220–222	.9279	1.4418	175.2	+0.34	71.60	10.79
24	222–224	.9284	1.4424	178.6	+0.38	71.79	11.02
25	224–226	.9290	1.4434	181.6	+0.48	71.99	10.86
26	226–228	. . .	1.4438	. . .	. . .	. . .	. . .

Fraction No. 8 contains heptanaphthene carboxylic ester, $C_7H_{13}COOCH_3$, which should contain 69.17% C and 10.33% H and the molar weight of which should be 156.1. Aschan found this ester to boil at 190°–192° and to have the specific gravity 0.9357 at 18°/18°. The methyl ester made from the silver salt of the octonaphthenic acid by Markownikow[1] boiled at 189°–190°. The fraction boiling 188°–192°, separated by Frangopol, had the density 0.9163 at 20°, and the refractive index 1.4423 at 25°.

The density of the fractions boiling above fraction No. 8 decreases until a minimum is reached in fractions No. 13 and No. 14. The analyses of these two fractions show that their composition agrees very closely with that calculated for the formula $C_8H_{15}COOCH_3$, which is C 70.53% and H 10.66%. Above these fractions the density rapidly increases up to fraction No. 18, which contains the octonaphthene carboxylic ester first isolated by Markownikow, and later described by Aschan.[2] Aschan's ester boiled at 211°–213° and had the specific gravity 0.9352 at 18.4°/18.4°. The fraction boiling 210°–215° obtained by Frangopol had the density 0.9398 at 20°, and the refractive index 1.4430 at 25°. It is quite evident that fractions No. 18 and No. 19 consist essentially of the same octonaphthene carboxylic ester as that heretofore known, slightly contaminated with the nononaphthene carboxylic ester which boils only 10° higher, since the percentage of carbon is 0.3% and 0.4% high, respectively.

The presence of at least one isooctonaphthene carboxylic ester, which has a lower density than either the heptanaphthene or octonaphthene carboxylic esters heretofore isolated is, therefore, clearly established.

Fractions No. 23 and No. 24 contain nononaphthene carboxylic ester, $C_9H_{17}COOCH_3$, composition C 71.68%, H 10.95%, calculated. This ester was first isolated by Markownikow in a fraction boiling 220°–225°. Frangopol also obtained a fraction boiling 223°–226°, having the density 0.9409 at 20°, and the refractive index 1.4485 at 25°.

Comparing the boiling points of all these esters, it is evident that the hexanaphthene, the heptanaphthene, and the octonaphthene carboxylic esters formerly isolated by Markownikow and Aschan are true homologues, while the nononaphthene car-

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[1] Jr. f. prakt. Chem., (2), *49*, 85 (1894).
[2] Berichte d. d. chem. Ges., *24*, 2723 (1891).

boxylic ester of Markownikow is a true homologue of the isomeric octonaphthene carboxylic ester isolated by us.

Ten liters of the partially esterified naphthenic acids, taken from the retorts as already described, were put into a copper still and subjected to distillation in a current of natural gas. Three fractions were collected; the first two being each 20% and the third 10% of the total volume. During the distillation of the first 40% the temperature of the liquid did not reach 285°, and during the distillation of the third fraction it was kept below 295°.

FREE NAPHTHENIC ACIDS (after 12 distillations)

No.	Boiling point	Sp. gr. 23°/15°	Ref. index at 20.8°	Optical rotation in a 20 cm. tube
	degrees			degrees
00	206–215	0.9246	1.4366	−0.35
0	215–220	0.9369	1.4362	−0.70
1	220–224	0.9467	1.4365	−0.64
2	224–227	0.9519	1.4382	−0.56
3	227–230	0.9565	1.4421	−0.42
4	230–232	0.9580	1.4440	−0.38
5	232–234	0.9615	1.4451	−0.32
6	234–236	0.9630	1.4462	−0.26
7	236–238	0.9627	1.4475	−0.22
8	238–240	0.9627	1.4481	−0.20
9	240–242	0.9629	1.4488	−0.18
10	242–244	0.9623	1.4496	−0.10
11	244–246	0.9626	1.4501	−0.07
12	246–248	0.9625	1.4510	−0.04
13	248–250	0.9617	1.4518	+0.01
14	250–252	0.9620	1.4524	+0.06
15	252–254	0.9622	1.4530	+0.12
16	254–256	0.9624	1.4534	+0.19
17	256–258	0.9623	1.4538	+0.30
18	258–260	0.9624	1.4523	+0.32

The first two fractions of the ethyl esters thus separated were redistilled from glass flasks, and the distillates were thereafter subjected to three successive fractional distillations in which a Wurtz dephlegmator was employed. The higher boiling residues from these distillations were united with the third, or 10%, fraction above mentioned, which is reserved for future examination. The distillates were collected in twenty-one fractions, each boiling within limits of 4°. The first ten fractions of these, boiling below 236°, were saponified in several separate portions with alcoholic potash. The soaps were then freed from hydrocarbons by steam distillation. The portion containing the soaps made from the 232°–236° fraction was also extracted with five successive portions of ether. However, not more than a drop of extract remained after the evaporation of the ether.

The acids were liberated from the purified soaps by hydrochloric acid, and then subjected to 12 successive fractional distillations. The use of a dephlegmator necessitated too high a temperature in the flask, so an ordinary Jena distilling flask was used, within the neck of which a platinum cone was suspended by a coil of heavy platinum wire, the upper end of the wire being hooked into the delivery tube of the flask. The weight of the platinum was about 10 gm. for a 100 c.c. or 200 c.c. flask.

By the aid of Fig. 1 the specific gravities of the naphthenic acid fractions may be compared with those of the corresponding methyl ester fractions. The naphthenic acids studied by Markownikow and Aschan boiled 49°–50° higher than the methyl esters from which they were prepared. In plotting the curves this difference has been made 50° for convenience.

In Fig. 2 the optical rotations of the various fractions of the naphthenic acids and their methyl esters are represented.

It will be observed that the maximum lævorotatory activity is shown in the two fractions, boiling 215°–220° and 165°–170°, which contain, respectively, hexanaphthene carboxylic acid and its methyl ester.

The methyl ester fraction boiling 196°–198° was inactive. The acid fractions No. 12 and No. 13 boiling approximately 50° higher are practically inactive. The neutral or inactive line cuts the methyl ester curve at a point about 9° above the boiling point of

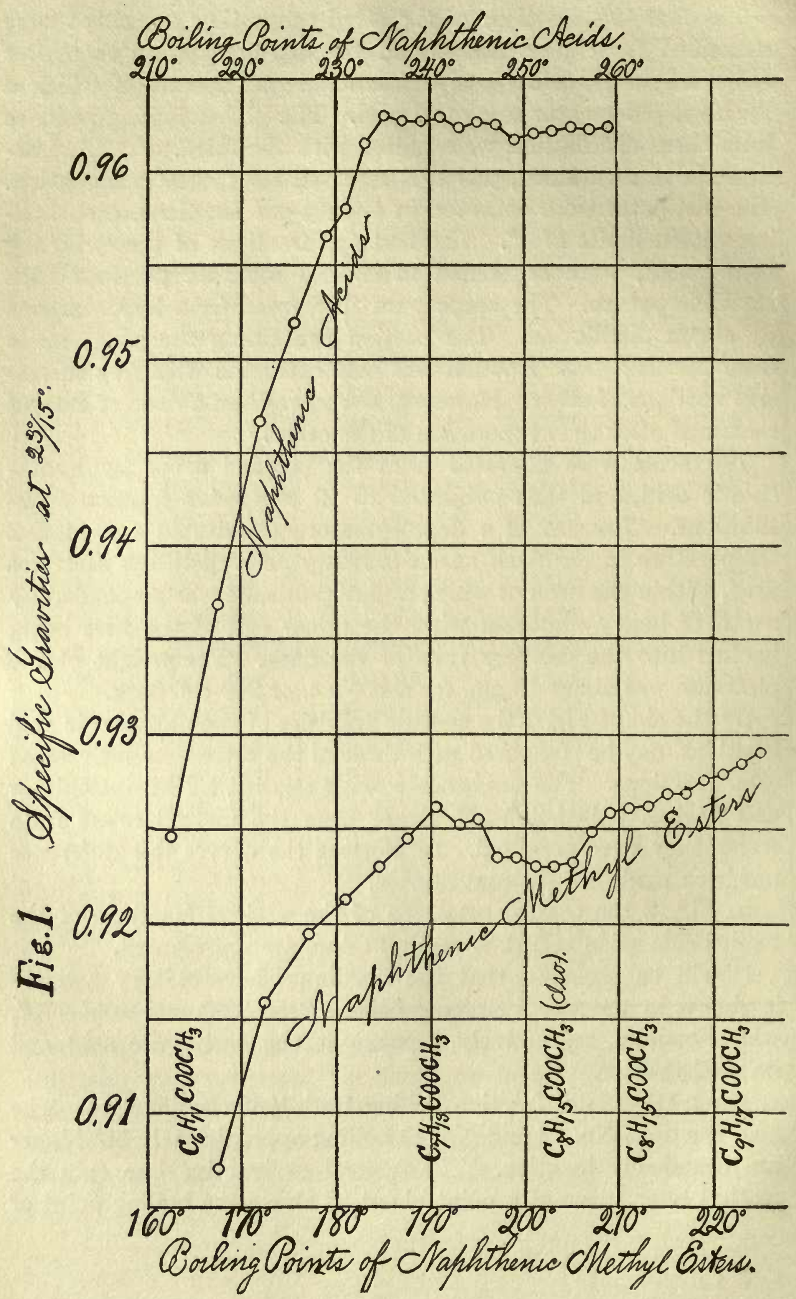
Boiling Points of Naphthenic Acids.
210° 220° 230° 240° 250° 260°
0.96
0.95
0.94
0.93
0.92
0.91
Specific Gravities at 25°/15°.
Naphthenic Acids
Naphthenic Methyl Esters
$C_6H_{11}COOCH_3$
$C_7H_{13}COOCH_3$
$C_8H_{15}COOCH_3$ (Iso).
$C_8H_{15}COOCH_3$
$C_9H_{17}COOCH_3$
160° 170° 180° 190° 200° 210° 220°
Boiling Points of Naphthenic Methyl Esters.

Fig. 1.

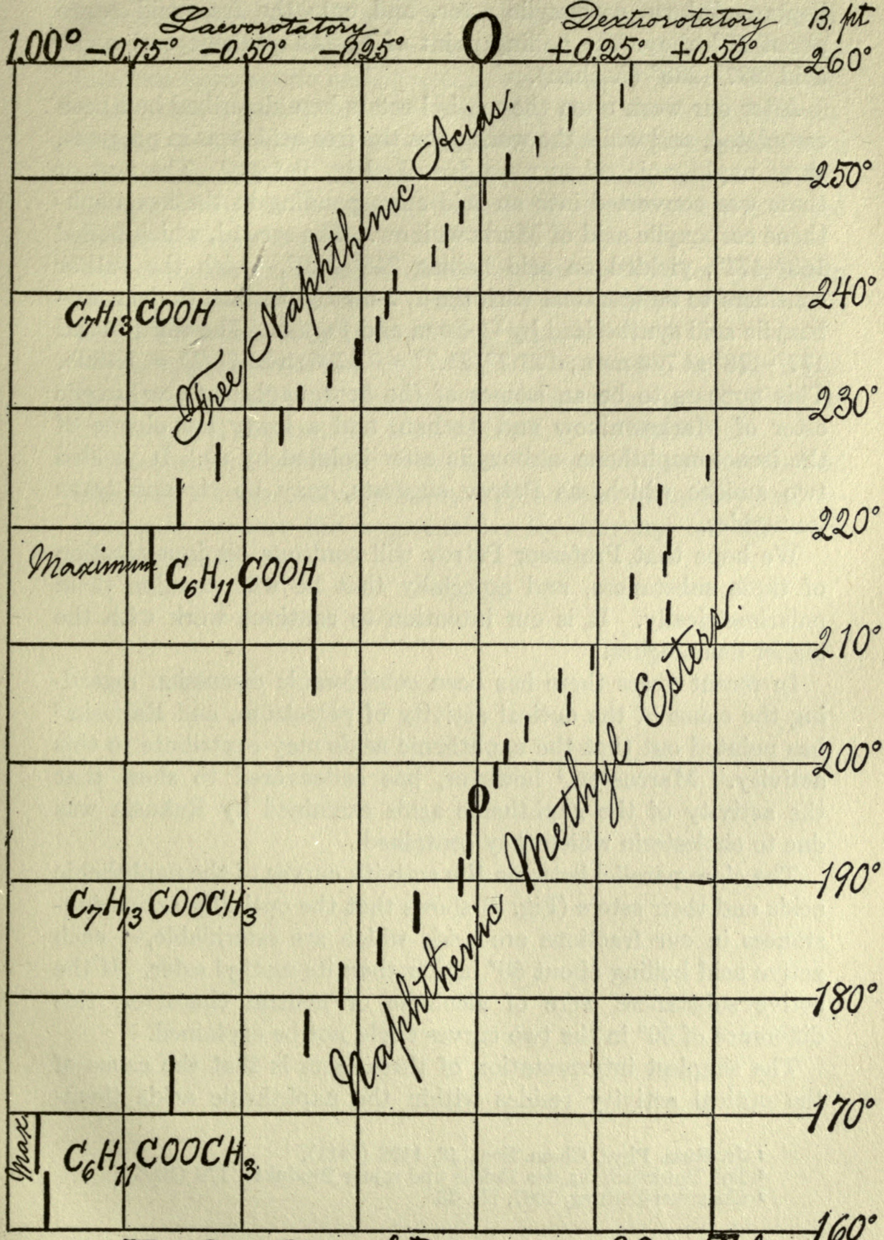

Fig. 2. Optical Rotation, in a 20 cm. Tube.

heptanaphthene carboxylic ester, and cuts the free acid curve about 10° above the boiling point of heptanaphthene carboxylic acid, 237°–239° (Aschan).

After our work upon the methyl esters here described had been completed, and while the work upon the free acids was in progress, three naphthenic esters were described by Petrov.[1] The first of these was converted into an acid corresponding to the hexanaphthene carboxylic acid of Markownikow. The second, which boiled 169°–171°, yielded an acid boiling 218°–220°, which the author considers to be identical with the 1, 2-methylpentamethylene carboxylic acid synthesized by Colman and Perkin. The third boiled 177°–178° at 736 mm.; $d\ 21.7°/21.7° = 0.9295$; $n\ 21.7°/D = 1.4305$. This appears to be an isomer of the heptanaphthene carboxylic ester of Markownikow and Aschan, and a lower homologue of the isooctonaphthene carboxylic ester isolated by us. It yielded two amides which, as Petrov suggests, may be cis and trans isomerides.

We hope that Professor Petrov will continue his investigation of these substances, and especially that he will examine them polarimetrically. It is our intention to continue work with the higher homologues.

In recent years there has been considerable discussion regarding the cause of the optical activity of petroleum, and Rakusin[2] has pointed out that the naphthenic acids may contribute to this activity. Marcusson,[3] however, has endeavored to show that the activity of the naphthenic acids examined by Rakusin was due to cholesterin which they contained.

The close parallel between the activity curves of the naphthenic acids and their esters (Fig. 2) shows that the optically active substances in our fractions are acids which are esterifiable, — each active acid boiling about 50° higher than its methyl ester. If the active substances were of alcoholic or neutral character, this difference of 50° in the two curves could not be explained.

The simplest interpretation of these facts is that the cause of the optical activity resides within the naphthenic acids them-

[1] Jr. Russ. Phys. Chem. Soc., *43*, 1198 (1911).
[2] Die Untersuchung des Erdöls und seiner Produkte, 178 (1906).
[3] Chemiker-Zeitung, 1907, Nr. 33.

selves. Theoretically the methylpentamethylene carboxylic acids, $CH_3 \cdot C_5H_8COOH$, which may exist in cis and trans forms, contain two asymmetric carbon atoms, and it is, therefore, to be expected that a natural product containing them should be optically active. A 1, 3-methylcyclopentane carboxylic acid prepared from active material by Zelinsky[1] gave the value $[a]_D = -5.89°$. Among the higher homologues the number of active isomers should correspondingly increase.

A complete explanation of the optical activity of petroleum cannot, therefore, be given until the constitution of the naphthenic acids can be established by synthesis.

The opportunities for the industrial utilization of the naphthenic acids and their derivatives appear to be as unlimited as the supply of the material from which they are obtained.

In conclusion we desire to express our gratitude to Dr. Robert Kennedy Duncan, through whose appreciative sympathy and enthusiastic support the opportunities for carrying on this work were secured.

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[1] Loc. cit.

REDUCTION OF KETONES TO THE CORRESPONDING HYDROCARBONS WITH AMALGAMATED ZINC AND HYDROCHLORIC ACID

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Aromatic Ketones

Aromatic ketones yield on treatment with the ordinary reducing agents usually pinacons or secondary alcohols. Klages and Allendorff[1] have, however, shown that the purely aromatic ketones (ketones in which the carbonyl group is connected with two aromatic groups) on treatment with sodium and absolute alcohol give the corresponding hydrocarbons in good yields after the equation:

$$R \cdot CO \cdot R + 2\,H_2 = R \cdot CH_2 \cdot R + H_2O$$

but that this reaction does not take place with the aliphatic-aromatic ketones (where the carbonyl group is attached to both an aliphatic and an aromatic group). In this case secondary alcohols are produced, thus 20 gm. of acetophenone gave 8 gm. of methyl phenyl carbinol, some styrol and only traces of ethyl benzene, and the other ketones investigated did not yield any hydrocarbons at all. Later Sabatier and Senderens introduced their elegant reduction method, by which vapors of the substance and hydrogen are conducted over finely divided nickel (or copper) prepared by reducing nickel oxide at different temperatures.

If this method be applied to aromatic ketones, a complete hydrogenation takes place, as not alone the carbonyl group, but also the benzene group, is reduced. Darzen[2] has, however, shown that in case the nickel be prepared at a high temperature (300°) and the reduction carried on at a comparatively low tem-

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[1] Ber., *31*, 998 (1898).

[2] Compt. rend., *139*, 868 (1904).

perature (190°–195°), the hydrogenation only takes place in the carbonyl group.

This method has, however, several disadvantages. It requires a complicated apparatus, the substance to be reduced and the hydrogen have to be absolutely free from halogens, as even minute quantities of these present prevent the catalytic action of the metal altogether. The nickel must be absolutely pure and prepared at a certain temperature, otherwise the reduction will go too far and, as by all contact processes, it requires the greatest care to prevent the catalytic agent from losing its activity. But, conducted in the right manner, the method gives good yields and is the only way in which aliphatic-aromatic ketones can be reduced to the corresponding hydrocarbons:

$$X \cdot CO \cdot Y + 2H_2 = X \cdot CH_2Y + H_2O$$

where X and Y represent, respectively, an aliphatic and aromatic group.

As already mentioned, these ketones give, on treatment with the ordinary reducing agents, such as zinc and acids, sodium amalgam, sodium and absolute alcohol, etc., either pinacons or secondary alcohols, and even prolonged boiling with zinc and acid does not produce any hydrocarbons. It appeared, however, that if the zinc was amalgamated superficially by immersion a short time in a dilute solution of mercuric chloride, the reduction of the ketones to the corresponding hydrocarbons took place with the greatest ease on heating with hydrochloric acid, and, furthermore, that the yields were excellent and the obtained hydrocarbons very pure, no by-product being formed at the same time.

The procedure is the simplest possible. The zinc employed is the granulated metal, which goes on the market under the name of mossy zinc. It is left in a 5% aqueous solution of mercuric chloride at ordinary temperature for about 1 hour. The liquid is then poured from the zinc, and, without washing and drying this, the ketone and then crude hydrochloric acid are added, and the whole heated in a flask with reflux condenser, so as to produce a brisk evolution of hydrogen. It is very essential to conduct the heating in such a manner that a thorough mixing of the two layers in the flask is established, and in order to maintain the evolution of hydrogen, small portions of hydrochloric acid are added now and then, through the condenser. When the reduction is completed, which generally takes from 5 to 8 hours, the hydrocarbon, which forms a colorless layer on top, can either be separated from the acid liquid, or, what sometimes is of advantage, the condenser can be turned down, a little water added to the reaction product, and the hydrocarbon distilled off with the water, separated from the aqueous distillate and dried. The hydrocarbons are thus obtained in a pure state distilling at their right boiling points. Even if the ketones are a little colored, the end products are usually colorless, a decoloration taking place along with the reduction.

The strength of the acid has some influence on the yield. In some cases the use of a comparatively strong acid will give rise to formation of resinous by-products, and thereby a lower yield, whereas, if a more dilute acid be employed, the reduction will go on gradually with a good yield. In other cases the reduction with dilute acid will proceed very slowly and require a long time before completed, while a stronger acid will give a complete reduction in a much shorter time. It is also of great advantage to use a liberal excess of zinc.

Methyl phenyl ketone to ethyl benzene.—Four hundred grams of granulated zinc were left 1 hour in 800 c.c. of a 5% aqueous solution of mercuric chloride. The liquid was then poured off, 100 gm. of methyl phenyl ketone (boiling point 200°–201°) added, and then so much hydrochloric acid (one part of crude hydrochloric acid mixed with three parts of water) that the zinc was just covered. The whole was then heated in a flask with reflux condenser for about 6 hours with occasional additions of small portions of the acid, so as to keep up a lively evolution of hydrogen. In all was used 1000 c.c. of the dilute acid. The ethyl benzene which formed a colorless layer on top of the liquid was then distilled off, separated from the aqueous distillate and dried, or it was simply separated from the acid liquid without distillation.

The yield was 70 gm. of ethyl benzene boiling at 135°–136°, which is about 80% of the theoretical.

If a more concentrated acid was used, for instance, equal parts of crude acid and water, a violent reaction took place after a few minutes' heating, and the reduction was over in less than 2 hours, but in this case the yield would go down to 50–60% of the theoretical.

Ethyl phenyl ketone $C_6H_5 \cdot CO \cdot CH_2 \cdot CH_3$ *to propyl benzene* $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CH_3$.—This ketone was made by heating acetophenone with methyl iodide and potassium hydrate to 100°.[1] Boiling point, 213°–215°.

Twenty-five grams of the ketone were mixed with 100 gm. of amalgamated zinc and hydrochloric acid added (equal parts of crude acid and water) in the usual way. After 5 minutes' heating a strong reaction occurred. The boiling was continued for 4 hours with successive addition of the dilute acid, of which was used 120 c.c altogether. A little water was then added to the reaction product, the colorless layer of propyl benzene distilled off, or separated from the acid liquid and dried. The yield was 20 gm. of propyl benzene boiling at 155°–160°, about 90% of the theoretical.

Propyl phenyl ketone $C_6H_5 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CH_3$ *to butyl benzene* $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$.—The ketone was made by heating a mixture of calcium benzoate and calcium butyrate. The distillation product was fractioned, and the portion boiling at 218°–222° employed. Twenty-five grams of the ketone were reduced in exactly the same way as the ethyl phenyl ketone. There resulted 20 gm. of butyl benzene boiling at 180°–185° and representing a yield of about 88% of the theoretical.

Methyl benzyl ketone $C_6H_5 \cdot CH_2 \cdot CO \cdot CH_3$ *to propyl benzene* $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CH_3$.—In order to obtain this ketone the classic method, dry distillation of the calcium salts, slightly modified, was employed. Dry calcium acetate and calcium phenylacetate were thoroughly mixed in molecular proportions and heated in an iron tube. This was an ordinary gas pipe 3 inches in diameter, closed at the ends with cork stoppers, through each of which went a glass tube, one for condensing the distillate, the other for dry carbonic acid, which was conducted through the apparatus during the whole operation. By carefully regulating the temperature it was possible to obtain a satisfactory yield with this very simple apparatus. The nearly colorless distillate was shaken with sodium

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[1] Nef., Ann., *310*, 318 (1900).

bisulphite solution, and the separated bisulphite compound washed with ether, dried, and the resulting crystalline product decomposed by warming with sodium carbonate solution. The methyl benzyl ketone was then obtained as a colorless liquid, boiling at 214°, in a yield of over 50% of the theoretical.

To 200 gm. of zinc, amalgamated in the usual way, were added 50 gm. of the ketone and 100 c.c. hydrochloric acid (equal parts of crude acid and water). This was boiled for 8 hours with occasional addition of undiluted crude acid; in all, 400 c.c. The propyl benzene which formed a colorless layer on top of the liquid, boiled at 157°–158°. The yield was 40 gm., which is about 90% of the theoretical.

Methyl phenethyl ketone $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CO \cdot CH_3$ *to butyl benzene* $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$.—The ketone was made like the preceding of calcium acetate and calcium hydrocinnamate, purified through the bisulphite compound, and thus obtained as a colorless liquid boiling at 234°. The yield was between 50 and 60% of the theoretical.

The reduction to the hydrocarbon was carried out in exactly the same way as with the methyl benzyl ketone. The resulting butyl benzene boiled constantly at 183°. The yield was practically the theoretical.

From this it will be seen that both ethyl phenyl ketone and methyl benzyl ketone are reduced to propyl benzene, propyl phenyl ketone, and methyl phenethyl ketone to butyl benzene about equally easily. But methyl benzyl ketone and methyl phenethyl ketone are much easier to make, and can, without difficulty, be obtained absolutely pure on account of their capability of uniting with sodium bisulphite, whereas ethyl phenyl ketone and propyl phenyl ketone can only be purified by fractional distillation.

Methyl α-naphthyl ketone to α-ethyl naphthalene. — The ketone was made by the aluminum chloride process and boiled at 293°–296°.

Twenty grams of the ketone were mixed with 80 gm. of amalgamated zinc, hydrochloric acid added (one part of crude acid and two parts of water) and heated for 4 hours with occasional addition of the dilute acid; in all, 120 c.c. The yield was 10 gm. of ethyl naphthalene, boiling at 250°–255°, which is about 55% of the theoretical, but could no doubt be improved considerably by varying the reduction conditions. However, I had no more material at my disposition.

Benzaldehyde to toluene.—In order to reduce benzaldehyde in the wet way it is necessary to heat it with a large excess of concentrated hydroiodic acid in sealed tubes to a high temperature. By this process a number of different hydrocarbons is produced in which also toluene can be detected.[1] Reduced by the contact method of Sabatier and Senderens, benzaldehyde yields both toluene and hexahydrotoluene.

With amalgamated zinc and hydrochloric acid the hydrogenation only takes place in the carbonyl group, and, toluene is produced as the sole volatile product, but, owing to the fact that aldehydes are so much more easily decomposed than the ketones, some resinous by-products are always formed, whereby the yield is decreased.

Two hundred grams of amalgamated zinc and 150 c.c. of crude hydrochloric acid were heated in a flask, and as soon as the evolution of hydrogen started, 50 gm. of benzaldehyde were added drop by drop through the condenser. After all had been added the boiling was continued for 2 hours with occasional addition of crude acid, the contents of the flask was then diluted with water, and the toluene distilled off. There were obtained 20 gm. of toluene boiling at 110°–111°, which is about 46% of the theoretical yield.

ALIPHATIC KETONES

Kraft[2] has converted the higher members of the ketones $C_nH_{2n}O$ to the hydrocarbons C_nH_{2n+2} by treating them with phosphorous pentachloride and heating the formed chlorides with concentrated hydroiodic acid and phosphorus in sealed tubes. A direct reduction has, however, never been done, and it would therefore be of interest to see if this could be accomplished with amalgamated zinc. Besides the above method Kraft[3] has also employed another for obtaining these hydrocarbons, namely,

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[1] Berthelot, Jahresbericht der Chemie, 346 (1867). Markownikoff, Ber., *30*, 1214 (1897).

[2] Ber., *15*, 1689 (1882).

[3] Loc. cit.

heating the fatty acids repeatedly with hydroiodic acid and phosphorus in sealed tubes to 210°–240°. These two methods seem to be the only available for synthesizing these hydrocarbons so extensively found in nature, and mixtures of which are important industrial products, and apart from the fact that these processes are very tedious to perform and can only be carried out with small quantities at a time, there is always, under those conditions, a possibility for decompositions taking place, giving rise to formation of mixtures of different hydrocarbons, which would be difficult to separate.

The reduction with amalgamated zinc and hydrochloric acid took place, however, quite easily, but required considerable more time than in the case of the aromatic ketones. It appeared also to be of advantage to change the zinc during the reaction. The yields were excellent and the obtained hydrocarbons very pure. I must admit, however, that the examined cases are too few to decide if the method can be applied on all the higher members of the series, and I beg to consider the work on the aliphatic ketones as preliminary, to which I will return later.

Methyl nonyl ketone $CH_3 \cdot CO \cdot C_9H_{19}$ *to normal undecane* $C_{11}H_{24}$.—The ketone was isolated from oil of rue. The oil was shaken with sodium bisulphite solution, and the double compound washed with ether, decomposed, and the ketone fractioned. The portion boiling from 224°–230° was employed.

To 200 gm. of granulated zinc were added 50 gm. of methyl nonyl ketone and 200 c.c. of hydrochloric acid (equal parts of crude acid and water). The whole was boiled for 24 hours with occasional addition of crude undiluted acid; in all, 500 c.c. The hydrocarbon which formed a colorless layer on top of the liquid was washed and dried. There were obtained 45 gm., boiling at 192°–210°. By fractional distillation this was separated into two portions. The main portion, 30 gm., boiled constantly at 193°–195°, had a specific gravity of 0.741 at 20°, and was thereby identified as pure undecane. (Kraft[1] gives for undecane, boiling point 194.5° and sp. gr. 0.741.) The smaller portion boiled all the way from 195°–210°, but by repeated fractionations a body boiling at 212°–214° could be obtained.

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[1] Ber., *15*, 1697 (1882).

These conditions are, however, not due to irregularities in the reduction, but no doubt to impurities in the ketone. Williams[1] has pointed out that oil of rue, besides methyl nonyl ketone, contains a little of a higher ketone, probably $C_{12}H_{24}O$ (boiling point 232°), which of course would be obtained together with the methyl nonyl ketone, and it has been my experience that it is not possible to isolate from oil of rue a ketone with an absolute constant boiling point. The presence of this ketone would naturally, by the reduction, give rise to formation of a hydrocarbon $C_{12}H_{26}$ and fully explain the presence of a higher boiling substance in the reduction product. (The boiling point of dodecane is given as 214.5°[2] and 216°.)[3]

The assertion of Williams is, however, doubted,[4] and it seems to be impossible to separate the ketones so as to come to a conclusion. If, on the other hand, it can be proven that normal dodecane is produced by the reduction, this certainly would be an absolute proof for the existence of methyl decyl ketone in oil of rue.

Methyl heptadecyl ketone $C_{17}H_{35}\cdot CO\cdot CH_3$ *to normal nonadecane* $C_{19}H_{40}$.—The ketone was made by distilling a mixture of dry calcium acetate and stearate *in vacuo*. The light yellow distillate solidified on cooling, and was recrystallized from boiling alcohol. The product was then dissolved in ether, whereby stearone (formed as a by-product by the distillation, and which is practically insoluble in ether) remained as white, lustrous plates, the ether evaporated and the residue twice crystallized from alcohol. The melting point of the thus obtained substance was 54°–55° (Kraft[5] gives for methyl heptadecyl ketone 55.5°), and was not changed by further recrystallizations.

Fifty grams of amalgamated zinc, 10 gm. of the ketone and 50 c.c. of hydrochloric acid (equal parts of crude acid and water) were heated in a flask, adding crude acid drop by drop, through the condenser. After 12 hours' boiling, the liquid in the flask was poured from the zinc and cooled. The solidified layer was taken off and mixed with 50 gm. of freshly amalgamated zinc, returned to the

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[1] Ann., *107*, 374.

[2] Kraft, Ber., *15*, 1698 (1882).

[3] Mabery, Am. Chem. J., *19*, 419 (1897).

[4] Gildemeister and Hoffmann, The Volatile Oils, 456 (1900).

[5] Ber., *15*, 1724 (1882).

flask, 50 c.c. acid (1:1) added, and again boiled for 12 hours. This operation was repeated once more. Care was taken to maintain a strong evolution of hydrogen and a thorough mixing of the two layers all the time by adding crude acid. The hydrocarbon formed a colorless layer, which, on cooling, solidified to a snow-white paraffin-like mass, melting at 30°–31°, boiling at 320° at ordinary pressure and with a specific gravity of 0.780 at 32° (Kraft's[1] data for nonadecane are, melting point 32°, boiling point 330° at 760 mm., sp. gr. 0.7774 at 32°). It was quite readily soluble in boiling alcohol, less so in cold, and easily soluble in ether. Shaken with concentrated sulphuric acid at the melting point, the acid was only slightly colored, and the hydrocarbon collected on the top as a water clear liquid. The yield was the theoretical.

Stearone $(C_{17}H_{35})_2 \cdot CO$ *to Normal Pentatriacontane* $C_{35}H_{72}$.—The ketone was made according to the convenient method of Kipping[2] by action of phosphorus pentoxide on pure stearic acid (melting point 69°). After two recrystallizations from boiling alcohol it melted at 86° (Kipping gives 88°).[3]

It was reduced exactly in the same way as the preceding ketone, and the hydrocarbon resulted as a colorless layer, solidifying to a snow-white crystalline mass, melting at 72°–73°. Dissolved in boiling alcohol, it crystallized on cooling in lustrous scales, which, after drying at 100°, melted sharply at 73° (Kraft[4] gives 74.7° for pentatriacontane), and this melting point was not changed on further recrystallizations from alcohol. The hydrocarbon was not in the least affected by concentrated sulphuric acid in the cold, but on warming to 70° for 8 hours some coloration occurred. On diluting with water the hydrocarbon was recovered perfectly white and with the same melting point, 73°. The yield was practically quantitative.

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[1] Ibid., *15*, 1704 (1882).

[2] J. Chem. Soc., *57*, 538 (1890).

[3] Loc. cit.

[4] Ber., *15*, 1715 (1882).

ON THE ESSENTIAL OIL OF JAMAICA GINGER

By Francis D. Dodge
Bayonne, N. J.

As constituents of the essential oil of Jamaica ginger, the following compounds have so far been identified:

1. Camphene, apparently the dextro-variety.[1]
2. Phellandrene, lævo.[2]
3. Sesquiterpene.[3]
4. Small amounts of aldehyde.[4]

In 1900 I observed the presence of an aldehyde, in relative small amount, which could be readily separated as bisulphite compound. This compound is distinctly crystalline, and exhibits the stability characteristic of saturated aldehydes.

On fractioning the oil, either by steam or *in vacuo*, the first sections, consisting largely of terpenes, and showing a dextro-rotation, are found to contain most of the aldehyde, and from these the latter can be most conveniently obtained; the last fractions, with high lævo-rotation, are principally sesquiterpene.

The content of aldehyde was found to be from 2 to 5%, the rich first sections showing up to 11%. To isolate the aldehyde, it was found best to shake the rich fractions with one fifth their volume of a 15% sodium bisulphite solution (free from excess of SO_2), and allow the mixture to stand at a low temperature for several days.

The precipitate can then be filtered by suction, and washed thoroughly with benzene, and dried in the air till free from odor.

The dry precipitate was then pulverized, mixed with a large bulk of water, and the calculated amount of sodium bicarbonate, and the aldehyde driven over with steam.

Thus obtained, it is a colorless mobile liquid, with the strong

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[1] Bertram and Walbaum, J., pr. II, *49*, 18 (1894).

[2] B. & W., J., pr. II, *49*, 18 (1894).

[3] Thresh, Pharm. J., 1881, 243. v. Soden, Pharm. Ztg., *45*, 414. Kremers & Schreiners, Ph. Arch., *4*, 141, 161.

[4] v. Soden, ibid.

characteristic orange odor of decylic aldehyde; S. G. .828 at 15°, optically inactive.

The aldehyde is very sensitive to alkali, and the quantitative separation from the bisulphite compound is not always successful.

The semi-carbazone was prepared in the usual way with semicarbazide hydrochloride and sodium acetate, and recrystallized twice from methyl alcohol. Fine white crystals, m. p. 98° (uncor.).

The preparation of the oxime from the aldehyde was attended with some difficulty, the product having usually a very low melting point. In one case, where the aldehyde had probably been somewhat altered by traces of alkali, a crystalline product, very difficultly soluble in alcohol, and melting at 37°, was obtained. This was evidently not an oxime, but may possibly be the polymer (?) (m. p. 43°) of decylic aldehyde, described by Bagard.[1]

By Mannich's method [2] the oxime was prepared directly from the bisulphite compound, and after recrystallizing from 70% alcohol, melted at 63° (uncor.).

It crystallizes in plates, resembling closely the oxime prepared from the synthetic decylaldehyde, which also was found to melt at 63° (uncor.).

The oxime was readily converted into the nitril by boiling 2 hours with twice its weight of acetic anhydride. The reaction product was washed, neutralized, and distilled with steam. Yield, about 80% of colorless oil, of ketonic odor, resembling oil of rue.

This was saponified by boiling about 50 hours with 15 volumes of $\frac{n}{2}$ alcoholic potassium hydrate, the solution then concentrated, decolorized by a little permanganate, and the acid liberated by a little hydrochloric acid.

The acid thus obtained was liquid at ordinary temperatures, crystallizing at 5°, and on titration showed an acid value of 313.9.

Calc. for $C_9H_{18}O_2$, 347.2
$C_{10}H_{20}O_2$, 325.3
$C_{11}H_{22}O_2$, 301.

The acid, however, was not perfectly pure, showing a slight turbidity on dilution of the alkaline solution, and may probably have contained a small amount of amide.

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[1] Bull. Soc. Ch., *41*, 346.

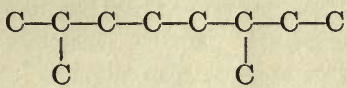
[2] Ber., 195 (1910).

Lack of material prevented further examination of the aldehyde and its denovations.

Although several discrepancies in melting points were observed, it seems probable that the aldehyde is identical with the decylic aldehyde, observed in oil orange;[1] oil cassie (Acacia farnesiana);[2] oil iris;[3] oil coriander.[4]

The structure of this decylic aldehyde is assumed to be normal, since it is stated to yield the normal decoic (capric) acid of m. p. 30°.

The aldehydes, citral and citronellal, however, are known to be derivatives of the nucleus:



$$\mathrm{C-\underset{\substack{|\\ C}}{C}-C-C-C-\underset{\substack{|\\ C}}{C}-C-C}$$

and it is not unreasonable that the natural decyl aldehyde might have the same configuration, in which case the corresponding acid should be identical with Wallach's decylic acid from menthone.[5]

The optical inactivity of the aldehyde, however, argues somewhat against this supposition.

As already noted, the aldehyde is unstable in presence of alkaline reagents. To 0.5 gm., in 2 c.c. methyl alcohol, was added 0.1 c.c. of saturated potassium carbonate solution, and the mixture allowed to stand several days, with occasional shaking. An oily layer gradually separated, and when its volume was constant, was precipitated by water, etc.

The product could not be made to crystallize on chilling, nor could a crystalline oxime or semi-carbazone be obtained.

The aldehyde also appears to undergo a spontaneous alteration on long standing.

A sample of steam-distilled aldehyde, which had been in a nearly full vial for over 9 years, was found to have acquired an odor resembling geraniol, and gave no precipitate with bisulphite solution. It was, however, mostly volatile with steam; the distilled product was readily soluble in 70% alcohol, but did not react

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[1] Schimmel & Co., Ber., Oct., 1900; Stephan, J., pr., *62*, 523.

[2] Walbaum, J., pr., *68*, 235.

[3] Schimmel & Co., Ber., April, 1907.

[4] Schimmel & Co., Ber., Oct., 1909.

[5] Ann., *296*, 126.

with bisulphite, nor with semi-carbazide, nor was it attacked by cold chromic acid solution.

The possibility here indicated of a conversion to a tertiary alcohol was interesting, but lack of material prevented further study of the reaction.

ON SOME DERIVATIVES OF 4-OXY-ISOPHTHALIC ACID

By Francis D. Dodge

Bayonne, N. J.

This acid was prepared by Ost[1] by the action of carbonic anhydride on di-sodic salicylate at 370°. Its occurrence, to a minute extent, in technical salicylic acid appears so far to have escaped attention, although its formation, under the conditions of the salicylic acid synthesis, might reasonably be expected.

At various times, in the steam distillation of large quantities of methyl salicylate, I have obtained, at the end of the operation, small amounts of a crystalline body slowly volatile with steam, and showing the usual reactions of a phenol. On closer examination this was found to be the dimethyl ester of the 4-oxy-isophthalic acid, melting at 96°, already described by Jacobsen.[2]

This compound, however, is, by no means, of uniform occurrence, and its formation must be ascribed to an irregularity in the manufacture of the technical acid.

Any appreciable amount of oxy-isophthalic acid in the synthetic salicylic acid would be indicated by a higher acid value on titration, the former being di-basic, and, in fact, I have frequently obtained titration values slightly above 100% (calculated as salicylic acid), on carefully checking the dry technical acid against the usual acidi-metric standards, or against recrystallized salicylic acid, either natural or synthetic.

Having accumulated some of the dimethyl ester, it appeared of interest to prepare other derivatives, in particular, the mono-ester, which should exist in two isomeric forms, analogous to the mono-esters of camphoric acid, described by Brühl.[3]

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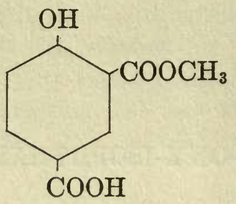
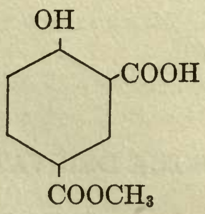
[1] J., pr. 2, *14*, 99.

[2] Ber., *11*, 378.

[3] Ber., *25*, 1806.



Ortho-ester



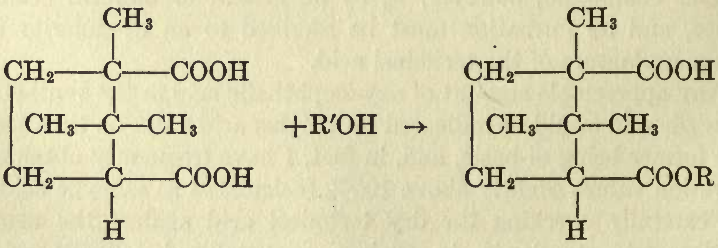
Para-ester

The influence of an ortho-substituent on the reactivity of the adjacent group is well known, and in the cases of di-ortho-substitution, studied especially by Victor Meyer, is so pronounced as to lead to the enunciation of his "ester-law"; a generalization somewhat modified, however, by more recent study.[1]

With a single ortho-group, the retarding effect ("sterische Hinderung") is less evident though, in general, observable.

For example, salicylic (ortho-oxy-benzoic) acid is less readily esterified than benzoic acid, and its esters are also less readily saponified.

In the case of the camphoric esters, Brühl [2] found that the carboxyl group more distant from the methyl was the first to be esterified by alcohol and hydrochloric acid, and also the first to be hydrolyzed by alkali.



By analogy we would expect that the product of partial esterification of 4-oxy-isophthalic acid would be principally the para-ester.

The result of partial hydrolysis of the di-ester could not be so confidently predicted, for, in spite of the probable greater mobility

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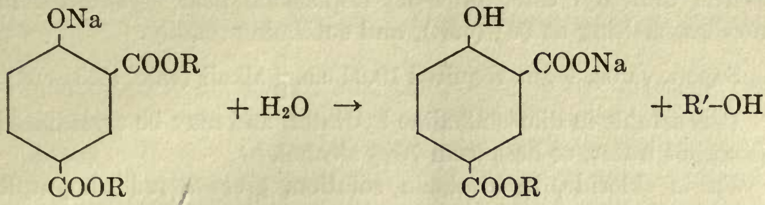
[1] Rosanoff, J., Am. Ch. Soc., 1908, 1895.

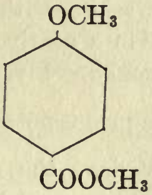
[2] Loc. cit.

of the para-alkyl, we might expect the phenolate, the first product formed, to react more readily with the adjacent ester-group.

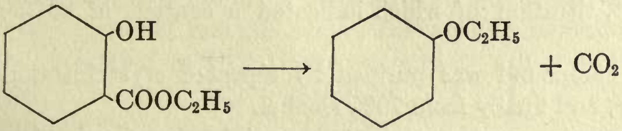


The latter reaction, in fact, appears to occur, the mono-ester being identical, whether obtained by esterification of the acid or hydrolysis of the di-ester. It was hoped that more definite evidence as to the orientation of the mono-ester could be obtained from the products of its destructive distillation; the ortho-ester should yield methyl salicylate, the para-ester, methyl p-oxybenzoate. The reaction here was found, however, to be more complicated, though no difference in the behavior of the two preparations could be observed.

The only recognizable decomposition product was methyl anisate, the formation of which is probably best explained by assigning the para-configuration to the mono-ester.



A somewhat similar reaction was noted by Baly,[1] in the distillation of ethyl salicylate over BaO:



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[1] Arm., *70*, 269.

EXPERIMENTAL

The dimethyl ester of 4-oxy-isophthalic acid crystallizes in needles, melting at 96° (cor.), and subliming readily.

Sapon. value, 1 gm. required 19.04 c.c. $\frac{n}{2}$ alkali (calc. 19.04 c.c.).

It is soluble in dilute alkaline hydrates, and may be crystallized from hot water, or best from 70% alcohol.

Ferric chloride, in alcoholic solution, gives a reddish purple coloration.

Oxy-isophthalic acid, obtained from the ester, showed the properties described by Ost.[1]

On titration, it gives the theoretical value for a dibasic acid, resembling in this respect salicylic acid, rather than the para- and meta-oxy-benzoic acids, which give anomalous results.[2] It is difficultly soluble in cold acetone.

The di-potassium salt is difficultly soluble in alcohol, which fact may be utilized for the purification of the crude acid.

If the latter is treated with a slight excess of $\frac{n}{2}$ alcoholic potassium hydrate, and warmed on steam bath till permanently alkaline, the potassium salt is obtained, as a crystalline precipitate, which can be purified by washing with cold alcohol. From this, the acid is readily obtained in a nearly pure condition.

Mono-ester, by Saponification.—Five grams pure di-ester were treated with 36 c.c. of $\frac{3n}{4}$ aqueous potassium hydrate, at the room temperature. After a few days the di-ester was nearly all in solution, and the mixture was warmed till neutral, and then made slightly alkaline by bicarbonate. On standing, a small amount of di-ester separated, which was filtered off. The filtrate, on acidifying with hydrochloric acid, yielded 4.5 gm. of crystalline product, titration of which indicated a content of 86% mono-ester.

The compound was purified by repeated crystallization from acetone, and finally from 70% alcohol.

It forms transparent plates, and contains 1 molecule of water of

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[1] Loc. cit.

[2] Traube, B., *31*, 1566.

crystallization, drying in the desiccator to an opaque powder, melting at 187° (uncor.).

Analysis: 1.286 gm. lost in desiccator, 0.1060 gm. or 8.3% (calc. for $C_9H_8O_5 \cdot H_2O$, 8.41%). Dry residue required 12.5 c.c. (calc. 12.04 c.c.).

Solubility: Easily soluble in alcohol, acetone, hot water. Ferric chloride gives reddish purple coloration in alcoholic solution.

Action of Heat. — One gram was heated to gentle boiling about 6 hours. The product was a thick oil, with slight odor of phenol. On distillation with water, a small amount of crystalline product was obtained, melting at 42°, and having the characteristic odor of methyl anisate. By saponification anisic acid, melting at 182°, was recognized. From the tarry residue, a white crystalline body, difficultly soluble in ether, was extracted by 70% alcohol. It melted at about 70° and has not yet been identified. No indications of salicylic acid were obtained.

Mono-ester, by Esterification of Acid. — Twenty grams of 4-oxy-isophthalic acid were treated with 40 gm. methyl alcohol and 1 gm. sulphuric acid, at a gentle heat for 5 days, until completely in solution.

The mixture was then filtered, precipitated by water and washed free from sulphuric acid. It was then dissolved in sufficient dilute sodium carbonate solution, filtered from a small amount of di-ester, and precipitated by hydrochloric acid, etc. The product showed, on titration, about 70% mono-ester, and was purified as before.

Analysis: 1.234 gm. lost in desiccator, 0.102 gm. or 8.3% (calc. 8.41%). The residue required 11.64 c.c. $\frac{n}{2}$ KOH (calc. 11.55 c.c.).

The compound melted at 186°–187°, and appeared to be identical with the mono-ester previously obtained.

Action of Heat. — The reaction proceeded as in the first case. Methyl anisate was found in the distillate, which also appeared to contain traces of salicylic acid. The crystalline product from the residue melted at 90°. Para-oxy-benzoic acid could not be detected.

THE OXIDATION ASSAY OF ESSENTIAL OILS

By Francis D. Dodge

Bayonne, N. J.

In a previous paper [1] the writer described a method for the determination of eucalyptol, based on its stability to permanganate solution, the other constituents of the oils in which eucalyptol occurs being, as a rule, oxidized to soluble products.

This process of selective oxidation having been found applicable in a number of other cases, a résumé of the results so far obtained may be of interest.

In general, the reaction was conducted as follows: 10 c.c. of oil are run into a liter flask having a narrow neck. The flask is kept ice-cold, while a saturated solution of potassium permanganate is added in small portions (25 c.c.) with continuous agitation, as long as the reagent is reduced. After the first rather vigorous reaction is over, the amounts added at a time may be increased, but it is well to keep the temperature low.

When the liquid ceases to be decolorized after a few hours' occasional shaking, the precipitated manganese oxide is dissolved by careful addition of a solution of sulphurous acid, or commercial bisulphite of soda, and hydrochloric acid.

Excess of sulphurous acid should be avoided, as it may lead to a separation of a crystalline manganese sulphite.

In general, about 10 c.c. of bisulphite is required for every 100 c.c. of permanganate used.

When all the brown oxide is in solution, the flask is filled with water, the oil allowed to collect in the neck, and later transferred by a capillary pipette to a graduated tube.

In case there is a doubt as to the complete oxidation, the oil obtained may be submitted to a further oxidation in the same way in a smaller flask, such as the well-known "cassia" flask.

[1] Read before N. Y. Section, Am. Chem. Soc., April 8, 1910.

Very few of the compounds, occurring in the volatile oils, are entirely unaffected by *cold* permanganate.

Camphor, fenchone, bornyl acetate, eucalyptol, paraffins, fatty ketones, and a few aromatic compounds are the ones most likely to be encountered.

Others show very different degrees of stability. In some cases, as with borneol and fenchyl alcohol, the oxidation is limited to one stage, the formation of a stable ketone; but, in general, the process is destructive and complete.

The benzene derivatives exhibit various peculiarities, which will be noted below.

For convenience, the various oils examined will be classified according to their principal constituents:

1. *Oils* containing *eucalyptol* (cineol).

Eucalyptus and *Cajeput:* results quantitative; no other stable compound present.

Rosemary: unoxidized oil, about 35%; contains also camphor and bornyl acetate, which can be determined by usual methods.

Spike (lavender): unoxidized, 41%, containing eucalyptol and camphor.

A check assay was made on a mixture of eucalyptol, 25%; bornyl acetate, 10%; borneol, 15%; pinene, 50% (all by weight); unoxidized, 46.5% (by vol.) (calc. 47.5%), showing that the removal of the terpenes, in this way, is complete.

2. *Oils* containing *Fenchone.*

Fennel: the oxidation process is troublesome, owing to the formation of anisic acid (from anethol) which separates as a crystalline precipitate, or as manganese anisate, which is also slightly soluble.

3. *Oils* containing *Borneol* and its esters. The esters are generally stable, while free borneol is converted into camphor.

Pine-Needles, Siberian: (S. G. .907 (25°), O. R. −39.60°, ester, 45.8%); unoxidized, 60% (showing 63.8% ester).

Spruce: (S. G. .919 (15°), O. R. −24.15°, ester, 38.9%); unoxidized, 45% (showing 72.8% ester).

Sage: unoxidized, 16% (not examined).

Valerian, Japanese: unoxidized, 62% (not examined).

Oils containing *Menthol* and *Menthone.*

Menthol is readily oxidized to menthone, which, in turn, is slowly but completely oxidized.

Menthyl acetate appears to be unaffected by the reagent.

Experiments with peppermint oil have not so far led to useful results.

Oils principally *terpenes.*

All terpenes are quickly attacked by the reagent, except camphene, which is slowly oxidized. Camphene seldom occurs in quantity, but its isolation in certain cases can be effected in this way.[1]

Lemon: unoxidized, traces, with a small amount of crystalline acid, probably terephthalic acid. Oxidation slow and apt to be incomplete.

Orange: behaves like lemon oil.

Juniper: unoxidized, 4%, thick oil (not examined).

Turpentine: unoxidized, traces.

Oils principally *olefinic.*

In general, the oxidation is practically complete.

Citronella, Java: unoxidized oil, 1%.

Lemongrass: unoxidized oil, traces.

Lignaloe: unoxidized oil, 0.

Coriander: unoxidized oil, 0.

Petitgrain, S. American: unoxidized oil, 0.

Lavender: unoxidized oil, 5–10%, in which eucalyptol can sometimes be detected. Much of the latter indicates an impure oil.

Oils principally *alicylic.*

Caraway: unoxidized, 0.

Cardamom: unoxidized, 8% (which is principally eucalyptol).

Pennyroyal: unoxidized, 5–10% (apparently menthone, or a similar ketone).

Savin: unoxidized, 9% (not examined).

Oils principally *aliphatic.*

Rue (S. G. .841 at 15°, congealing point 8.1°): unoxidized, 90%.

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[1] Wallach, Ann., *357*, 79.

The oxidized oil showed a congealing point of 9.25°, indicating a concentration of the ketone.

Oils principally *sesquiterpenes* and their derivatives.

The oxidation is slow, and seldom complete.

Cedar: 40% thick oil (not examined).

Copaiba Para: 24% (not examined).

Sandal, East Indian: yielded a mixture of oil, and a crystalline acid, not yet identified.

Oils containing *aromatic* compounds.

1. Hydrocarbons.

Cymene is very slowly oxidized at the ordinary temperature. The principal product is terephthalic acid, with traces of methyl para-tolyl ketone. Cymene can be roughly separated from terpenes in this way.

2. Aldehydes.

Bitter Almond and *Cassia* oils are completely oxidized to benzoic acid.

Cumin yielded about 20% cymene, with terephthalic acid.

3. Phenols.

No general rule can be stated for the behavior of the phenols. Some are readily and entirely oxidized to simple compounds, while others yield intermediate products, which are being examined.

Methyl salicylate and *birch:* unoxidized, 0.

Bay: unoxidized, 0.

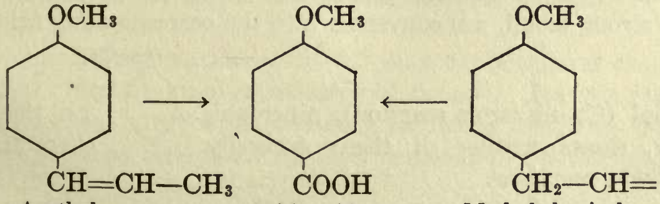
Pimento: unoxidized, 0.

Cloves: unoxidized, 0.

4. Phenolic ethers.

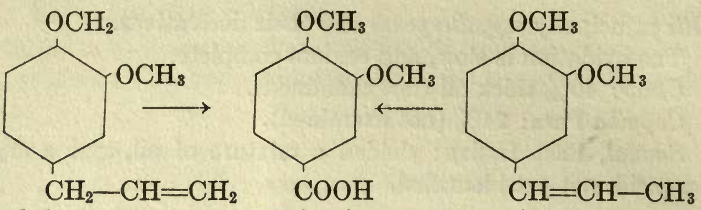
The phenolic ethers occurring in the oils show rather interesting peculiarities on oxidation.

Anethol and its isomer, methyl chavicol, are converted almost quantitatively into the corresponding anisic acid.



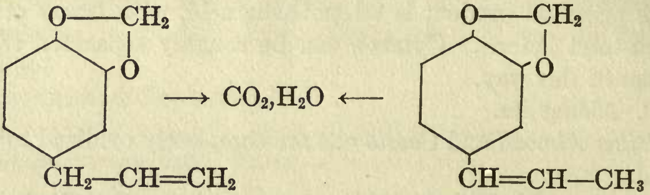
Anethol Anisic acid Methyl chavicol

Methyl eugenol and methyl iso-eugenol also give a fair yield of veratric acid.



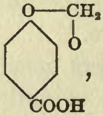
Methyl eugenol Veratric acid Methyl iso-eugenol

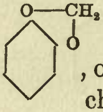
But safrol and iso-safrol are destructively oxidized to soluble products.



Safrol Iso-safrol

It is evident that the methylene radical does not confer a similar stability to the phenol group, which is effected by a substitution of methyl, or other alkyl, for hydrogen. Whether this is due to a condition of strain in the five-atom ring, is a question which may be left for future consideration.

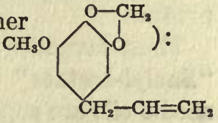
A similar difference in behavior is shown by the acids mentioned. Thus, anisic and veratric acids are not attacked by permanganate, while piperonic acid, , is readily and completely oxidized.

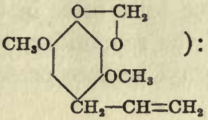
It is also rather remarkable that, while benzaldehyde and anisaldehyde are quickly oxidized on exposure to the air, and, with strong alkali, are converted into the corresponding acid and alcohol (Cannizzaro's reaction), piperonal, , on the contrary, shows neither of these generally characteristic aldehyde reactions.

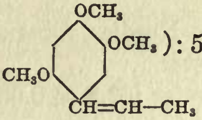
The examination of oils containing anethol, or methyl chavicol, by this method, is inconvenient, as was noted in the case of oil fennel.

Sassafras: yielded 5% of oil, in which camphor could be detected.

Cinnamon-leaf (containing about 10% methyl eugenol): yielded a small amount of veratric acid.

Nutmeg (containing myristicin, a methylen-ether ): yields traces of oil, with cymene odor.

Parsley (containing apiol, ): 5–6% oil (not further examined).

Calamus (containing asarone, ): 5–6% oil, with a little crystalline acid.

In conclusion, a few useful applications of this method may be noted:

1. For the detection of petroleum products in commercial spirits of turpentine.

Ten cubic centimeters of oil require 800–850 c.c. of the permanganate solution. Little regard may be paid to the temperature, except to prevent loss by evaporation; and the possible formation of cymene, etc., by the usual polymerization, with sulphuric acid, is eliminated.

2. For the detection of petroleum products in oil of citronella.

As is well known, the Ceylon oil is apt to contain products from Russian petroleum, which can be conveniently detected by this method.

The unoxidized portion of the oil may contain some camphor (borneol being a normal constituent of the oil). This may be removed by treatment with cold 80% sulphuric acid, and the insoluble paraffins recognized by their immiscibility with castor oil at 0°.

3. To differentiate between bornyl acetate and the isomeric linalyl-, geranyl-, and terpinyl-acetates.

Of these esters, bornyl acetate alone is stable to the reagent, and the method supplies a means of determining this compound when necessary.

The ester content of many of the oils is generally reported as a single ester, whereas, in all probability, a mixture of such is present.

Thus, lavender and bergamot oils are valued largely by their "linalyl-acetate" content, while rosemary, spruce, and pine-needle oils are supposed to contain "bornyl-acetate."

If we determine total ester in the oil, and, after oxidation, the ester content of the remainder, we have data for the estimation of the actual bornyl acetate present.

For example:

Oil of Pine-Needles, Siberian (previously noted).

Total ester	45.8%
Stable ester (63.8 × 0.60)	38.3
Oxidizable ester	7.5%

(which may be terpinyl-acetate)

Oil Spruce (previously noted).

Total ester	38.9%
Stable ester (72.8 × 0.45)	32.7
Oxidizable ester	5.2%

Oil Rosemary, 0.903(25°).

Total ester	5.78%
Stable ester (3.8 × 0.35)	1.33
Oxidizable ester	4.45%

Fenchyl acetate, if present, would probably show the same stability as bornyl acetate, but its detection is not easy.

The same method has been used by Hesse[1] for differentiating benzyl- and linalyl-acetates in his analyses of the oil of jasmine.

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[1] Ber., *32*, 565.

THE REACTION BETWEEN SELENIC ACID AND TOLUENE

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In 1909 one of us published an account[1] of the reaction between benzene and selenic acid. This reaction resulted in the formation of benzeneselenonic acid and was accomplished by heating selenic acid with benzene for many hours on the water bath or in sealed tubes at 120°.

In 1910 the senior author, with the assistance of Mr. Pierre Drewsen, began a study of the corresponding reaction between selenic acid and toluene. We heated the reacting substances together in an Erlenmeyer flask, fitted with return condenser, on a water bath. A rather violent reaction took place before the water bath had reached the boiling temperature. This reaction subsided after a time, and the heating was continued during several working days. During the heating a colorless crystalline product appeared, but gradually disappeared as the heating progressed. The product after heating consisted of an acid layer, dark red in color, and a layer of unchanged toluene. When the acid layer was poured into water, a yellow insoluble substance was deposited which was practically insoluble in all the ordinary solvents, but could be oxidized by nitric acid, forming a yellow acid which would dissolve in sodium carbonate. This substance has not been identified. The acid solution contained what appeared to be tolueneselenonic acids, but the work was interrupted at this point by the graduation of Mr. Drewsen from college. In the following year the work was taken up by the present writers.

As a violent reaction had taken place when toluene and selenic

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[1] Am. Chem. J., *41*, 326.

acid were heated together, we decided to try the effect of allowing the substances to stand in contact during the summer at ordinary temperatures. Enough selenic acid was placed in an Erlenmeyer flask to cover the bottom and an excess of toluene was added. An outlet from the flask was provided through a U tube containing barium hydroxide, suitably protected from the carbon dioxide of the air by a second similar tube. Within a few hours there was evidence of pressure within the flask, and after a day or two a precipitate of barium carbonate formed in the first U tube. Carbon dioxide is, therefore, one of the products of the reaction, but its production was not attended by any precipitation of selenium or any evidence of carbonization. An explanation of this part of the reaction will be offered presently.

The flasks containing the reacting substances were allowed to stand for 4 to 6 months at room temperature. Probably equilibrium is reached in considerably less time than this, but we have no data on this point. At the end of the time mentioned the flasks contained a lower dark red viscous layer containing the selenic acid and products of reaction, and an upper clear layer of toluene containing practically nothing else. The acid layer, which originally consisted of about 75 gm. of selenic acid, sp. gr. 2.54, was separated from the toluene layer and added to about 500 c.c. of water. A relatively small amount of red oil separated, most of the acid layer going into solution in the water. Filtering through a wet filter removed the red oil, which also contained a solid crystalline substance also insoluble in water. For convenience of reference we shall speak of these products as A, B, and C respectively.

A. *The Acid Solution.*—This solution was exactly neutralized with barium hydroxide solution, using phenolphthalein as indicator. The precipitated barium selenate was filtered off and the resulting solution of barium salt evaporated to dryness on the water bath. The crystalline, slightly reddish-brown residue was then pulverized and extracted with chloroform for several days, using a Sohxlet apparatus. This treatment removed a red oily substance that proved to be identical with the red oil, B, referred to above. The residual barium salt was dissolved in water, recrystallized and analyzed. It is very soluble in water, dissolving in about twice its weight of water. Analysis shows it to be the barium salt of tolueneselenonic acid crystallizing with 2 molecules of water.

Air-dried salt, 0.7502: H_2O lost at 160° 0.0430.

Substance	H_2O Calculated for $C_{14}H_{14}O_6Se_2Ba \cdot 2H_2O$	H_2O Found
0.7502	5.90 per cent	5.73 per cent

Anhydrous salt, 0.7072; $BaSO_4$, 0.2872

Substance	Calculated for $C_{14}H_{14}O_6Se_2Ba$	Found
0.7072	Ba 23.91 per cent	23.90 per cent

In order to obtain the free tolueneselenonic a weighed amount of the barium salt was dissolved in water and the calculated amount of 0.1 N sulphuric acid was added. The solution was filtered from barium sulphate, evaporated to dryness *in vacuo* over sulphuric acid, crystallized from chloroform and finally washed with ether. The solid residue had no definite melting point. It began to melt at 68° and finally became clear at about 100°. Evidently the substance was a mixture, and since the analysis of the barium salt corresponded so exactly to the theoretical amounts for the barium tolueneselenonate, it seemed probable that the substance was a mixture of the ortho and para tolueneselenonic acids. By recrystallizing from chloroform a very little of a product was finally obtained which melted at 197°–198° with decomposition. There was not enough of it to do anything further with it. So far as we could discover the solubilities of the two isomers are so nearly alike that it will be necessary to work on a larger scale in order to effect a satisfactory separation.

Having failed to separate the tolueneselenonic acids, we determined to try reducing them to the seleninic acids, hoping that sufficient difference in solubility would be manifested to enable us to effect a separation. In this we were not disappointed. We passed hydrogen chloride gas into a concentrated solution of the tolueneselenonic acids. Considerable heat was developed and a white precipitate formed, which became yellow, and chlorine was evolved. Subsequent investigation showed that the precipitation was practically complete. The precipitate was filtered off, dissolved in boiling water and allowed to cool. During the boiling the yellow color entirely disappeared. On cooling a beautifully crystalline product separated in long silky white needles, m. p. 160°. This product is rather difficultly soluble in boiling water and almost quantitatively insoluble in cold water. It is also soluble in alcohol, chloroform, and benzene.

The mother-liquor from the product just described was evaporated to a small volume and allowed to cool. Another product separated in wart-like masses of short white needles, m. p., 99°–101°. This product also dissolves in alcohol, chloroform, and benzene, but not in ether or petroleum ether. Both products are acids and appear to contain water of crystallization (?), but attempts to remove this water resulted in more or less decomposition.

The product melting at 160° gave the following results on analysis: Titrated with 0.1 N sodium hydroxide; 0.5580 gm. required 25.02 c.c.; calculated, 25.22 c.c.; 0.2799 gm. required 12.35 c.c.; calculated, 12.65 c.c. for $CH_3 \cdot C_6H_4 \cdot SeO_2H \cdot H_2O$.

The acid melting at 99°–101° when titrated with 0.1 N sodium hydroxide gave the following results: 0.4300 gm. required 20.20 c.c.; calculated, 20.25 for $CH_3 \cdot C_6H_4 \cdot SeO_2H\frac{1}{2}H_2O$.

The products obtained by reducing the tolueneselenonic acids with hydrogen chloride appear, therefore, to be hydrates of the tolueneseleninic acids. Work with these substances has been temporarily interrupted, so that we are not able to say definitely which of them is ortho and which para tolueneseleninic acid, but since an oxidation product of the higher melting seleninic acid did not give salicylic acid when fused with potassium hydroxide, it seems probable that the acid melting at 160° is para tolueneseleninic acid, and the one melting at 99°–101° is ortho tolueneseleninic acid. Further work on these acids and their derivatives is in progress and will be reported in a subsequent communication.

Seventy-eight grams of selenic acid with excess of toluene gave 30 gm. of the anhydrous barium tolueneselenonates, corresponding to about 23 gm. of the mixed tolueneselenonic acids.

B. *The Red Oil.*—The red oil obtained as described above was removed from the crystals (C) by washing with ether, in which the crystals are very slightly soluble. The product of the chloroform extraction of the barium tolueneselenonate was also added. After distilling off the ether about 5 gm. of a heavy very viscous red syrup remained in the flask. This was distilled under diminished pressure (18–20 mm.), and boiled at 201°–202°. The distillate solidified in the receiver to a light yellow crystalline mass, which when crystallized from ether melted at 69.5°–70.5°. About 1 gm. of this distillate was boiled for a few minutes with 10 c.c. of concentrated nitric acid. It dissolved and a white precipitate was formed when the nitric acid solution was poured into 40 c.c. of water. This precipitate redissolved on warming. About 10 c.c. of concentrated hydrochloric acid were added and a heavy pale yellow precipitate formed. This substance, dried and washed with ether, melted at 177°–178° with decomposition.

In 1895 Zeiser[1] prepared ortho and para ditolyl selenides by the action of mercury ditolyl on selenium when heated in closed tubes. Ortho ditolyl selenide boils at 186° under 16 mm. pressure. Para ditolyl selenide boils at 196°–196.6° under the same pressure. By heating with nitric acid and precipitating with concentrated hydrochloric acid he obtained the dichlorides of these selenides. Ortho ditolyl selenide dichloride melts at 152°–153° with decomposition. The para compound melts at 177°–178° with decomposition. There is therefore no doubt that the red oil, referred to as B, is para ditolyl selenide.

Thirteen grams of para ditolyl selenide were heated with 45 gm. of potassium permanganate and 1500 c.c. of water for 24 hours. The permanganate was then completely decolorized, and subsequent examination showed that about 2 gm. of the selenide remained unchanged. The manganese dioxide and unchanged selenide were filtered off from the alkaline solution. The latter was evaporated to about 200 c.c. and acidified with 28 c.c. of concentrated hydrochloric acid. A heavy white precipitate was formed. This substance proved to be an acid, insoluble in water, almost insoluble in boiling alcohol, and insoluble in the ordinary organic solvents. It was titrated with boiling 0.1 N sodium hydroxide with the following result: 0.3510 gm. required 19.63 c.c. of 0.1 N sodium hydroxide. Calculated for $(HO_2C \cdot C_6H_4)\ SeO_2$, 19.72 c.c.

The selenium determination was less satisfactory, but serves at least to show the nature of the compound. About 5 gm. of solid sodium hydroxide and 1 c.c. of water were placed in a nickel crucible together with a weighed amount of the substance. The

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[1] Ber., *28*, 1671.

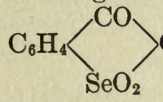
crucible was heated in an air bath until the mass was fused. Sodium peroxide was then added in small portions, heating between each addition, the temperature being gradually raised. The mass was finally heated to quiet fusion. The crucible and contents were boiled with water, and the selenium finally precipitated from the solution, after filtering, by means of hydrochloric acid and sodium bisulphite. The portion left on the filter was dissolved in nitric acid, evaporated to dryness, dissolved in water, and the selenium precipitated as in the case of the other solution. The selenium from both precipitations was weighed on a Gooch filter as usual. This method is a modification of the well-known sodium peroxide method for determining sulphur in organic compounds. It seems to promise an excellent method of determining selenium in organic compounds, but evidently requires more experience than I have yet had with it before perfectly satisfactory results are obtainable. 0.6015 gm. of the substance gave 0.1288 gm. of selenium, or 21.41% Se. Calculated for $(HO_2C \cdot C_6H_4)_2SeO_2$, 22.41% Se.

This oxidation product of para ditolyl selenide seems, therefore, to be diphenyleneselenone-*pp'*-dicarboxylic acid. It is practically insoluble in all of the ordinary solvents except alcohol, in which it is very slightly soluble. It melts at 283° with decomposition.

C. *The Crystals Insoluble in Water.*—The crystals that were formed in the original reaction between the selenic acid and toluene dissolved easily in chloroform and in boiling alcohol. They were dissolved in the latter solvent and boiled with animal charcoal. The filtered solution was clear and almost colorless. From it the substance crystallized in colorless stout hexagonal prisms with well-marked pyramidal ends. They melted at 183° without decomposition. The substance is insoluble in water, ether, or petroleum ether, but dissolves very easily in chloroform, hot alcohol, and ethyl acetate. It is also fairly soluble in benzene. It is not affected by heating to 250°, but at some temperature not greatly above this point it decomposes very rapidly with evolution of gas, making it difficult to analyze by combustion. The substance is perfectly neutral. It is not dissolved or changed by boiling with sodium hydroxide. It does not reduce potassium permanganate. The alcoholic solution is neutral to litmus. The yield was about 10% of that of the tolueneselenonic acids.

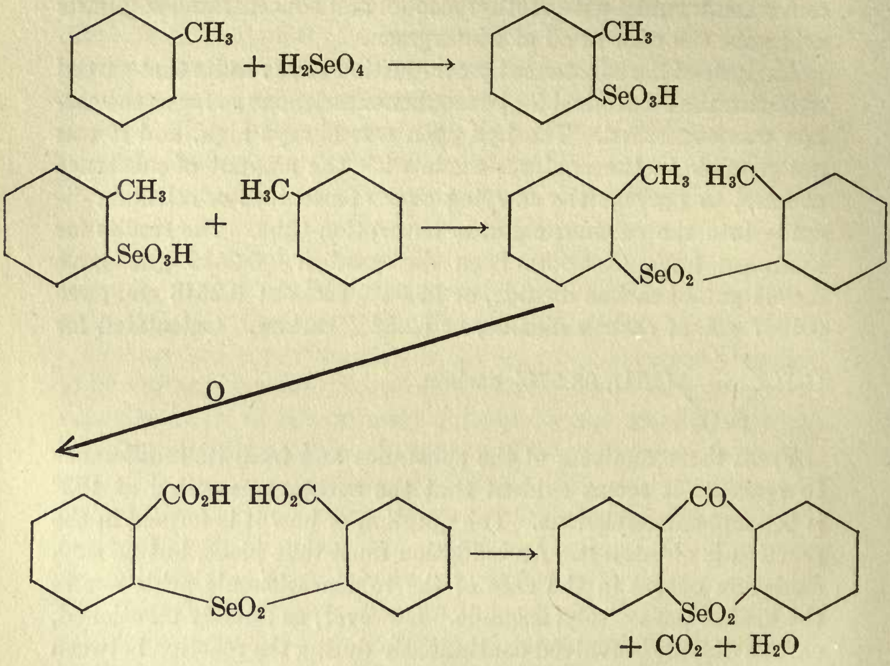
A gram of the substance melting at 183° was fused for 6 hours with potassium hydroxide at 180°. The reaction product was dissolved in water, acidified with hydrochloric acid, and shaken with ether. The ether, on evaporation, deposited a few crystals which were not pure enough to give a satisfactory melting point, but gave the characteristic test for salicylic acid with ferric chloride, and when warmed with methyl alcohol and concentrated sulphuric acid gave the odor of oil of wintergreen.

Analysis of the substance by combustion gave results that agreed well with the theoretical for benzophenoneselenone so far as the carbon was concerned. The hydrogen was always high, and it was not possible in the analyses made with the amount of substance at hand to prevent the carrying over of selenium or selenium dioxide into the calcium chloride absorption tube. The results for hydrogen have therefore been disregarded. 0.2536 gm. gave 0.4931 gm. of carbon dioxide, or 53.04% carbon; 0.2548 gm. gave 0.4937 gm. of carbon dioxide, or 52.82% carbon. Calculated for



$C_6H_4\left\langle\begin{array}{c}CO\\SeO_2\end{array}\right\rangle C_6H_4$, 53.57% carbon.

From these analyses of the substance and from its indifference to reagents it seems evident that the substance melting at 183° is benzophenoneselenone. The question of how it is formed in the reaction is of interest. An oxidation must take place, but no such oxidation occurs in the case of the tolueneselenonic acids nor in the case of para ditolyl selenide. However, as already mentioned, carbon dioxide is evolved continuously during the reaction between selenic acid and toluene, and it seems improbable that this carbon dioxide comes from the breaking down of the benzene ring. There is no deposition of either carbon or selenium, as is generally the case when organic selenium compounds are destructively oxidized. The following explanation is offered as being in harmony with the observed facts in the case. There should be a chance for the formation of ortho ditolyl selenide as well as of the para compound, but none of the ortho compound has been found. Supposing that the ortho compound was formed, if it were oxidized to the corresponding dicarboxylic acid, then this acid could lose water to form an anhydride, since it is a diortho compound. This anhydride would consist of an eight-membered ring, however, while, if carbon dioxide is also eliminated, the resulting ketone ring would contain only 6 atoms, the case being analogous to the formation of cyclopentanone from adipic acid. The following equations show the probable course of the reaction, according to this explanation:



In beginning this investigation we had in mind the possibility of the oxidation of the methyl group of the toluene, and rather expected that we should obtain dibasic acids corresponding to sulphobenzoic acids. Had such oxidation taken place before substitution, it should have resulted in the formation of a meta selenobenzoic acid. Such oxidation does not take place except in the case just discussed.

CONCLUSIONS

When toluene and concentrated selenic acid are allowed to stand in contact, a reaction takes place at room temperature, which is complete after some months. Four products of this reaction have been found, not including carbon dioxide, which is also a product of the reaction. These products are as follows: Ortho and para *tolueneselenonic acids*, very soluble in water, and not possible to separate, working with the quantities at our disposal. Para ditolyl selenide, m. p. 69°–70°, which oxidizes smoothly by means of potassium permanganate to *diphenyleneselenone-pp′-dicarboxylic acid, m. p.* 283°. *Benzophenoneselenone, m. p.* 183°.

The tolueneselenonic acids are reduced by hydrochloric acid to the corresponding seleninic acids, which are still under investigation. They appear to be hydrated acids melting at 99°–101° and 160° respectively. The acid melting at 160° is easily oxidized by potassium permanganate to a dibasic acid, the acid potassium salt of which melts and decomposes at 264°. Since this substance when fused with potassium hydroxide does not yield salicylic acid, it is probably a para compound.

No evidence of the oxidation of methyl groups to carboxyl by selenic acid is found, except in the formation of benzophenoneselenone, for the formation of which an explanation is offered, which also explains the evolution of carbon dioxide.

THE CHANGE IN REFRACTIVE INDEX WITH TEMPERATURE — III

BY K. GEORGE FALK

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The refractive indices for a number of organic liquids were measured for the sodium and three hydrogen lines of the spectrum at temperatures ranging from 15° to 75° and the results communicated in the two preceding articles.[1] These were discussed briefly in connection with the three expressions for refractive power, I $(n^2-1)/d$, II $(n-1)/d$, and III $(n^2-1)/(n^2+2)d$, and it was pointed out that I gave decreasing values as the temperature increased, II in some cases increasing, in others decreasing values, and III increasing values for substances not tautomeric. The results obtained from expression III (multiplied by the molecular weight of the substance studied) were compared with the values calculated from Brühl's constants for atomic refractions.

Recently Eisenlohr,[2] at the suggestion of Professor Anwers, determined more accurate values for the atomic refractions, using the best data available and supplementing and completing them with work of his own. These will be used here for a more careful comparison with the refractions determined experimentally over the range of temperature indicated.

The manner in which the experimental data given in the first two papers were obtained may be reviewed briefly. A Pulfrich refractometer with hot water jacket, etc., was used, and the refractive indices were measured for the four lines (three hydrogen α, β, γ, and one sodium D_1) at from 27 to 47 temperatures between 15° and 75° for each substance. The refractive indices for each line plotted against the temperatures indicated straight line functions for which the equations were calculated. The results

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[1] Jour. Amer. Chem. Soc., *31*, 86, 806 (1909).
[2] Z. physik. Chem., *75*, 585 (1910).

to be quoted here are taken from these equations (or plots), as in this way accidental errors are eliminated to a great extent. For the densities, referred in every case to the density of water at 4°, about six measurements for each substance through the same temperature range sufficed for the calculation of an equation (straight line) for the relation between density and temperature.

The substances to be discussed contain carbon, hydrogen, and oxygen, and no conjugate system of double bonds. They include a hydrocarbon, an alcohol, an acid, a ketone, and three esters.[1]

The comparison of the experimental results with those calculated by the use of the atomic refractions and dispersions of Eisenlohr is shown in Table I. Column 1 contains the name of the substance, its empirical formula, and the spectrum lines for which the molecular refractions and dispersions are given in the succeeding columns. Column 2 contains the values calculated by use of the atomic refractions and dispersions, columns 3 and 4 the values found experimentally at 20° and at 80° respectively. In column 5 are shown the percentage deviations of the experimental values at 20° from the calculated referred to the latter, and in column 6 the percentage deviations of the experimental values at 80° from the calculated (at 20°). In columns 7 and 8 are shown the numerical differences between the molecular refractions found at 20° and 80° respectively (given in columns 3 and 4) and the corresponding molecular refraction as calculated (column 2).

In considering the results shown in Table I, the percentage differences and then the numerical differences between the calculated and observed results will be taken up first for the molecular refractions and then for the molecular dispersions.

At 20° the greatest difference between the observed and calculated results for the molecular refractions is 0.50% (M_γ for isobutyl acetate). The agreement between the two sets is practically perfect for *n*-heptyl alcohol; the experimental values are smaller than the calculated values for two substances (*n*-butyric acid, 0.1%, and ethyl *n*-butyrate, 0.2–0.3%) and larger for four sub-

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[1] The substances containing benzene rings for which results were given in the first two papers are not included here in view of the extended study of benzene and its substitution products promised by Eisenlohr (Z. physik. Chem., *79*, 129 (1912).

TABLE I. — COMPARISON OF THE EXPERIMENTAL AND CALCULATED VALUES FOR THE MOLECULAR REFRACTIONS AND DISPERSIONS.

		Calc. 20°	Fd. 20°	Fd. 80°	$\frac{\text{Fd. }20^\circ - \text{Calc. }20^\circ}{\text{Calc. }20^\circ} \times 100$	$\frac{\text{Fd. }80^\circ - \text{Calc. }20^\circ}{\text{Calc. }20^\circ} \times 100$	Fd. 20° −Calc. 20°	Fd. 80° −Calc. 20°
Diisoamyl ($C_{10}H_{22}$)	M_α	48.15	48.29	48.57	0.29	0.87	0.14	0.42
	M_D	48.38	48.51	48.81	0.27	0.89	0.13	0.43
	M_β	48.91	49.05	49.34	0.29	0.88	0.14	0.43
	M_γ	49.34	49.51	49.82	0.34	0.97	0.17	0.48
	$M_\beta - M_\alpha$	0.76	0.76	0.76	0	0	0	0
	$M_\gamma - M_\alpha$	1.20	1.22	1.25	1.7	4.2	0.02	0.05
n-Heptyl alcohol (C_7H_{10})	M_α	35.89	35.90	36.07	0.03	0.50	0.01	0.18
	M_D	36.05	36.05	36.27	0	0.61	0	0.22
	M_β	36.44	36.43	36.61	−0.03	0.47	−0.01	0.17
	M_γ	36.76	36.77	36.95	0.03	0.52	0.01	0.19
	$M_\beta - M_\alpha$	0.55	0.53	0.54	−3.6	−1.8	−0.02	−0.01
	$M_\gamma - M_\alpha$	0.87	0.87	0.88	0	1.2	0	0.01
n-Butyric acid ($C_4H_8O_2$)	M_α	22.10	22.09	22.27	−0.05	0.77	−0.01	0.17
	M_D	22.21	22.18	22.39	−0.14	0.81	−0.03	0.18
	M_β	22.45	22.42	22.63	−0.14	0.80	−0.03	0.18
	M_γ	22.65	22.63	22.84	−0.09	0.84	−0.02	0.19
	$M_\beta - M_\alpha$	0.35	0.33	0.36	−5.7	2.9	−0.02	0.01
	$M_\gamma - M_\alpha$	0.55	0.55	0.57	0	3.6	0	0.02
Methyl hexyl ketone (C_8H_{10})	M_α	38.97	39.07	39.37	0.26	1.03	0.10	0.40
	M_D	39.16	39.23	39.55	0.18	1.00	0.07	0.39
	M_β	39.59	39.67	40.02	0.20	1.09	0.08	0.43
	M_γ	39.95	40.05	40.40	0.25	1.13	0.10	0.45
	$M_\beta - M_\alpha$	0.63	0.60	0.64	−4.8	1.6	−0.03	0.01
	$M_\gamma - M_\alpha$	0.99	0.99	1.03	0	4.0	0	0.04
Isobutyl-acetate ($C_6H_{12}O_2$)	M_α	31.41	31.56	31.80	0.48	1.24	0.15	0.39
	M_D	31.56	31.69	31.95	0.41	1.24	0.13	0.39
	M_β	31.90	32.03	32.30	0.41	1.25	0.13	0.40
	M_γ	32.19	32.35	32.59	0.50	1.24	0.16	0.40
	$M_\beta - M_\alpha$	0.50	0.48	0.50	−4.0	0	−0.02	0
	$M_\gamma - M_\alpha$	0.78	0.79	0.79	1.3	1.3	0.01	0.01
Ethyl *n*-butyrate ($C_6H_{12}O_2$)	M_α	31.41	31.35	31.59	−0.19	0.57	−0.06	0.18
	M_D	31.56	31.49	31.73	−0.22	0.54	−0.07	0.17
	M_β	31.90	31.81	32.09	−0.28	0.60	−0.09	0.19
	M_γ	32.19	32.11	32.38	−0.25	0.59	−0.08	0.19
	$M_\beta - M_\alpha$	0.50	0.47	0.50	−6.0	0	−0.03	0
	$M_\gamma - M_\alpha$	0.78	0.77	0.79	−1.3	1.3	−0.01	0.01
Isoamyl-acetate ($C_7H_{14}O_2$)	M_α	36.01	36.15	36.36	0.39	0.97	0.14	0.35
	M_D	36.18	36.29	36.56	0.30	1.05	0.11	0.38
	M_β	36.57	36.69	36.94	0.33	1.01	0.12	0.37
	M_γ	36.90	37.03	37.30	0.35	1.08	0.13	0.40
	$M_\beta - M_\alpha$	0.57	0.55	0.57	−3.5	0	−0.02	0
	$M_\gamma - M_\alpha$	0.89	0.89	0.94	0	5.6	0	0.05

stances (diisoamyl, 0.3%, methyl hexyl ketone, 0.2–0.25%, isobutyl acetate, 0.4–0.5%, and isoamyl acetate, 0.3–0.4%). It is interesting to note for the three esters, that the values for the two isomers deviate in opposite directions from the calculated result, while the two acetic esters (homologues) deviate in the same direction.

At 80° the experimental values are greater throughout than the calculated values (for 20°), the difference varying from 0.47% to 1.25%. The relative differences for the experimental 20° and 80° values are perhaps of more significance. The average change for the seven substances is 0.74% of the calculated value (varying from 0.52% for *n*-heptyl alcohol to 0.91% for *n*-butyric acid). The smallest change for the difference in temperature (0.47% for M_α for *n*-heptyl alcohol) is larger with one exception (0.50% for M_γ for isobutyl acetate) than the largest difference between the experimental and calculated results at 20°.

At 20° the numerical deviations between the experimental and calculated results for the molecular refractions range from -0.09 to 0.17, with a mean value for all the substances of 0.06. At 80° the numerical deviations range from 0.17 to 0.48, with a mean value of 0.31. The average difference between the means for the difference in temperature of 60° is therefore 0.25.

The percentage differences between the experimental and calculated values for the molecular dispersions, $M_\beta - M_\alpha$, range from 0% to -6.0%, mean -3.9%, at 20°; and -1.8% to 2.9%, mean 0.4%, at 80°. The differences between the calculated and experimental results for $M_\gamma - M_\alpha$, at 20°, range from -1.3% to 1.7%, mean 0.2%; and at 80°, from 1.2% to 5.6%, mean 3.0%. The numerical differences are perhaps a fairer comparison. For $M_\beta - M_\alpha$, at 20°, the largest difference is -0.03, mean -0.02; at 80°, $+0.01$, mean 0.001. For $M_\gamma - M_\alpha$, at 20°, the largest difference is $+0.02$, mean 0.003; at 80°, $+0.05$, mean 0.027.

To sum up the results which have been given, it will be seen that there is a small and in most cases negligible difference between the experimental and calculated values for the molecular refractions at 20°. This difference is greater for the molecular refractions determined at 80° compared with the values calculated for 20°, but the difference is always in the same direction and does not vary greatly in magnitude. It would appear, therefore, that the determination of the molecular refraction at temperatures higher than the ordinary would give results as useful for the determination of chemical structure as those obtained at the ordinary temperature, if the small but (more or less) regular increase in the refractive power with the temperature be taken into account. The calculation of temperature coefficients for the constants of atomic refraction of Eisenlohr would doubtless be of value, but at present the data at hand are not of sufficient extent and accuracy to warrant this. For the molecular dispersions the agreement for $M_\beta - M_\alpha$ between the experimental and calculated values at 20° is poor. The experimental values for 80° agree much better with the calculated values. For $M_\gamma - M_\alpha$ there is a very good agreement between the two sets at 20°, while at 80° the experimental values show an increase. In the use of the molecular dispersions at different temperatures, this increase with the rise in temperature must be taken into account.

The study of the change in refractive index with temperature was undertaken initially with the object of investigating tautomeric substances. The isolation of the two forms of aceto acetic ester [1] and the probable isolation of the different forms of acetyl acetone [2] make the further prosecution of this part of the subject unnecessary.[3] The results given in the first paper for these substances will therefore not be discussed further.

One more phase of the subject will be taken up. Since the Lorentz-Lorenz expression for molecular refraction does not give constant values for different temperatures, various modified expressions have been proposed. The expression $(n^2-1) / (n^2+a) d$, which may be derived from Maclaurin's dispersion formula [4] for transparent media under certain assumptions, and in which a depends for its value "on the influence of the electrons in the immediate vicinity of the point where the disturbance is considered," was spoken of in the second paper and the average values of a

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[1] Knorr, Rothe, and Averbeck, Ber., *44*, 1138 (1911).

[2] Knorr, Ber., *44*, 2771 (1911).

[3] Cf. the work of K. H. Meyer, Lieb. Ann., *380*, 212 (1911); Anwers, Ber., *44*, 3514–42 (1911); Ber., *45*, 963 (1912); and Hantzsch, Ber., *45*, 559 (1912) along these lines.

[4] "On Optical Dispersion Formulæ," Proc. Roy. Soc., A, *81*, 367 (1908).

which will give constant values in the above expression listed. The values of *a* for each line of the seven substances discussed in this paper which when substituted in the above expression will give a constant value for the temperature range of 20° to 80° for that line are given in Table II.

TABLE II. — VALUES OF *a* IN THE EXPRESSION $(n^2-1)/(n^2+a)\,d$

	a	*d*	β	γ
Diisoamyl	3.9	3.8	3.6	4.0
n-Heptyl alcohol	3.7	4.6	3.7	3.9
n-Butyric acid	5.7	6.6	6.9	6.6
Methyl hexyl ketone	5.2	5.7	5.7	5.3
Isobutyl acetate	4.5	4.7	4.4	4.3
Ethyl *n*-butyrate	4.4	4.3	4.7	4.5
Isoamyl acetate	3.9	4.3	4.2	3.5

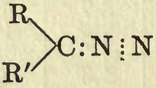
The values of *a* are seen to range from 3.6 to 6.9. The only marked regularity apparent is the fair agreement between the values of *a* for the isomeric esters, isobutyl acetate and ethyl *n*-butyrate. The comparatively large value of *a* as compared with the corresponding term of the Lorentz-Lorenz expression is of interest.

STRUCTURE OF THE AZOIMIDE NUCLEUS

By Martin Onslow Forster

Royal College of Science, London

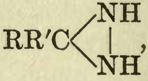
Nearly twelve months have elapsed since the appearance of a paper by Thiele[1] advocating the representation of aliphatic diazo-compounds and of organic azoimides by the formulæ



$$\begin{matrix}R\\R'\end{matrix}\!\!>\!C\!:\!N\vdots N \qquad \text{and} \qquad R\cdot N\!:\!N\vdots N$$

respectively, instead of the hitherto accepted cycloids. In absence of any published argument to the contrary there is danger of the case going by default, and it is desirable, therefore, that certain considerations which appear to militate against Thiele's views should be carefully weighed.

It may first be pointed out that, as Thiele himself has since acknowledged,[2] others have already made the same suggestion,[3] whilst the limitations of the conventional formula for azoimide and its aryl derivatives were discussed still earlier by Mendeléef and by H. E. Armstrong.[4]

Thiele's arguments appear to be founded on experiments which have not yet been published indicating that the condensation products of hydrazine with ketones should be regarded as hydrazones, $RR'C\!:\!N\cdot NH_2$, rather than hydrazi-compounds,  $RR'C\!<\!\begin{matrix}NH\\|\\NH\end{matrix}$, and although not mentioned by Thiele, this view has been already

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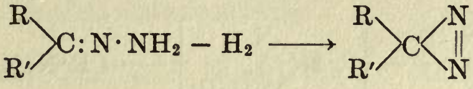
[1] Ber., *44*, 2522 (1911).
[2] Loc. cit., 3336.
[3] Angeli, Real. Accad. dei Lincei, *16*, ii, 790 (1907), and *20*, i, 626 (1911); Forster and Fierz, Trans., *93*, 75 (1908); Philip, ibid., 923.
[4] Proceedings, *9*, 57 (1893).

expressed in connection with the hydrazones of camphorquinone;[1] a paper by Staudinger and Kupfer,[2] to which Thiele does refer, also bears on this point. He concludes that the facility with which aliphatic diazo-compounds arise from these hydrazones by oxidation supports the open-chain in preference to the cycloid structure, but the "analogy" drawn between the formulæ

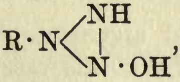
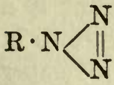
$$RR'C{:}N{\vdots}N \qquad \text{and} \qquad C_6H_5{\cdot}NCl{\vdots}N$$

is surely fallacious, because the diazonium formula represents nitrogen as singly linked with carbon and as associated, moreover, with an ionizable halogen. The alternative, and it seems to me more probable, explanation is that the transformation



is an arrested Hofmann-Curtius reaction, which, in its completed form, is typified by the changes

$$X{\cdot}CO{\cdot}NHBr - HBr = X{\cdot}N{:}CO$$
$$X{\cdot}CO{\cdot}N_3 - N_2 = X{\cdot}N{:}CO$$

Proceeding now to examine Thiele's arguments against the cyclic arrangement of the nitrogen atoms in the azoimide nucleus, it is difficult to see why the necessity of explaining the production of amine and nitrous oxide, in addition to an azoimide, by the decomposition of a nitrosohydrazine, should require a new representation for the more familiar change; this difficulty is increased by the fact that the explanation furnished by Thiele actually involves the cycloid, , from which the passage to  is surely as simple and reasonable as could be desired, and far more simple and reasonable than a change to $R{:}N{:}N{\vdots}N$.

Dimroth's work on the interaction of azoimides and the Grignard agents is next quoted by Thiele as favoring the open-chain

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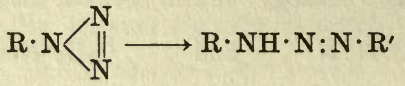
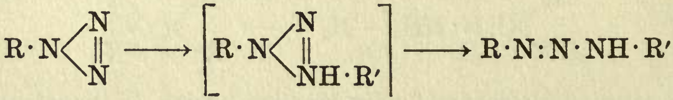
[1] Forster and Zimmerli, Trans., *97*, 2156 (1910).
[2] Ber., *44*, 2197 (1911).

formula. It is stated that "mit der Ringformel müsste man die sehr unwahrscheinliche Annahme machen (I), dass bei der Anlagerung die Doppelbindung intakt bleibt, während die einfache gesprengt wird. Die neue Formulierung lässt die Enstehung der Diazoamidoverbindungen leicht voraussehen (II):

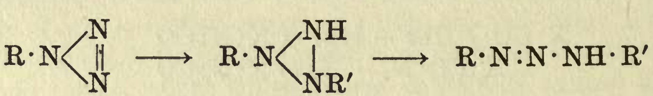
I


II $R\cdot N:N\vdots N \longrightarrow R\cdot N:N\cdot NH\cdot R'$"

But in Thiele's own explanation the double linking between nitrogen atoms is left intact, and therefore, using his own process of addition, the change might be represented as



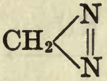
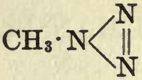
whilst another likely course is indicated as follows:

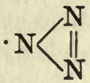


Furthermore, if Dimroth's discovery is to be taken as in favor of an open chain in the azoimide nucleus, it would stand for $X\cdot N:N\cdot N$, corresponding to the carbylamines, $X\cdot N:C$, rather than for $X\cdot N:N\vdots N$, corresponding to the carbimides $X\cdot N:C:O$ and ketens, $X_2\cdot C:C:O$, in which the additive process follows a course different from that pursued by the carbylamines and azoimides.

Summing up the principal arguments brought forward by Thiele, it cannot be claimed that the case they represent is a strong one. It appears to be based entirely on analogy, which in places is faulty; for example, in the closing sentence of his paper he declares that "Die vorgeschlagenen Formeln weichen von den bisherigen Ringformeln übrigens, wie ich glaube, nicht allzusehr ab, sie verhalten sich zu diesen wie die Diazoniumformel zu der Kekuléschen Diazoformel."

Since the communication under discussion makes no attempt to demolish the evidence in favor of the conventional cycloid, it is only proper that some points which support this arrangement should be indicated. In the first place it may be stated that the stability of the azoimides accords more completely with the cycloid representation than with a chain of unprotected nitrogen atoms. It is true that hydrazoic acid itself is a violent explosive, but replacement of the hydrogen by alkyl or aryl groups leads to comparatively harmless materials; methylazoimide, for example, may be heated above 500° before explosion occurs,[1] and phenylazoimide has been distilled at 161° (754 mm.) without exploding,[2] although this is only possible with pure specimens. Furthermore, it has been shown recently by Staudinger [3] that pure diazomethane is dangerously explosive, and on comparing it structurally with the relatively harmless methylazoimide

$CH_2:N\vdots N$ and $CH_3\cdot N:N\vdots N$ or  and 

it may be urged that there is greater reason for this disparity in behavior to be found in the cycloid representation than in the open chain. Another point in connection with the stability of the azoimides must be noted with regard to the diazonium azides, which would have to be represented, according to Thiele, as having the structure $X\cdot N(N:N\vdots N)\underline{\vdots}N$. These materials change spontaneously into arylazoimide and nitrogen, but there seems to be no reason why an isomeric product, $X\cdot N(N)\underline{\vdots}N$, should not be formed, and it is hardly conceivable that this would have a separate existence without becoming transformed into 

The question of nitrogen quinquivalence independent of an ionizable atom must next be considered. It is true that Thiele recognizes this difficulty, and rightly states that objections are not raised to the representation of nitro-compounds in this way; but, so far as I am aware, all those compounds which have been represented as containing non-ionizable quinquivalent nitrogen

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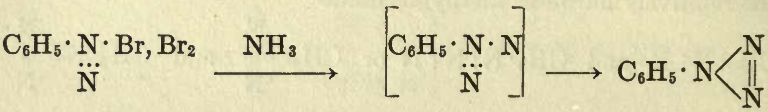
[1] Dimroth and Wislicenus, Ber., *38*, 1576 (1905).
[2] Forster, Trans., *89*, 232 (1906).
[3] Ber., *45*, 501 (1912).

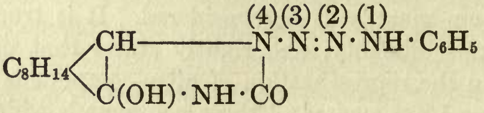
have that nitrogen associated with at least one univalent group, as, for example, in dimethylaniline oxide, $C_6H_5\cdot N(CH_3)_2:O$, and the *n*-methyl ethers of the oximes, $X\cdot CH:N(CH_3):O$. Certainly no case is known where quinquivalent nitrogen is satisfied by the equivalent amount of a single element, or of groups having the same polarity; diversity among the attached groups appears to be necessary for the existence of quinquivalent nitrogen,[1] but Thiele ignores this aspect of the question.

The original method of producing aromatic azoimides discovered by Griess in 1866 appears to favor the conventional representation. Here ammonia deprives the diazonium perbromide of halogen, putting nitrogen in its place, and the most straightforward view of this change is as follows:



$$C_6H_5\cdot\underset{\overset{\vdots}{N}}{N}\cdot Br, Br_2 \xrightarrow{NH_3} \left[C_6H_5\cdot\underset{\overset{\vdots}{N}}{N}\cdot N\right] \longrightarrow C_6H_5\cdot N\left\langle\begin{matrix}N\\ \|\\ N\end{matrix}\right.$$

Rearrangement of the nitrogen atoms to $C_6H_5\cdot N:N\vdots N$ seems less probable. Another important method of preparation points in the same direction. Emil Fischer[2] observed that benzenediazonium nitrate or sulphate, acting on phenylhydrazine, gives phenylazoimide and aniline, whilst Curtius found[3] that benzenediazonium sulphate and hydrazine give, according to circumstances, aniline and hydrazoic acid or phenylazoimide and ammonia; Curtius deduced therefrom the presence, at an intermediate stage, of the hypothetical substance phenylbuzylene, $C_6H_5\cdot NH\cdot N:N\cdot NH_2$. Derivatives of phenylbuzylene have actually been isolated, namely, hippurylphenylbuzylene[4] and benzenediazo-ψ-semicarbazinocamphor.[5] Now the last-named substance, which probably has the constitutional formula



$$C_8H_{14}\left\langle\begin{array}{l}CH\text{———————}\overset{(4)(3)\,(2)\,(1)}{N\cdot N:N\cdot NH}\cdot C_6H_5\\ |\qquad\qquad\qquad\quad\ \ |\\ C(OH)\cdot NH\cdot CO\end{array}\right.$$

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[1] Cf. Lachman, Amer. Chem. J., *20*, 283 (1898), and Ber., *33*, 1035 (1900).
[2] Annalen, *190*, 94 (1878).
[3] Ber., *26*, 1263 (1893).
[4] Curtius, Loc. cit.
[5] Forster, Trans., *89*, 222 (1906).

since it does not yield a diazonium salt with ice-cold mineral acid, is resolved quantitatively by alkalies into camphoryl-ψ-carbamide and phenylazoimide, whence it is surely reasonable to conclude that after hydrogen has been transposed between nitrogen atoms (1) and (4), the consequent separation of (4) from (3) would cause the latter to combine with (1). This seems, at least to me, a more probable course for the change to follow than the sudden development of quinquivalence on the part of nitrogen atom (2) in a system free from acid.

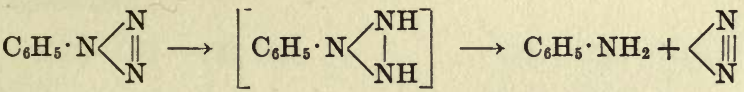
Next it may be inquired why, since the reduction of a diazonium salt to an arylhydrazine,

$$C_6H_5\cdot NCl\vdots N \longrightarrow C_6H_5\cdot NH\cdot NH_2$$

leads to enormous increase of stability, the transformation

$$C_6H_5\cdot N{:}N\vdots N \longrightarrow C_6H_5\cdot N{:}N\cdot NH_2 \quad \text{or} \quad C_6H_5\cdot NH\cdot N{:}NH$$

involves, under normal conditions, the production of aniline and nitrogen instead of phenyltriazane, $C_6H_5\cdot NH\cdot NH\cdot NH_2$, or at least phenylhydrazine and ammonia. There is much to be said in favor of the alternative explanation,



$$C_6H_5\cdot N\left\langle\begin{matrix}N\\ \|\\ N\end{matrix}\right. \longrightarrow \left[C_6H_5\cdot N\left\langle\begin{matrix}NH\\ |\\ NH\end{matrix}\right.\right] \longrightarrow C_6H_5\cdot NH_2 + \left\langle\begin{matrix}N\\ |||\\ N\end{matrix}\right.$$

since the aryl-substituted nitrogen atom may be expected to display much greater attraction for hydrogen than is exerted by the remaining ones; support for this is to be derived from the fact that when a diazonium salt is coupled with an aliphatic amine the product is

$$C_6H_5\cdot NH\cdot N{:}NX \quad \text{instead of} \quad C_6H_5\cdot N{:}N\cdot NHX$$

Another aspect of the triazo-group which is not in accord with the proposed formula is revealed by the behavior of the iodophenylazoimides towards chlorine. In collaboration with Mr. J. H. Schaeppi I have lately found that excess of chloride may be passed into chloroform solutions of ortho-, meta-, and para-iodophenylazoimide without any change other than the production of the iodochloride; the latter may then be converted, through the iodoso- and iodoxy-compounds, into the corresponding di-triazophenyliodonium iodide. It is difficult to believe that the azoimide nucleus could survive the series of transformations

$$N_3\cdot C_6H_4\cdot I \longrightarrow N_3\cdot C_6H_4\cdot ICl_2 \longrightarrow N_3\cdot C_6H_4\cdot IO \longrightarrow$$
$$N_3\cdot C_6H_4\cdot IO_2 \longrightarrow (N_3:C_6H_4\cdot)_2I\cdot I$$

if the arrangement of atoms were that advocated by Thiele.

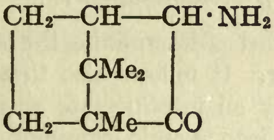
Enough material has now been brought forward to indicate that considerable risk of error is incurred by an acquiescent attitude towards the open-chain formula. It is not suggested that the arguments here enumerated offer conclusive proof of the cycloid arrangement. It may even be doubted whether such proof can be furnished until more definite views prevail as to the valency conditions of the nitrogen atom, but it may be safely contended that existing knowledge on this point is less inimical to the cycloid than to the alternative advocated by Thiele.

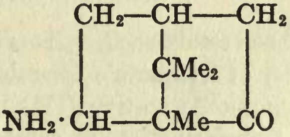
ORIENTATION OF TIEMANN'S *ISO*AMINOCAMPHOR

BY MARTIN ONSLOW FORSTER AND HUBERT ARTHUR HARRY HOWARD

Royal College of Science, London

Two amino-derivatives of camphor are known at present, namely, α-aminocamphor (I), arising from α-nitrocamphor or from *iso*nitrosocamphor by reduction, and *iso*aminocamphor, which Tiemann produced from camphoroxime by the action of hydriodic acid.[1] The constitution of the latter base has not been established because Tiemann's representation of its structure is rendered inapplicable by Bredt's formula for camphor, now generally accepted. Consideration of the existing evidence led us to suspect that it belongs to the β-series, and experiments suggested by this possibility have confirmed the view here presented. Accordingly, we use the expression β-aminocamphor in place of *iso*aminocamphor, and represent the base by the structural formula (II):


I


II

The production of β-aminocamphor from the source indicated most probably depends on the principle invoked to explain the formation of β-bromocamphor (VIII) and β-chlorocamphor by the action of halogens on hydroxycamphene,[2] namely, that the β-position approaches the ketonic carbon in space; the production from camphoroxime of an intermediate *cyclo*imino-derivative (III),

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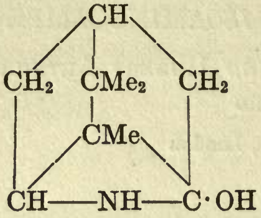
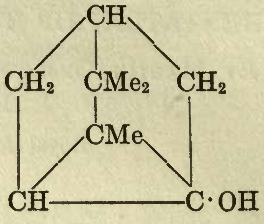
[1] Ber., *28*, 1082 (1895), and *30*, 321 (1897).
[2] Forster, Trans., *81*, 268 (1902).

corresponding closely to the hydroxycamphene (IV), which is the source of β-halogen camphor derivatives, is thus facilitated.



III



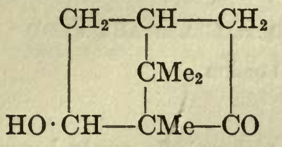
IV

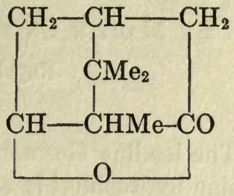
A substance of this structure (III) might be expected to pass readily into β-aminocamphor (II) or to be produced easily from it, and we find that when the solid hydrochloride of Tiemann's base is heated under reduced pressure there distills a compound, $C_{10}H_{17}ON$, melting at 71°, slowly changing at ordinary temperatures into the isomeric β-campholenamide (m. p. 52°), converted by bromine into β-bromocamphor and by chlorine into β-chlorocamphor. Moreover, when β-bromocamphor is heated with alcoholic ammonia it is transformed into β-aminocamphor. Thus the relationship,

$$\beta\text{-aminocamphor} \rightleftarrows \beta\text{-bromocamphor},$$

has been established, and may be regarded as determining the orientation of Tiemann's *iso*aminocamphor. It follows also that the *cyclo*imino-derivative (III) is probably an intermediate stage in the transformation of camphoroxime into β-aminocamphor, and is actually the substance $C_{10}H_{17}ON$, melting at 71°, for we find that the latter yields campholenonitrile and β-aminocamphor with hydriodic acid, the agent which produces these materials from camphoroxime.

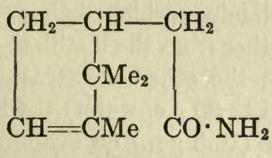
The most conspicuous difference in the behavior of the amino-group when occupying the α- or the β-position is the remarkable facility with which it is eliminated in the latter case. Tiemann found that hydroxylamine gives rise to two isomeric oximes of the corresponding hydroxycamphor, but was not able to isolate the hydroxyketone itself. By carrying out the analogous change with semicarbazide, however, and hydrolyzing the resulting semicarbazone with aqueous oxalic acid, we have isolated β-hydroxycamphor (V), and find that it is rapidly transformed into dihydrocampholenolactone (VI) by a spontaneous change:

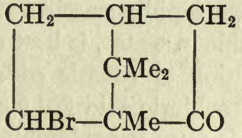

V


VI

The facility with which this alteration takes place precludes the possibility of converting β-hydroxycamphor into β-bromocamphor by existing processes, and all such attempts have led to dihydrocampholenolactone.

Another observation which supports the view that β-aminocamphor belongs to the category which includes the β-halogen derivatives and Reychler's camphorsulphonic acid is connected with the action of benzenesulphonyl chloride on the base. This leads to α-campholenamide (VII) and thus corresponds to the transformation of β-bromocamphor (VIII) into α-campholenic acid under the influence of alcoholic alkali.[1]


VII


VIII

The experimental details arising out of this investigation will be communicated to the Chemical Society.

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[1] Trans., *81*, 270 (1902).

NOTE ON THE PREPARATION OF BENZYLAMINE

By Martin Onslow Forster and Hilda Mary Judd

Royal College of Science, London

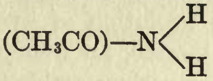
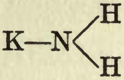
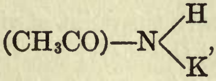
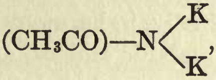
The leading German producers of fine chemicals quote benzylamine hydrochloride at 33 marks per 100 gm., and we are therefore led to describe a simple, small-scale, laboratory process by which we have prepared considerable quantities of this salt at a cost approximating to one third of this figure for materials only.

Benzyl chloride (20 gm.) in 96% alcohol (100 c.c.) is mixed with sodium azide (15 gm.) dissolved in the minimum of water, and shaken at intervals during three days at air temperature. Strong brine is then added and the precipitated benzylazoimide extracted with ether; this having been removed on the water bath, the residue, without further purification, is mixed with 50% acetic acid (100 gm.), and reduced with zinc dust (18 gm.) while the liquid is cooled with water. The metal must be added in small quantities during at least 1 hour, otherwise the yield of base is greatly impaired. Excess of caustic soda having been added, a current of steam rapidly carries over the benzylamine, which, being freely soluble in water, is best extracted by ether from the distillate after addition of caustic soda; on shaking the ethereal extract with hydrochloric acid (20 c.c. concentrated to 20 c.c. water) the latter yields pure benzylamine hydrochloride (16.5 gm.) on evaporation to dryness.

THE ORGANIC ACID AMIDES AND THEIR METALLIC DERIVATIVES AS ACIDS AND SALTS OF THE AMMONIA SYSTEM OF ACIDS, BASES, AND SALTS

By Edward Curtis Franklin

Treasury Department, Washington, D. C.

The discovery of the many striking analogies between liquid ammonia and water as electrolytic solvents[1] has led the writer to the conception of a system of acids, bases, and salts[2] in which ammonia occupies a position strictly analogous to that occupied by water as the typical substance from which the ordinary oxygen acids, bases, and salts are derived. The compounds which are related to ammonia as the oxygen acids, bases, and salts are related to water are respectively the acid amides and imides, the metallic amides and imides, and the metallic derivatives of the acid amides and imides. Recalling the familiar fact that the ordinary oxygen acids, bases, and salts may be formulated as derivatives of water as represented by the formulas $(CH_3CO)\text{–}O\text{–}H$ for acetic acid, $K\text{–}O\text{–}H$ for potassium hydroxide, and $(CH_3CO)\text{–}O\text{–}K$ for potassium acetate, the above statements with respect to the ammonia derivatives may be exemplified by the formulas  $(CH_3CO)\text{—}N\left\langle\begin{matrix}H\\H\end{matrix}\right.$ for acetamide, $(CH_3CO)_2 = N\text{–}H$ for diacetamide,  $K\text{—}N\left\langle\begin{matrix}H\\H\end{matrix}\right.$ for potassium amide, and  $(CH_3CO)\text{—}N\left\langle\begin{matrix}H\\K\end{matrix}\right.$,  $(CH_3CO)\text{—}N\left\langle\begin{matrix}K\\K\end{matrix}\right.$, and $(CH_3CO)_2 = N\text{–}Na$ for monopotassium acetamide, dipotassium acetamide, and sodium diacetamide respectively.

Now it is an established fact that the relationships thus indicated

[1] Am. Chem. J., *21*, 8 (1899).

[2] For an exposition of the writer's theory of an ammonia system of acids, bases, and salts, cf. Am. Chem. J., *47*, 285 (1912).

are by no means purely formal. It has been shown, for example, that just as potassium hydroxide and acetic acid in solution in water react with each other to give potassium acetate and water in accordance with the familiar equation

$$CH_3COOH + KOH = CH_3COOK + H_2O$$

so potassium amide and acetamide in solution in liquid ammonia interact to form either the one or the other of the two potassium derivatives of acetamide, monopotassium acetamide or dipotassium acetamide, and ammonia in accordance with the equations

$$\begin{aligned} CH_3CONH_2 + KNH_2 &= CH_3CONHK + NH_3 \\ CH_3CONH_2 + 2KNH_2 &= CH_3CONK_2 + 2NH_3 \end{aligned}$$

Moreover the familiar reciprocal color changes produced by the action of acids and bases in aqueous solutions on the ordinary indicators are found to be characteristic of liquid ammonia solutions of the acid amides and the soluble metallic amides. Phenolphthalein, for example, dissolves in pure, dry liquid ammonia to form a practically colorless solution.[1] The addition of a small quantity of potassium amide brings out the red color characteristic of alkaline solutions of phenolphthalein, and this color may then be discharged by the addition of a sufficient quantity of acetamide.

The acid properties of the acid amides are further shown by the fact that their liquid ammonia solutions attack certain metals with the formation of metallic derivatives of the acid amides and the evolution of hydrogen gas. A liquid ammonia solution of acetamide, for example, reacts with metallic magnesium, forming a magnesium amide in accordance with the equation

$$2CH_3CONH_2 + Mg + 4NH_3 = (CH_3CONH)_2Mg \cdot 4NH_3 + 2H$$

Finally, in harmony with the point of view that the acid amides, the metallic amides, and the metal derivatives of the acid amides are compounds belonging to an ammonia system of acids, bases, and salts, is the fact that their solutions in liquid ammonia are

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[1] The fact is to be emphasized that ammonia is not a base, that it is only in the presence of water that ammonia exhibits basic properties. It is consequently not surprising to find that the dry liquid behaves almost, if not quite, as indifferently as water itself toward the ordinary indicators.

conductors of electricity. Some of the acid amides, it must be confessed, form solutions which are very poor conductors; others, however, approach the salts in the facility with which their solutions permit the passage of the electric current.[1] Liquid ammonia solutions of ammono salts should be, and probably are, good conductors of electricity, although, unfortunately, this has been proved experimentally for but one representative of the class. Liquid ammonia solutions of mercuric succinimide are excellent conductors.[2]

Nomenclature.—The writer has proposed to designate the acids, bases, and salts of the ammonia or nitrogen system as ammono acids, ammono bases, and ammono salts respectively, and when on occasion clearness demands, to refer to the members of the water system as aquo acids, aquo bases, and aquo salts. Accordingly the first equation given above may be described in words as representing the action of aquoacetic acid on the aquo base, potassium hydroxide, to form potassium aquoacetate and water; the two succeeding equations as representing the action of an ammono acetic acid on the ammono base, potassium amide, to form monopotassium ammonoacetate and ammonia in the one case, and dipotassium ammonoacetate and ammonia in the other.

Organic Ammono Acids.—The ammono acids as a class must be assumed to include all those compounds related to ammonia as the oxygen acids are related to water. It therefore follows that, just as is the case with the water derivatives, it is those containing an electronegative atom or radical in place of one hydrogen atom of the water molecule which exhibit acid properties and con-

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[1] It is not the acid amides alone which act as acids in ammonia solution, for it has been found that the ordinary oxygen and halogen acids in solution in liquid ammonia show to a conspicuous degree all the acid properties described above as characteristic of liquid ammonia solutions of the acid amides. Ammonium nitrate and ammonium bromide, for example, discharge the red color of alkaline solutions of phenolphthalein much more sharply than do most acid amides, they react with potassium amide to form potassium nitrate and potassium bromide respectively, their solutions attack metallic magnesium with the evolution of hydrogen and the formation of the corresponding magnesium salts, and their solutions in liquid ammonia are excellent conductors of electricity. Even in aqueous solution the acid properties of ammonium salts are frequently in evidence. Among other familiar examples may be mentioned the action of ammonium chloride on metallic zinc in the Le Clanche cell and the solution of certain metallic oxides and hydroxides in aqueous solutions of ammonium salts.

[2] J. Am. Chem. Soc., *27*, 196 (1905).

stitute the class of aquo acids, so it is true that similar replacement of either one or two of the three hydrogen atoms of ammonia gives rise to compounds belonging to the class of ammono acids. Many hundreds of such compounds are described in the chemical literature, and it is well known that some acid amides are possessed of acid properties quite equal to that of the stronger aquo acids. The acid properties of other ammono acids are so inconspicuous that they are usually not looked upon as acids at all. At one extreme in respect to acid strength are such ammono acids as acetamide, benzamide, and urea, for example, whose liquid ammonia solutions show scarcely more than an appreciable electrical conductance and whose salts—easily made in liquid ammonia solution—are incapable of existence in aqueous solution. Stronger ammono acids are such compounds as cyanacetamide, nitroacetamide, cyanamide, thiobenzamide, nitrobenzamide, benzenesulphonamide, phthalimide, isatin, etc., some of which are capable of forming salts in the presence of water, while among the compounds, nitrobenzenesulphonamide, tribrombenzenesulphonamide, saccharine,benzenesulphonnitramide, etc., are ammono acids which are not excelled in strength by the strongest aquo organic acids.

These compounds and many others which might be mentioned are acid amides derived from the carboxylic and sulphonic acids; one of them, saccharine, is an amide derived from a mixed compound which is simultaneously a carboxylic acid and sulphonic acid.

The members of another interesting group of organic ammono acids are to be looked upon as acid esters of Thiele and Lachman's nitramide,[1] which, if the fairly high conductance of its solutions in liquid ammonia [2] is any criterion, must be assumed to be an ammono acid of considerable strength. It is the nitric acid of the ammonia system.[3]

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[1] Ann. Chem. (Liebig), *288*, 267 (1905).

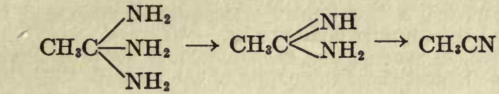
[2] J. Am. Chem. Soc., *27*, 196 (1905).

[3] In earlier papers the writer has frequently referred to the amides of acetic, nitric, sulphuric, and carbonic acids as ammono acetic acid, ammono nitric acid, ammono sulphuric acid, and ammono carbonic acid respectively; and as a matter of fact such names are justified, for in exactly the same sense that acetic acid, for example, is an acetyl derivative of water, so are acetamide and diacetamide similar derivatives of ammonia. More perfect ammonia analogues of the aquo acids, however, would be compounds entirely devoid of oxygen

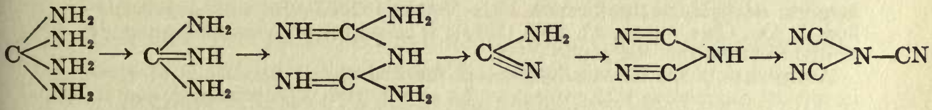
Two acid esters of ammono nitric acid are methyl nitramine, CH_3NHHO_2, and phenyl nitramine, $C_6H_5NHNO_2$, which are

and in which all the functions of oxygen in the aquo acids are performed by nitrogen.

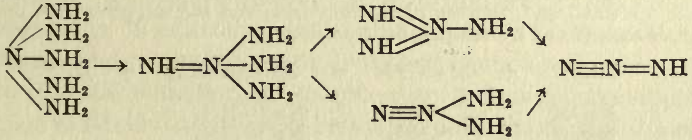
If, after the familiar manner, acetic acid, carbonic acid, and nitric acid and their anhydrides are assumed to be derived from the normal acids of the respective formulas, $CH_3C(OH)_3$, $C(OH)_4$, and $N(OH)_5$ by successive dehydration, then formulas for strictly analogous ammono acids and their anammonides may be deduced from the hypothetical ammono acids of the formulas $CH_3C(NH_2)_3$, $C(NH_2)_4$, and $N(NH_2)_5$. Normal ammono acetic acid and its deammonation products are then represented by the formulas



normal ammono carbonic acid and its deammonation products by the formulas



and normal ammono nitric acid and its deammonation products by the formulas



Of the compounds whose formulas are thus derived the first, acetamidine, appears not to be capable of forming metallic salts; and in view of the much weaker acidifying power of nitrogen as compared with oxygen, it is of course safe to predict that should the amidines ultimately be found to possess acid properties they will be less pronounced than even those of the weak acetamide. Acetonitrile is an acid anammonide.

The deammonation products of normal ammono carbonic acid show distinct acid properties; guanidine and diguanidine to the extent at least of forming, the one a silver salt, the other a copper salt, while cyanamide and dicyanamide are possessed of sufficiently marked acid properties to form each a series of well-defined metallic salts. Cyanamide has been found also to form solutions in liquid ammonia which are fair conductors of electricity.

The indicated successive deammonation of nitrogen pentamide is especially interesting in view of the fact that the formula of the final product is identical with that recently proposed by Thiele (Ber. Chem. Ges., *44*, 2522 (1911)) and by Turrentine (J. Am. Chem. Soc., *34*, 385 (1912)) for hydronitric acid. The experimental work of Turrentine shows very clearly the analogy between hydronitric acid and nitric acid as acids respectively of the ammonia and water systems, and proves to a practical certainty the correctness of the formula $HN=N\equiv N$ for hydronitric acid. Mendelejeff (Ber. Chem. Ges., *23*, obviously related to nitramide as methyl nitrate and phenynitrate are related to nitric acid. The former, however, as derivatives of a dibasic acid are acid esters, whereas the latter, being derivatives of a monobasic acid, are neutral esters. Both methyl nitramine and phenyl nitramine form salts in the presence of water,

3469 (1890)), although avoiding, as was his wont, the use of structural formulas, apparently came to the same conclusion concerning the constitution of hydronitric acid when he discusses this acid as the nitrile of diammonium nitrate $NO(OH)(ONH_4)(ONH_4)$, but this is not so clear when he comes to illuminate his formula in the language of the "structurists." Mendelejeff suggests further that hydronitric acid is to be looked upon as the nitrogen analogue of phospham, a long-known phosphorous compound to which is generally ascribed the formula $N \equiv P = HN$.

It may be noted, in passing, that the ammonium salt of hydronitric acid is isomeric with the hypothetical compound of the formula $N \equiv N(NH_2)_2$ which Mendelejeff has suggested may be found to exist—although this seems doubtful in view of the large amount of attention which has been devoted to the study of hydronitric acid—and that the ammonia addition product of ammonium trinitride of the formula $NH_4{-}N{=}N{\equiv}N \cdot 2NH_3$ (Browne and Houlehan, J. Am. Chem. Soc., *33*, 1742 (1911)) is isomeric with nitrogen pentamide or may even be this compound itself.

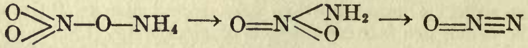
Acceptance of the formula $N \equiv N = NH$ for hydronitric acid leads to some important conclusions with respect to the constitution of nitrous oxide and nitramide which may be set forth briefly here. The formation of hydronitric acid by the action of nitrous oxide on sodium amide is explained, and at the same time the analogy between the action of nitrous oxide on sodium amide on the one hand and between nitric anhydride and sodium hydroxide on the other, is exemplified by the parallel equations

$$NaNH_2 + O{=}N{\equiv}N = NaN{=}N{\equiv}N + H_2O$$

$$\begin{matrix} NaOH \\ NaOH \end{matrix} + O{<}\begin{matrix} NO_2 \\ NO_2 \end{matrix} = \begin{matrix} NaO{-}NO_2 \\ NaO{-}NO_2 \end{matrix} + H_2O$$

if it be assumed that the constitution of nitrous oxide is represented by the formula $O = N \equiv N$.

Nitrous oxide, therefore, appears to be a mixed acid anhydride-acid anammonide, that is to say, it is a compound possessing simultaneously the properties of an acid anhydride and a nitrile, and this conclusion is furthermore in accord with the view of Mendelejeff (Loc. cit.) who saw in nitrous oxide the nitrile of ammonium nitrate. Had Mendelejeff been in the habit of using structural formulas, he would undoubtedly have formulated the familiar decomposition of ammonium nitrate in accordance with the scheme



$$\begin{matrix} O \\ O \end{matrix}{\gg}N{-}O{-}NH_4 \longrightarrow O{=}N{<}\begin{matrix} NH_2 \\ O \end{matrix} \longrightarrow O{=}N{\equiv}N$$

in which the pentavalent nitrogen of the ammonium nitrate persists in the final dehydration product.

If there is good reason to conclude that one of the nitrogen atoms in each ammonium nitrate and nitrous oxide is pentavalent, it follows that one of the nitrogen atoms in nitramide must likewise be pentavalent and that consequently the formula of Thiele and Lachman for their compound is in all probability the correct one.

and the former has been shown to form solutions in liquid ammonia which are excellent conductors of electricity.

Examples of other important derivatives of nitramide which exhibit conspicuous acid properties are nitrourea, nitroguanidine, nitrourethane, and phenyl nitramide. Such compounds are mixed acid amides related to ammonia as the mixed acid anhydride acetyl nitrate, $CH_3CO–O–NO_2$ is related to water, with the important difference that whereas the former compounds by virtue of the presence of amide hydrogen are acids, the latter compound, in the absence of acid hydrogen, is devoid of acid properties. Nitrourea, $NH_2CONHNO_2$, a mixed carbamide-nitramide; nitrourethane, $C_2H_5OCONHNO_2$, a mixed aquo ester-carbamide-nitramide and benzene sulphonnitramide, $C_6H_5SO_2NHNO_2$, a mixed sulphonamide nitramide, are good conductors of electricity in aqueous solution[1] and form salts capable of resisting hydrolytic decomposition. Nitroguanidine and nitrourethane have also been found to form solutions in liquid ammonia which are excellent conductors.

Representatives of another class of ammono acids are the nitranilines, which are compounds related to ammonia as the nitrophenols are related to water. Just as the acid properties and electrical conductance of aqueous solutions of phenol and its nitro substitution products increase rapidly with the number of nitro groups present in the benzene ring, so in the case of the former compounds it has been found that while liquid ammonia solutions of aniline are nonconductors, dinitraniline gives solutions which are good conductors, and trinitraniline forms solutions which approach salt solutions in the facility with which they carry the electric current. Although salts of picramide are not known, Franklin and Stafford[2] have shown the probable existence of a potassium salt.

A large number of cyclic compounds containing the imide group are known to exhibit acid properties and must therefore, in so far at least as those containing oxygen do not act as the tautomeric aquo acids, be included in the class of ammono acids.

As interesting examples of monocyclic ammono acids, in addition

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[1] Baur, Z. physikal. Chem., *23*, 410 (1897).

[2] Am. Chem. J., *28*, 102 (1902).

to such compounds as succinimide, may be mentioned the cyclic nitrogen compounds, pyrrol (C_4H_4)–NH, pyrazol (C_3H_3N)–NH, triazol $(C_2H_2N_2)$–NH and tetrazol (CHN_3)–NH, and many of their derivatives which, although varying greatly in acid strength, are in general capable of forming metallic salts. Reference may also be made to such familiar pyrimidine derivatives as barbituric acid, uramil, alloxan, etc.

A large number of bicyclic nitrogen compounds are also known to form metallic salts. In addition to such compounds as phthalimide, isatin, and saccharine which have already been referred to above, purine and its large family of important derivatives may be mentioned. Purine[1] itself, $(C_5H_3N_3)$–NH, forms metallic salts very readily, and in view of the fact that it is a compound devoid of oxygen it seems impossible to interpret such behavior otherwise than as that of an ammono acid. The numerous oxypurines are tautomeric compounds which may act toward bases either as ammono acids or as aquo acids.

Ammono Bases.—Apparently no organic ammono bases have been prepared,[2] although a very considerable number of inorganic ammono bases and their deammonation products, such as potassium amide, sodium amide, and zinc amide, zinc nitride, and other metallic nitrides have long been known, and others, such as silver amide, lead imide, and bismuth nitride, for example, have recently been prepared by the interaction of potassium amide and soluble salts of the respective metals in liquid ammonia solution. A few attempts have been made to prepare ammono bases

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[1] In sharp contrast with the behavior of purine as an acid is the apparently entire absence of acid properties on the part of pyrimidine. The presence of the imide group in one and its absence in the other as shown by their familiar structural formulas explain the difference in the behavior of those two compounds in this respect.

[2] It is of course clear that such compounds as the alkylamines and arylamines are not ammono bases. They are the ammonia analogues of the alcohols and phenols. Methylamine shows alcohol-like properties to the extent at least that it forms a potassium derivative of the formula CH_3NHK, analogous to potassium methylate, it unites with many salts as methylamine of crystallization as do water, alcohol, and ammonia, to form salts with solvent of crystallization. It dissolves salts to form solutions which are good conductors of the electric current, and especially it exhibits a solvent power for organic compounds (Gibbs, J. Am. Chem. Soc., *28*, 1395 (1906)) which certainly equals and probably exceeds the power of methyl alcohol in this respect.

analogous to the familiar quaternary ammonium bases, the sulphonium bases, and the iodonium bases, by the action of potassium amide on certain quaternary ammonium, sulphonium, and iodonium salts in solution in liquid ammonia, but as yet without success.

Ammono Salts.—Excepting for certain silver and especially mercury salts the metallic derivatives of the weakest ammono acids are generally incapable of existence in the presence of water and are consequently compounds which are not very well known. Representatives of readily hydrolyzable ammono salts were apparently first obtained by Gal,[1] who prepared the zinc salts of acetamide, butyramide, benzamide, carbamide, and oxyamide by the action of zinc ethyl on the respective acid amides in ethereal solutions. Following upon this earlier work, Curtius[2] prepared the sodium salts of benzamide, dibenzamide, and diacetamide by the action of metallic sodium on benzene or xylene solution of the acid amides, and Blacher[3] prepared the sodium salts of acetamide, benzamide, and phenylurea and acetanilide by the action of metallic sodium on xylene solutions of the respective acid amides. Finally, Titherley has obtained the salts of formamide, acetamide, propionamide, and benzamide by the continued action of hot benzene solutions of the acid amides on sodium amide. Of the reactions whereby these products were obtained the first is analogous to the action of zinc ethyl on acetic acid and the others are identical with those studied by Franklin and Stafford,[4] with the difference in conditions that the experiments of Curtius, Blacher, and Titherley were conducted in the presence of nonionizing solvents and gave amorphous or microcrystalline and frequently impure products, whereas the preparations obtained by Franklin and Stafford separated from liquid ammonia in beautiful crystalline form and were consequently obtainable in pure condition. Being salts of very weak acids, Gal's, Blacher's, and Titherley's compounds, like those prepared by Franklin and Stafford, are completely hydrolyzed in the presence of water.

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[1] Bull. Soc. Chim., *39*, 647 (1883).
[2] Ber. Chem. Ges., *23*, 3037 (1890).
[3] Ber. Chem. Ges., *28*, 432 and 2352 (1895).
[4] Am. Chem. J., *28*, 83 (1902).

Salts of stronger ammono acids, that is to say, the metallic derivatives of acid amides containing stronger electronegative groups, are capable of resisting the hydrolytic action of water to a greater or less extent, which accounts for the fact that large numbers of such compounds,—as, for example, metallic salts of succinimide, phthalimide, saccharine, the nitrobenzenesulphonamides, and the nitramines, nitrourea, nitrourethane, nitroguanidine benzenesulphonnitramide, etc.,—have been prepared in the past from aqueous and alcoholic solutions.

The metallic derivatives of the acid amides have been discussed above as members of the class of ammono salts. The fact has not been forgotten, however, that the amides of oxygen acids, including the oxygen derivatives of pyrimidine and purine, mentioned above, are tautomeric substances which sometimes behave as amido or imido compounds, at other times as hydroxy compounds. It may therefore well be that certain metallic derivatives of the acid amides, for example, acetamide mercury, are true ammono salts, whereas others, such as the mercury salt of methylnitramine as claimed by Ley and Kissel, are aquo salts.[1] Certainly, however, in such a compound as dipotassium benzamide one of the potassium atoms must be in combination with nitrogen, and is to that extent an ammono salt, and there can be no question of the propriety of including such compounds as the metallic derivatives of hydronitric acid, cyanamide, succinimidine, pyrrol, purine, etc., among the ammono salts.

Ammono Esters, Mixed Ammono Acids, and Acid Anammonides.—Just as ordinary oxygen esters are prepared by the action of sodium salts of aquo acids on the halogen substituted hydrocarbons or on potassium alkyl sulphates, so it has been found[2] that the same halogen compounds, or potassium alkyl sulphates, when heated with metallic salts of the acid amides, give rise to the formation of compounds which are related to ammonia as the ordinary esters are related to water and which are consequently to be looked upon as ammono esters. For example, the sodium salts of benzamide, succinimide, and acetanilide have been found

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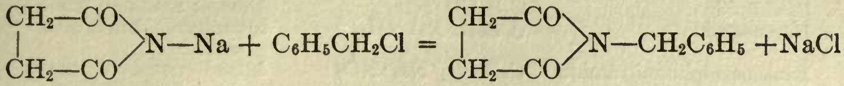
[1] Ber. Chem. Ges., *32*, 3457 (1899).

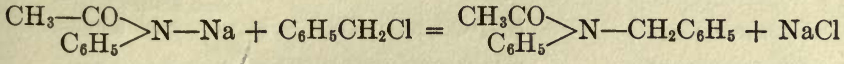
[2] Blacher, Ber. Chem. Ges., *28*, 432 and 2352 (1895). Titherley, J. Chem. Soc., *79*, 391 (1901); *81*, 1520 (1902), and *89* ,708 (1906).

to react with benzylchloride to form benzyl esters of the respective acid amides in accordance with the equations

$$C_6H_5CONHNa + C_6H_5CH_2Cl = C_6H_5CONHCH_2C_6H_5 + NaCl$$



$$\left.\begin{array}{l}CH_2—CO \\ | \\ CH_2—CO\end{array}\right> N—Na + C_6H_5CH_2Cl = \left.\begin{array}{l}CH_2—CO \\ | \\ CH_2—CO\end{array}\right> N—CH_2C_6H_5 + NaCl$$



$$\left.\begin{array}{l}CH_3—CO \\ \quad C_6H_5\end{array}\right> N—Na + C_6H_5CH_2Cl = \left.\begin{array}{l}CH_3CO \\ \quad C_6H_5\end{array}\right> N—CH_2C_6H_5 + NaCl$$

and with potassium ethyl sulphate to form ethyl esters in accordance with equations which are obvious.

Of the compounds formed in the reactions represented by the above equations the first still contains an acid hydrogen atom and is therefore an acid ammono ester, the second and third are devoid of acid hydrogen and are therefore neutral ammono esters. Either of the names, acid benzylammonobenzoate or monobenzylammonobenzoate, may be given to the acid ester, and the name phenylbenzylammonoacetate to the second of the neutral esters.[1]

Furthermore, as sodium benzoate reacts with benzoyl chloride to form benzoic anhydride, so benzamide sodium when treated with benzoyl chloride has been found to form dibenzamide in accordance with the equation

$$C_6H_5CONHNa + C_6H_5COCl = C_6H_5CONHCOC_6H_5 + NaCl$$

Dibenzamide, however, is not a true analogue of benzoic anhydride, for the reason that it contains an amide hydrogen atom and in consequence possesses acid properties. The true analogue of benzoic anhydride is tribenzamide or benzoica nammonide, a compound which Blacher prepared.

Nomenclature Again.—The ordinary names, the formulas, and general class names which may be given to a number of representative compounds are tabulated herewith by way of recapitulation

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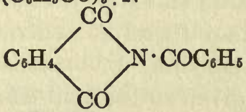
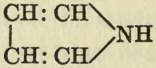
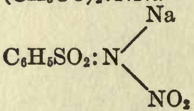
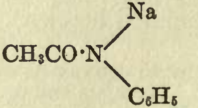
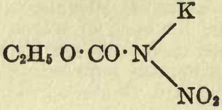
[1] It is not so simple a matter to derive a name for benzylsuccinimide as an ester of the ammonia system. There are two or even three compounds which are to be looked upon as ammono succinic acids, viz., succinamide, succinimidine, and succinimide, for each of which a distinguishing designation must be decided upon before their salts and esters can be given unequivocal names. The writer does not venture suggestions along this line at the present time.

of the considerations advanced in the above pages. No attempt has been made to make the list comprehensive.

Ammono Acids and Anammonides

Benzamide	$C_6H_5CO\cdot NH_2$	Dibasic ammono acid.
Dibenzamide	$(C_6H_5CO)_2:NH$	Monobasic ammono acid.
Benzenesulphonnitramide	$C_6H_5SO_2\cdot NH\cdot NO_2$	Mixed monobasic ammono acid.
Nitrourea	$NH_2\cdot CO\cdot NH\cdot NO_2$	Mixed tribasic ammono acid.
Benzylbenzamide	$C_6H_5CO\cdot NH\cdot CH_2C_6H_5$	Acid ammono ester.
Benzylacetamide	$CH_3CO\cdot NH\cdot CH_2C_6H_5$	Acid ammono ester.
Phenetolacetamide	$CH_3CO\cdot NHC_6H_4OC_2H_5$	Acid ammono ester.
Urethane	$C_2H\cdot_5O\cdot CO\cdot NH_2$	Aquo ester dibasic ammono acid.
Nitrourethane	$C_2H_5\cdot O\cdot CO\cdot NH\cdot NO_2$	Aquo ester mixed ammono acid.
Tribenzamide	$(C_6H_5CO)_3\vdots N$	Acid anammonide.
Benzoylphthalimide		Mixed acid anammonide.
Pyrrol		Monobasic ammono acid.
Hydrazoic acid	$N\vdots N:NH$	Monobasic ammono acid.
Hydrocyanic acid	$C:NH$	Monobasic ammono acid.
Dicyanamide	$(N\vdots C)_2:NH$	Monobasic ammono acid.
Cyanamide	$N\vdots C\cdot NH_2$	Dibasic ammono acid.
Acetonitrile	$CH_3C\vdots N$	Acid anammonide.

Ammono Salts

Monopotassium benzamide	$C_6H_5CO\cdot NHK$	Acid ammono salt.
Dipotassium benzamide	$C_6H_5CO\cdot NK_2$	Normal ammono salt.
Sodium acetimide	$(CH_3CO)_2:NNa$	Normal ammono salt.
Sodium benzenesulphonnitramide		Salt of a mixed ammono acid.
Sodium acetanilide		Salt of an acid ammono ester.
Potassium nitrourethane		Salt of an aquo ester mixed ammono acid.

ON THE INTERACTION OF DIKETONES AND ACID AMIDES

BY L. H. FRIEDBURG

New York, N. Y.

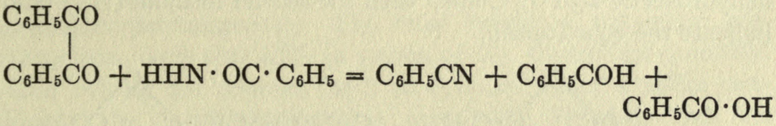
In the pursuit of this general reaction I found a remarkably easy way of preparing practically quantitative benzonitrile.

It is merely necessary to distill together molecular quantities of benzil and benzamide.

Both substances were used in a very pure state, the outcome of many recrystallizations.

As a result of the reaction, benzonitrile, benzaldehyde, and benzoic acid were obtained, which were separated and identified in the usual manner.

The reaction evidently is accomplished in the following sense:



$$\begin{array}{l} C_6H_5CO \\ \quad | \\ C_6H_5CO + HHN \cdot OC \cdot C_6H_5 = C_6H_5CN + C_6H_5COH + \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad C_6H_5CO \cdot OH \end{array}$$

The yield of benzonitrile is quantitative.

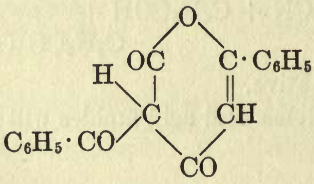
The general reaction between diketones and acid amides will be pursued farther.

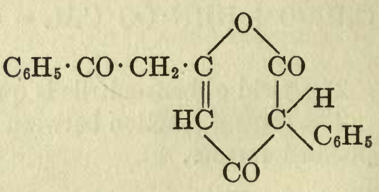
PARABROMBENZOYLACETIC ESTER

By William J. Hale and Lambert Thorp
Ann Arbor, Mich.

The investigations by one of us[1] upon the constitution of dehydroacetic acid proved conclusively the correctness of v. Pechmann's[2] interpretation on the formation of this acid. Further than this, the manner in which acetoacetic ester condensed with itself was shown to proceed exactly in accord with the Feist hypothesis.[3]

Benzoylacetic ester was first prepared by Baeyer[4] and later shown by Perkin[5] to be converted, upon heating, into a compound closely resembling dehydroacetic acid in properties, namely, dehydrobenzoylacetic acid. The formula of this acid, in accordance with the Feist interpretation, would be as indicated below (I). If, however, this acid should accord in formula with that assigned to dehydroacetic acid by Collie,[6] then the second formula (II) would indicate the constitution.


I


II

In the light of recent work we may now assume that the first formula alone accounts for all of the characteristic properties of dehydrobenzoylacetic acid, as it also does for dehydroacetic acid.

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[1] J. Amn. Chem. Soc., *33*, 1119 (1911).
[2] Ber., *24*, 3600, 4098 (1891); Ann., *273*, 186 (1893).
[3] Ann., *257*, 253 (1890).
[4] Ber., *15*, 2705 (1882); Ber., *17*, 64 (1884).
[5] J. London Chem. Soc., *47*, 277 (1885).
[6] J. London Chem. Soc., *59*, 179, 617 (1891).

In fact the formation of dehydrobenzoylacetic acid from benzoylacetic ester cannot be explained upon the Collie hypothesis.

In order that complete and sufficient data may be at hand for the study of the less known dehydrobenzoylacetic acid it was thought best to prepare and study a few derivatives of benzoylacetic ester itself. The first derivative of this class to claim our attention is para-brombenzoylacetic ester.

For the preparation of this ester p-bromtoluene was first oxidized by potassium permanganate to para-brombenzoic acid and this in turn converted into the corresponding acid chloride. This latter was carried through an acetoacetic ester synthesis to obtain the sodium salt of p-brombenzoylacetoacetic ester, which was then transformed into p-brombenzoylacetic ester by the action of dilute ammonia.

Para-brombenzoic Acid.—For the preparation of this acid Beilstein recommends the oxidation of p-bromtoluene by means of chromic acid, as described by Jackson and Rolfe.[1] The method, however, is tedious, and the average yield does not exceed 50% of the theoretical. The following procedure was found to give better results. Into a copper vessel were introduced 1500 c.c. of water, 66 gm. of p-bromtoluene, and 55 gm., or a one-third portion, of potassium permanganate. The total weight of potassium permanganate used was 30% in excess of the theoretical quantity. After boiling the mixture for 2 to 3 hours under a reflux condenser, the permanganate was completely reduced, and the second of the one-third portions of permanganate, 55 gm., then added. Again, after the reduction of this portion, the last 56 gm. of permanganate were added. By the time this portion was reduced the oxidation was practically complete. The slight amount of bromtoluene remaining may be removed by steam distillation if desired. After settling of the manganese dioxide the clear solution was poured through a filter, and the manganese dioxide boiled up twice with water, 400 c.c. at each time, and filtered by aid of suction. These washings were combined with the main filtrate and the whole evaporated in a porcelain dish to a volume of about 500 c.c. After cooling, the calculated quantity of concentrated hydrochloric acid was added and p-brombenzoic

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[1] Amer. Chem. Jour., *9*, 84 (1887).

acid at once precipitated. When filtered off and dried, the yield amounted to 52 gm., a value calculating to 72% of the theoretical.

Para-brombenzoyl Chloride.—In general, the method of Sudborough[1] was here followed. Thirty-five grams of p-brombenzoic acid were placed in a 500 c.c. flask and treated with one equivalent of phosphorus pentachloride. The reaction was brought to completion by gentle warming on the water bath and the products then separated by distillation under diminished pressure. Sudborough gives 154°–155° as the boiling point of the acid chloride at 50 mm. pressure. In our work a pressure of 20 mm. was employed, and at this point all of the acid chloride distilled over at 135°–138°, solidifying completely in the receiver. The yield came to 92% of the theory.

Para-brombenzoylacetoacetic Ester.—The preparation of this ester in the form of its sodium salt was carried out in the manner described by Claisen[2] for the preparation of benzoylacetoacetic ester, p-brombenzoyl chloride here taking the place of the benzoyl chloride in Claisen's synthesis. According to this method one half of the sodium acetoacetic ester present is liberated as free ester, consequently further additions of sodium ethylate in half the previous portions must be added to re-form the sodium salt, and this in turn be allowed to react with the acid chloride simultaneously added. The reaction involved may be indicated as follows:

2 Na · acetoacetic ester + 1 p-brombenzoyl chloride =
1 Na · p-brombenzoylacetoacetic ester + 1 acetoacetic ester + NaCl

In Claisen's work the benzoyl chloride was dropped into the flask directly, whereas in this work the p-brombenzoyl chloride was employed in an ether solution. The following proportions were used: 9.15 gm. of sodium (2 mol.) dissolved in 150 c.c. of absolute alcohol; 25.8 gm. acetoacetic ester (1 mol.); 42.8 gm. p-brombenzoyl chloride (1 mol.) dissolved in 400 c.c. ether.

Seventy-five cubic centimeters of the sodium ethylate solution were mixed with the entire quantity of acetoacetic ester. Into this solution, alcohol to 5°, were then admitted gradually from a burette 200 c.c. of the ethereal solution of p-brombenzoyl

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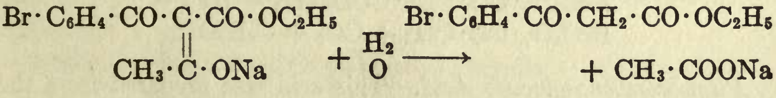
[1] J. London Chem. Soc., *67*, 591 (1895).

[2] Ber., *20*, 651 (1887).

chloride. The solution, constantly stirred, was kept under 10° as its upper limit. After standing for one-half hour a second portion of the sodium ethylate solution, 37.5 c.c., was poured into the beaker containing the reaction mixture, and the corresponding second portion of acid chloride in ether solution, 100 c.c., gradually run in. After the lapse of another half-hour the third portions of these solutions, 18.75 c.c. of sodium ethylate and 50 c.c. of acid chloride, were similarly added. In like manner were added the fourth and fifth portions (each consisting of 9.4 c.c. of sodium ethylate solution and 25 c.c. of acid chloride solution), thus completing the operation. The entire reaction mixture was now allowed to stand in a cool place for 24 hours, when the separation of the yellow sodium salt of p-brombenzoylacetoacetic ester (already begun after the second addition above) was complete. Filtered off and washed with dry ether, the product weighed 58 gm.

Para-brombenzoylacetic Ester.—This ester was obtained from the sodium salt of p-brombenzoylacetoacetic ester just described by gentle warming with aqueous ammonia. The reaction may be indicated as follows:



$$\begin{array}{l} Br\cdot C_6H_4\cdot CO\cdot C\cdot CO\cdot OC_2H_5 \\ \qquad\qquad\quad \| \\ \qquad CH_3\cdot C\cdot ONa \end{array} + \begin{array}{c} H_2 \\ O \end{array} \longrightarrow Br\cdot C_6H_4\cdot CO\cdot CH_2\cdot CO\cdot OC_2H_5 + CH_3\cdot COONa$$

The 58 gm. of sodium salt were mixed with 600 c.c. of water, in which this salt is only slightly soluble. Sixty cubic centimeters of concentrated ammonia water and 30 gm. of ammonium chloride were then added. The mixture was kept at 40°–45° for one-half hour with constant shaking. In the course of this time the yellow sodium salt had gone completely into solution and a heavy oil had separated out at the bottom of the flask. This oily product was removed by extraction with ether and the ethereal solution dried over $CaCl_2$. Upon removal of ether by distillation the heavy oil was allowed to dry in desiccator over H_2SO_4. The yield of oil was 28 gm.

Para-brombenzoylacetic ester in extremely small quantities gives, in alcoholic solution, a deep red color with ferric chloride. The test is practically as delicate as the well-known test for ferric iron by ammonium sulphocyanate. The bromine in the ester was determined by Bacon's[1] modification of Stepanow's method.

$C_{11}H_{11}O_3Br$	Calculated	Br	29.49
	Found		29.32

Attempts to distill p-brombenzoylacetic ester, even at 5 mm. pressure, resulted in its decomposition. A considerable quantity of carbon dioxide was evolved when the distillation was conducted slowly, and in the distillate the presence of alcohol and p-brombenzoic ethyl ester detected. A small quantity of a yellow granular solid was left as residue in the distilling flask. When the heating was carried out quickly, scarcely any carbon dioxide was evolved and the proportion of this yellow substance considerably increased. This product was found to be dehydro-p-brombenzoylacetic acid as expected.

When the ester is heated with water for a short time, the decomposition products consisted entirely of p-bromacetophenone, carbon dioxide, and alcohol:

$$BrC_6H_4 \cdot CO \cdot CH_2 \cdot COOC_2H_5 + H_2O =$$
$$BrC_6H_4 \cdot CO \cdot CH_3 + CO_2 + C_2H_5OH$$

Para-brombenzoylacetic Acid.—This acid was prepared from the ester by allowing the latter to stand, at room temperature, with a slight excess of a 3% potassium hydroxide solution. After 24 hours the mixture was mixed with a little boneblack and filtered. The clear filtrate, cooled by addition of ice, was carefully acidified with dilute sulphuric acid and the white gelatinous precipitate of free acid then taken up in ether. This ethereal solution was dried, carefully evaporated to small volume, and then a sufficient quantity of low-boiling ligroin added to it. Almost immediately the fine needle-like plates of the free acid were precipitated. This p-brombenzoylacetic acid is readily soluble in ether, acetone, acetic ester, or alcohol; only fairly soluble in benzene and almost insoluble in ligroin, carbon disulphide, or water. Owing to its tendency to decomposition, the best method for its purification consisted in bringing it into solution in alcohol, or, better, ether,

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[1] J. Amer. Chem. Soc., *31*, 49 (1909).

without the aid of heat, and then precipitating the substance in crystalline form by the addition of ligroin as already described. The pure product melts, when quickly heated, at 106°–107°, with evolution of carbon dioxide and production of p-bromacetophenone.

This acid dissolved in alcohol gives with ferric chloride a beautiful violet color, just as is noted with acetoacetic acid. A determination of bromine in the acid in the same manner as with the ester resulted as follows:

$C_9H_7O_3Br$	Calculated	Br	32.90
	Found		33.04

Dehydroparabrombenzoylacetic Acid.—As previously stated, this substance was found in the residues left after attempts to distill p-brombenzoylacetic ester under diminished pressure. When, however, this ester is heated quickly to boiling in an open test-tube, the same product is produced in almost quantitative yield. In properties this substance closely resembles those of dehydrobenzoylacetic acid obtained by Perkin in the rapid heating of benzoylacetic ester. The reaction for its production may be indicated as follows:

$$2\ BrC_6H_4 \cdot CO \cdot CH_2 \cdot COOC_2H_5 = 2\ C_2H_5OH + C_{18}H_{10}O_4Br_2$$

Dehydroparabrombenzoylacetic acid is insoluble in ligroin or water and only very slightly soluble in alcohol, acetic ester, ether, benzene, or carbon disulphide; it is fairly soluble in glacial acetic acid, from which it crystallizes in small yellow needles melting at 261°.

A determination of bromine in this acid by the sodium peroxide method gave the following result:

$C_{18}H_{10}O_4Br_2$	Calculated	Br.	35.55
	Found		35.67

Further investigations upon this acid are now in progress.

THE RELATIVE YIELDS OBTAINED BY THE DESTRUCTIVE DISTILLATION OF DIFFERENT FORMS AND SPECIES OF HARDWOODS

By L. F. Hawley and R. C. Palmer

Forest Products Laboratory, Madison, Wis.

Introduction

The purpose of this work was to determine the commercial value of different species of hardwood as raw material for distillation. Mixtures of beech, birch, and maple in various proportions have been commonly used for hardwood distillation in this country, these three species forming probably 90% of the raw material for this industry. There has been no information available, however, in the relative values of these species or on the possibility of utilizing other hardwoods by distillation.

The standard commercial woods, beech, birch, and maple, were included in the experiments not only in order to determine their relative values but for the more important purpose of furnishing a basis of comparison for the other species. This was necessary, because it is well known that the conditions of distillation influence the yields of the products, and, since it is difficult to reproduce commercial conditions in the laboratory, laboratory results cannot be compared directly with commercial results. It is recognized that both in the distillations and in the determinations of yields the methods do not duplicate commercial practice, and the work must, therefore, be considered simply as a comparison of different species under the same conditions. There is, however, sufficient data on commercial species to show the relation between commercial yields and laboratory yields.

Apparatus and Methods

The Retort.—The retort in which the distillations were made consisted of a horizontal iron cylinder 3 feet long and 15 inches in diameter surrounded by a 4-inch oil jacket. The oil bath was heated by a row of gas burners and served to distribute the heat and equalize the temperature. The temperature was measured in two pyrometer tubes, one reaching to the center of the retort, the other lying next to the inside shell of the retort near the top. Temperature measurements were made only at this one place on the surface of the retort, because it was found that at other places on the surface the temperatures were always slightly lower. The outlet pipe connected the end of the retort near the top with an ordinary worm condenser.

Preparation of Material.—In the case of most of the species the material was taken from several different trees, and in some cases from trees from different localities, but no effects due to these differences were noted. The bolts were sawed into slabs and bodywood in about the same proportion as would occur in practice, but the percentage of bark in the slabs was also roughly determined. Sticks just less than 18 inches long and from 2 to 4 inches in diameter were prepared. From each charge of wood just before weighing six 1-inch sections were taken for moisture determinations, each section being cut from a different stick and from a different part of a stick.

Temperatures.—The maximum temperatures obtained in different distillations varied from 327° C. to 415° C., and the maximum temperatures in different parts of the retort in the same distillation often varied as much as 60° C. It was found, however, that these differences did not appreciably affect the yields of alcohol and acetic acid; there was no apparent relation between maximum temperatures and yields of alcohol or acid, and it was also found that the charcoal from low temperature distillations produced only very small amounts of acid when small samples were redistilled at higher temperatures. As long as all parts of the charge were heated to 320° C. the distillations were practically complete as far as the alcohol and acid were concerned.[1]

In most of the distillations the temperature at the center of the retort finally became higher than at the surface, indicating the exothermic character of the reaction. It was the heat developed

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[1] For confirmation of this statement see Klason, von Heidenstam, and Nörlin, Arkiv for Kemi Min. och Geol., *3*, 9 (1908).

during the exothermic reaction which made it difficult to obtain the same maximum temperatures in all distillations; after the reaction was once well started at the surface its progression toward the center was spontaneous and could not be readily controlled.

Collection and Analysis of Products.—The distillate was caught in 500 c.c. fractions and the fractions were mixed for analysis. The temperatures and the time were read as every fraction was taken. The tar and pyroligneous acid were separated by decantation after settling for at least 24 hours, and the volume and weight of each were determined.

Pyroligneous Acid.—The acetic acid and wood alcohol were determined by the methods described by Klar,[1] the former by titration after a distillation to remove tar, and the latter by three distillations, twice in the presence of excess sodium hydroxide, with the determination of the specific gravity of the last distillate. The residue from the distillation in the acid determination was weighed and computed as dissolved tar.

Charcoal. — The charcoal was allowed to cool in the retort over night and was weighed after separation from the tar coke.

Gas.—The gas was determined by difference and no attempt was made to determine its composition.

Computation of Results.—All the yields (see Tables I–VI) are computed to the basis of percentage weight of the dry material distilled, and the results are strictly comparable on this basis. For comparison with commercial conditions, however, the average yields from slabs and bodywood of each species, expressed in terms of the commercial products 82% crude alcohol and 80% acetate of lime, are computed to the basis of a cord of wood with 15% moisture (Table VII). A cord of wood is assumed to contain 90 cubic feet of actual wood, and the weight of a cord is computed from the average weight per cubic foot of air-dry wood as given in Snow [2] (assumed to contain 15% moisture).

DISCUSSION OF RESULTS

The data obtained in each of the distillations, together with the average yields of alcohol and acid from each form of material,

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[1] Technologie der Holzverkohlung, 337.

[2] The Principal Species of Wood.

are given in Tables I to VI for beech, birch, maple, gum chestnut, and hickory, respectively. These tables require no special explanation, and only a few of the more important considerations will be mentioned.

In general the slabs give as good yields as the bodywood without bark; in the case of the beech the slabs give considerably higher yields of acetic acid than the bodywood, this being due to the relatively high yields of acid from the sapwood (Runs 38 and 39, Table I); in the case of the maple the slabs with 25% bark still yield almost the same amount of alcohol as the bodywood, this being due to the relatively high yields of alcohol from the bark (Runs 27 and 28, Table III). The birch slabs give slightly higher yields of both alcohol and acid than does the bodywood (Table II).

The yield figures obtained by parallel runs on similar material show large variations, but the largest variations are found in such products as the tar, gas, and charcoal which are influenced by the maximum temperature of the distillation to a greater extent than the alcohol and acetic acid which are not produced in appreciable amounts after the exothermic reaction is complete. There are considerable variations, however, in the yields of alcohol and acid which cannot be accounted for readily, since there are not a sufficient number of runs in which all the variables except one are constant. The average yields are probably correct within 4 or 5%.

Table VII is a summary of the yields from the previous tables expressed in commercial units; it includes also the total yields of acetate of lime when the acetic acid in the settled tar is recovered and added to that from the pyroligneous acid. It will be seen that of the standard commercial species birch yields the least alcohol and the most acid, while beech and maple are very similar except that the former yields slightly more acid.

Red gum yields slightly less of both alcohol and acid than the average of beech, birch, and maple, the low yields being due largely to the lower weight per cord.

Chestnut gives very low yields of both alcohol and acid, especially of the former; the low yields of the acid are largely due to the low weight per cord, but the low alcohol yields are due also to the composition of the wood (see Table V).

TABLE I. — DESTRUCTIVE DISTILLATION, BEECH

Form.	Moisture per cent of dry weight.	Maximum temperature per cent C.		Total pyroligneous acid.	Pyroligneous acid minus moisture.	Settled tar.	Tar coke.	Dissolved tar.	Total tar.	Charcoal.	Acetic acid.	Wood alcohol 100%.	Gas by difference.	Run No.
		Surface	Center											
Bodywood	22.6	331	372	49.0	26.4	6.7	0.7	4.6	11.1	40.7	5.10	1.93	25.8	7
"	20.6	317	354	52.5	31.9	3.6	0.7	4.5	8.8	42.8	5.46	2.03	17.8	8
"	20.8	321	327	54.3	33.5	5.5	0.5	4.6	10.7	43.5	5.27	1.90	17.9	9
"	4.7	337	368	39.7	35.0	3.3	0.9	5.0	9.1	45.3	5.08	1.95	15.7	37
13% slabs bark	15.0	369	398	51.0	36.0	5.7	0.5	5.3	11.4	38.4	5.76	1.80	17.9	10
"	15.7	350	367	51.2	35.5	5.8	0.6	6.1	12.5	37.5	5.93	1.74	20.3	11
"	15.9	354	362	50.7	34.6	3.8	0.8	4.0	8.5	42.4	5.76	1.84	17.4	12
Bark	7.3	341	357	31.2	23.9	5.3	. .	1.6	6.9	56.5	2.66	1.38	14.0	29
"	9.4	342	346	31.5	21.1	3.7	. .	1.3	5.1	57.5	2.68	1.11	16.7	30
Sapwood	16.5	326	349	52.8	36.3	3.5	0.9	4.1	8.5	42.2	6.58	1.98	16.8	38
"	14.1	310	329	47.7	33.6	2.1	1.5	3.2	6.8	47.3	6.37	1.96	. . .	39
Average bodywood	. . .	. .	. .	. . .	. . .	. .	. .	. .	. .	. .	5.23	1.95	. .	. .
Average slab	. . .	. .	. .	. . .	. . .	. .	. .	. .	. .	. .	5.82	1.79	. .	. .
Average bark	. . .	. .	. .	. . .	. . .	. .	. .	. .	. .	. .	2.67	1.25	. .	. .
Average sapwood	. . .	. .	. .	. . .	. . .	. .	. .	. .	. .	. .	6.47	1.97	. .	. .
Average species bodywood and slabs	. . .	. .	. .	. . .	. . .	. .	. .	. .	. .	. .	5.55	1.87	. .	. .

TABLE II. — DESTRUCTIVE DISTILLATION, BIRCH

Form.	Moisture per cent of dry weight.	Maximum temperature ° C.		Total pyroligneous acid.	Pyroligneous acid minus moisture.	Settled tar.	Tar coke.	Dissolved tar.	Total tar.	Charcoal.	Acetic acid.	Wood alcohol 100%.	Gas by difference.	Run No.
		Surface.	Center.											
Bodywood	39.1	356	340	75.5	36.4	3.6	1.2	3.3	8.1	41.9	6.20	1.44	16.9	40
Bodywood	25.8	354	344	61.5	35.7	3.8	1.2	4.9	9.9	41.7	6.75	1.36	17.6	41
Slabs . .	16.8	346	363	53.8	37.0	4.5	1.2	4.2	9.9	41.2	6.50	1.50	16.1	42
Slabs . .	18.1	351	325	55.2	37.1	3.8	0.9	3.5	8.2	41.0	6.70	1.60	17.2	43
Bodywood	45.8	337	329	81.8	36.0	4.8	1.6	4.5	10.9	46.3	6.22	1.49	11.3	54
Bodywood	28.9	358	355	68.0	39.1	6.1	1.6	5.1	12.8	38.5	6.39	1.51	14.7	55
Average bodywood											6.39	1.45		
Average slab . .											6.60	1.55		
Average species .											6.50	1.50		

TABLE III. — DESTRUCTIVE DISTILLATION, MAPLE

Form.	Moisture per cent of dry weight.	Maximum temperature ° C.		Total pyroligneous acid.	Pyroligneous acid minus moisture.	Settled tar.	Tar coke.	Dissolved tar.	Total tar.	Charcoal.	Acetic acid.	Wood alcohol 100%.	Gas by difference.	Run No.
		Surface.	Center.											
Bodywood	26.9	348	374	60.0	33.0	7.2	1.8	6.9	15.9	36.4	4.80	. . .	21.2	1
Bodywood	21.6	334	378	53.4	31.8	3.9	1.8	5.3	11.0	40.7	4.97	2.00	21.5	2
Bodywood	22.2	336	364	54.0	31.8	4.5	2.0	4.3	10.9	42.6	5.00	2.04	17.2	3
Slabs with 25% bark	20.4	348	379	52.5	32.1	5.1	0.4	4.6	10.2	42.6	4.96	. . .	19.8	4
	21.5	343	357	53.3	31.8	4.3	1.5	4.2	10.1	45.2	4.90	1.81	17.2	5
	18.8	331	376	49.4	30.6	3.2	0.8	3.5	7.5	47.4	4.80	2.02	18.0	6
Bark . .	9.1	357	360	30.2	21.1	1.3	. .	1.3	2.6	53.7	2.81	1.83	23.9	27
Bark . .	8.4	352	369	31.0	22.6	5.7	. .	2.0	7.7	54.6	3.00	1.92	17.1	28
Bodywood	24.3	343	345	60.6	36.3	6.6	1.2	5.0	12.8	39.6	5.37	1.74	16.0	52
Factory waste .	11.3	347	385	46.8	35.5	6.6	1.2	6.9	14.7	43.0	4.75	1.57	14.7	56
Small blocks .	11.3	349	350	46.0	34.7	2.4	2.6	3.8	8.8	45.0	5.25	2.36	16.5	57
Average bodywood											5.02	1.94		
Average slab . .											4.89	1.91		
Average species .											4.95	1.93		

TABLE IV. — DESTRUCTIVE DISTILLATION, RED GUM

Form.	Moisture per cent of dry weight.	Maximum temperature ° C.		Total pyroligneous acid.	Pyroligneous acid minus moisture.	Settled tar.	Tar coke.	Dissolved tar.	Total tar.	Charcoal.	Acetic acid.	Wood alcohol 100%.	Gas by difference.	Run No.
		Surface.	Center.											
Bodywood	20.5	351	361	58.8	38.3	5.4	0.8	5.1	11.3	37.6	5.19	1.80	17.9	33
Bodywood	16.2	346	376	54.3	38.1	5.8	1.0	5.3	12.1	36.0	5.43	1.72	19.1	34
Slabs, 15–20% bark	13.3	339	368	47.1	33.8	4.1	1.1	4.2	9.4	44.7	5.12	1.74	16.3	35
Slabs, 15–20% bark	14.7	328	338	44.7	30.0	1.9	1.0	2.7	5.6	50.2	4.92	1.73	16.9	36
Average bodywood											5.30	1.76		33, 34
Average slab . .											5.02	1.73		35, 36
Average species .											5.16	1.75		33–36

TABLE V. — DESTRUCTIVE DISTILLATION, CHESTNUT

Form.	Moisture per cent of dry weight.	Maximum temperature ° C.		Total pyroligneous acid.	Pyroligneous acid minus moisture.	Settled tar.	Tar coke.	Dissolved tar.	Total tar.	Charcoal.	Acetic acid.	Wood alcohol 100%.	Gas by difference.	Run No.
		Surface.	Center.											
Bodywood	35.9	363	353	72.3	36.2	1.3	1.3	2.1	4.8	47.1	5.48	.92	14.1	44
Bodywood	33.8	351	335	69.7	35.9	1.1	1.1	2.3	4.5	48.2	5.36	.88	13.7	45
Slabs, 20% bark . .	37.1	354	381	67.3	30.2	0.6	1.4	1.7	3.7	52.2	5.43	.85	15.6	46
Slabs, 20% bark . .	36.8	374	337	65.5	28.7	0.9	1.2	1.5	3.6	53.7	5.00	.88	15.5	47
Limbs, 11% bark	40.4	345	344	73.3	32.9	4.3	1.5	1.6	7.4	47.7	6.13	.96	13.6	48
Limbs, 11% bark	43.1	342	365	75.4	32.3	4.4	1.4	2.7	8.5	49.4	6.10	.96	12.5	49
Average bodywood											5.42	.90		44, 45
Average slab . .											5.22	.87		46, 47
Average limb . .											6.11	.96		48, 49
Average bodywood and slabs											5.32	.88		44–47

Hickory gives high yields of both alcohol and acid, especially of the former; the high yields of acid are largely due to the high weight per cord, but the high alcohol yields are also due to the composition of the wood (see Table VI).

TABLE VI. — DESTRUCTIVE DISTILLATION, HICKORY

Form.	Moisture per cent of dry weight.	Maximum temperature ° C.		Total pyroligneous acid.	Pyroligneous acid minus moisture.	Settled tar.	Tar coke.	Dissolved tar.	Total tar.	Charcoal.	Acetic acid.	Wood alcohol 100%.	Gas by difference.	Run No.
		Surface.	Center.											
Small blocks factory waste .	6.4	365	415	46.3	39.9	5.9	.7	5.9	12.5	36.9	4.65	2.02	22.7	25
	7.8	360	404	42.7	34.9	6.9	1.5	5.2	13.6	38.3	4.56	2.14	18.5	26
Average .											4.61	2.08		

TABLE VII. — DESTRUCTIVE DISTILLATION, OAK

Form.	Moisture per cent of dry weight.	Maximum temperature ° C.		Total pyroligneous acid.	Pyroligneous acid minus moisture.	Settled tar.	Tar coke.	Dissolved tar.	Total tar.	Charcoal.	Acetic acid.	Wood alcohol 100%.	Gas by difference.	Run No.
		Surface.	Center.											
Bodywood	42.48	376	312	76.10	33.62	2.62	.945	2.72	6.25	48.10	5.23	1.40	16.20	50
Bodywood	25.36	366	328	58.70	33.34	1.25	1.42	3.29	5.96	46.70	5.01	1.26	18.60	53
Bodywood	46.09	361	327	77.20	31.11	3.67	.75	2.20	6.62	53.50	4.13	1.36	9.85	60
Slab-wood 17–30% bark .	28.57	347	330	57.25	28.68	2.93	1.18	1.74	5.85	52.20	4.68	1.38	15.15	51
	43.22	358	358	73.80	30.58	1.06	.72	2.19	3.97	48.10	4.75	1.28	18.40	58
	32.20	354	334	66.25	34.05	1.33	.59	2.28	4.10	50.80	4.42	1.31	14.80	59
Average bodywood											4.79	1.34		50, 53, 60
Average slab . .											4.62	1.33		51, 58, 59
Average species .											4.70	1.335		50–60

The average yields of alcohol for the standard species are only slightly higher than those obtained in practice, but the acid yields are very much higher. Probably 225 pounds of acetate of lime per cord of wood is the maximum obtained in commercial practice. The analyses of the pyroligneous acid for the determination of acetic acid have been checked in several cases by the preparation and analysis of an acetate of lime by methods similar to commercial practice.

The other commercial product, charcoal, is not included in Table VII, since the composition of the charcoal obtained by the comparatively low temperature of the laboratory method would not be the same as commercial charcoal and comparisons of yields would be of no value.

TABLE VIII. — YIELDS — PERCENTAGE OF DRY WEIGHT SUMMARY TABLES I TO VII

Species.	Wood alcohol, 100%.			Acetic acid, 100%.		
	Bodywood.	Slabs.	Average.	Bodywood.	Slabs.	Average.
Beech	1.95	1.79	1.87	5.23	5.82	5.55
Birch	1.45	1.55	1.50	6.39	6.60	6.50
Maple	1.94	1.91	1.93	5.02	4.89	4.95
Red gum . . .	1.76	1.73	1.75	5.30	5.02	5.16
Chestnut . . .	.90	.87	.88	5.42	5.22	5.32
Hickory . . .	2.08	...	2.08	4.61	...	4.61
Oak	1.34	1.33	1.335	4.79	4.62	4.70

TABLE IX. — AVERAGE YIELDS PER CORD

Species.	Wood alcohol, 82%, gallons.			Acetate of lime, 80%, pounds.				Wood with 15% moisture weighs per cord.
	Bodywood.	Slabs.	Average.	Bodywood.	Slabs.	Average.	Average including settled tar.	
Beech . .	11.8	10.9	11.4	283	315	299	318	3785
Birch . .	8.3	8.9	8.6	329	340	334	349	3600
Maple .	11.8	11.6	11.7	278	271	275	292	3875
Red gum	9.4	9.2	9.3	253	236	245	258	3330
Chestnut	3.7	3.6	3.6	196	189	193	195	2520
Hickory .	15.3	...	15.3	304	...	304	338	4590
Oak . .	9.2	9.2	9.2	295	286	291	300	4320

RESEARCHES ON PYRIMIDINES: THE CATALYTIC ACTION OF ESTERS IN THE CLAISEN CONDENSATION

(Fifty-fifth paper.)

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α-unsubstituted β-ketone esters $RCOCH_2CO_2R'$ have been prepared by several methods, of which the following are the most important: (1) by the condensation of esters with ethyl acetate in the presence of sodium, sodium ethylate, or sodium amide (Claisen's condensation):

$$RCOOC_2H_5 + CH_3COOC_2H_5 + Na = C_2H_5OH + RC(ONa):CHCOOC_2H_5$$

(2) by the hydrolysis of C-acyl derivatives of ethyl acetoacetate[1] I,

$$\underset{\text{I}}{C_3H_7COCH(COCH_3)COOC_2H_5} \xrightarrow{\text{NaOH}} CH_3COONa + C_3H_7COCH_2COOC_2H_5$$

(3) by the action of aldehydes on ethyl diazo-acetate[2] II,

$$C_6H_5CHO + \underset{\text{II}}{N_2CHCOOC_2H_5} = N_2 + C_6H_5OCH_2COOC_2H_5$$

(4) by the action of Grignard's reagents upon ethyl cyanacetate[3] III,

$$C_3H_7MgI + \underset{\text{III}}{CNCH_2COOC_2H_5} \longrightarrow C_3H_7COCH_2CO_2C_2H_5$$

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[1] Elion, Bull. Soc. Chim., (2), *44*, 523; Rec. Trav. Chim., *3*, 248; Bouveault, Compt. rend., *131*, 45; Bouveault and Bongert, Ibid., *132*, 701; Bull. Soc. Chim., (3), *27*, 1046.

[2] Curtius and Buchner, Ber. d. Chem. Ges., *18*, 2371; Schlotterbeck, Ibid., *40*, 3000.

[3] Blaise, Compt. rend., *132*, 978; Chem. Centralb., *1*, 1195 (1901).

and (5) by the addition of water to propiolic acids, when β-ketone acids are formed. The esters are then prepared by esterification.[1]

$$\underset{\text{IV}}{RC\equiv C\cdot COOH} + H_2O = RCOCH_2COOH \longrightarrow RCOCH_2COOC_2H_5$$

Of these five methods of synthesis, Method 1 has received the most attention, and consequently the widest application. Notwithstanding its successful employment in a great number of cases, it is not, however, a general method of preparation, because only certain types of esters are capable apparently of undergoing this condensation. For example, while the esters of aromatic acids—ethyl benzoate, diethyl phthalate, ethyl hexahydrobenzoate,[2] etc., and the esters of strongly negative aliphatic acids—formates and oxalates—condense smoothly, on the other hand, the higher fatty esters have been shown to be remarkably inert and do not condense smoothly with ethyl acetate according to the equation given above.

Boesken[3] attempted to generalize this reaction and investigated the action of esters of propionic, phenylacetic, isobutyric, and trimethylacetic acids on ethyl acetate in the presence of sodium and sodium ethylate. He obtained, however, no conclusive evidence of the formation of the corresponding β-ketone ester in any case. In fact, it has been generally admitted, since this work, that condensations of this character cannot be effected. Contrary to this prevailing view, however, it has been recently shown by Wahl[4] that the reaction can be applied with ethyl propionate and ethyl butyrate. He actually succeeded in condensing them with ethyl acetate, in the presence of sodium, and isolated in a pure state ethyl propionyl- and butyryl-acetates V and VI respectively. The yields, however, were poor, being only about 20% of the theoretical.

$$\underset{\text{V}}{C_2H_5COCH_2COOC_2H_5} \qquad \underset{\text{VI}}{C_3H_7COCH_2COOC_2H_5}$$

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[1] Moureu and Delange, Compt. rend., *136*, 753; Chem. Centralb., *1*, 1018 (1903).

[2] Claisen and Lowman, Ber. d. Chem. Ges., *20*, 653; Wislicenus, Ann. Chem. (Liebig), *246*, 349; Zelinsky and Schwedoff, Ber. d. Chem. Ges., *40*, 3055.

[3] Rec. Trav. Chim., *15*, 161 (1896); Bull. Soc. Chim., (3), *15*, 1223.

[4] Compt. rend., *152*, 95 (1911).

In the summary of his investigation Wahl[1] writes as follows: "En résumé, contrairement à ce qui était admis jusqu'ici, la condensation de l'ether acétique avec ses homologues au moyen du sodium est possible."

It was necessary before taking up an investigation now in progress in this laboratory to determine whether ethyl phenoxyacetate VII will condense with ethyl acetate in a similar manner as the corresponding propionate and butyrate, which were investigated by Wahl, giving the corresponding β-ketone ester—*ethyl γ-phenoxyacetoacetate* IX. We found that sodium

$$\underset{\text{VII}}{C_6H_5OCH_2COOC_2H_5} + CH_3COOC_2H_5 + Na = C_2H_5OH + C_6H_5OCH_2C\cdot(ONa)CH:COOC_2H_5$$

$$\longrightarrow \underset{\text{IX}}{C_6H_5OCH_2COCH_2COOC_2H_5}$$

reacted immediately when suspended in an ether solution of a mixture of these two esters, with evolution of hydrogen. The sodium completely dissolved within a few hours, and a practically colorless sodium salt was deposited.

In fact, the reaction appeared to be very smooth and the yield of sodium salt was excellent. The results obtained by analysis of this salt showed, however, that we were not dealing with a definite substance. They were not uniform and the percentages of sodium were always too high. Furthermore, when this salt was decomposed by acids, a yellow viscous oil was obtained which showed no signs of crystallization on cooling. We did not attempt to purify this oil by distillation for fear of decomposing the ketone ester. Hantzsch[2] has prepared ethyl α-phenoxyacetoacetate $CH_3COCH(OC_6H_5)CO_2C_2H_5$, and states that it cannot be distilled without decomposition. We observed also that sodium reacts with ethyl phenoxyacetate alone, in ether solution, but it was very apparent that the reaction in this case was slower and the condensation product not as pure as when a mixture of the two esters was subjected to the same treatment. In this experiment, also, on decomposing the salt with hydrochloric acid a viscous oil was obtained, which showed no tendency to crystallize on long standing.

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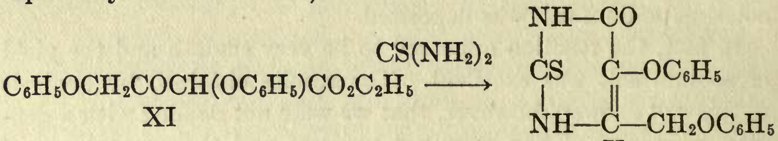
[1] Loc. cit.

[2] Ber. d. Chem. Ges., *19*, 1293.

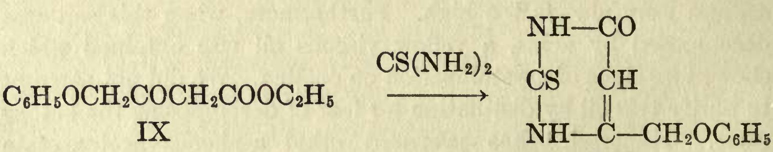
It was apparent from these results that ethyl phenoxyacetate can undergo a Claisen condensation. This assumption has been confirmed, and the constitution of the β-ketone esters formed, established by digesting the crude condensation products with an excess of thiourea, in alcohol solution and in the presence of sodium ethylate. We obtained, in this manner, from the condensation product of ethyl phenoxyacetate alone and that formed in the presence of ethyl acetate, the same pyrimidine derivative, viz., 2-thio-4-phenoxymethyl-5-phenoxy-6-oxypyrimidine X. In fact, we obtained no evidence of the formation of 2-thio-4-phenoxymethyl-6-oxypyrimidine XII, or 2-thio-4-methyl-5-phenoxy-6-oxypyrimidine XIV, which would be expected to be formed if the ketone esters—ethyl-γ-phenoxyacetoacetate IX and ethyl α-phenoxyacetoacetate XIII—were present. In other words, ethyl phenoxyacetate does not condense, under the conditions employed, with ethyl acetate forming ethyl-γ-phenoxyacetoacetate IX, but undergoes a Claisen condensation forming ethyl α-γ-diphenoxyacetoacetate XI,



$$C_6H_5OCH_2COCH(OC_6H_5)CO_2C_2H_5 \xrightarrow{CS(NH_2)_2}$$

XI

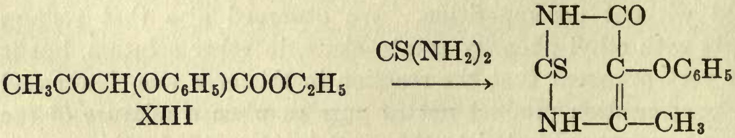
X



$$C_6H_5OCH_2COCH_2COOC_2H_5 \xrightarrow{CS(NH_2)_2}$$

IX

XII



$$CH_3COCH(OC_6H_5)COOC_2H_5 \xrightarrow{CS(NH_2)_2}$$

XIII

XIV

The new pyrimidine derivative X proved to be a very suitable compound for measuring indirectly the amount of the β-ketone ester formed, because of its insolubility in water and the common organic solvents. We intend to apply this method in some other cases where it has not been demonstrated conclusively that ketone esters are formed. We not only expect to obtain in this manner some new and interesting pyrimidines, but also to acquire, indirectly, new data regarding the mechanism of the Claisen condensation, which will be of interest.

As previously stated, we observed in our preliminary experiments that the condensation of ethyl phenoxyacetate was influenced decidedly by the presence of ethyl acetate. In fact, the difference in behavior was so marked that we were led to investigate the cause of this change.

We now find that this effect is produced by the ethyl acetate. After the completion of about thirty experiments, which were conducted under definite conditions, we have obtained evidence which proves that ethyl acetate acts here as a catalyzer. This was established by condensing the salt formed in each condensation with thiourea and determining quantitatively the amount of 2-thio-4-phenoxymethyl-5-phenoxy-6-oxypyrimidine X formed. In fact, in two experiments, where special precautions were taken in purifying the ether and the two esters, the yields of β-ketone ester were increased over 100% by the incorporation of ethyl acetate.

Working with constant proportions of ethyl phenoxyacetate and sodium, we have examined the influence of varying amounts of ethyl acetate from one-eighth of a molecule up to two molecular proportions, and have found that the effect is the same, to increase the yield, whether we incorporate one or a fractional part of a molecular proportion of the ester. By increasing the amount of ethyl acetate, there is a corresponding increase in the amount of β-ketone ester formed until four to five eighths mole is added, when the maximum yield is obtained. The yield is then practically constant, until more than one molecular proportion of acetate is introduced. Secondary reactions then apparently set in, and the yield of β-ketone ester falls, and approaches a minimum.

The results of twenty-one of our experiments are recorded in the two tables below. The only change in the conditions of the two series of experiments was that in one series we used one molecular proportion of sodium and in the other one half. It will be observed that the effect is practically the same in both series

TABLE I

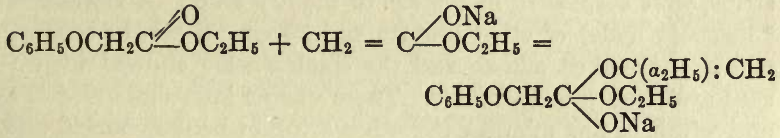
Experiment.	Moles of the catalyzer (ethylacetate).	Weight of (ethylphenoxy-acetate).	Weight of sodium.	Weight of sodium salt deposited in ether A.	Weight of pyrimidine obtained from salt A.	Weight of sodium salt soluble in ether B.	Weight of pyrimidine obtained from salt B.	Total yield of pyrimidine.	Per cent of theoretical.	Percentage increase.
		gm.	gm.	gm.	gm.	gm.	gm.	gm.		
1	0.000	25	3.2	12.2	4.0	11.0	1.0	5.0	44.0	..
2	0.125	25	3.2	17.0	7.0	9.0	0.0	7.0	62.0	40
3	0.250	25	3.2	15.0	7.0	6.0	0.0	7.0	62.0	40
4	0.250	25	3.2	18.0	6.5	8.0	0.0	6.5	57.5	30
5	0.375	25	3.2	21.7	8.0	5.7	0.0	8.0	69.0	56
6	0.500	25	3.2	21.5	9.0	1.5	0.0	9.0	79.6	80
7	0.625	25	3.2	21.5	10.5	4.5	0.0	10.5	92.9	110
8	0.625	25	3.2	24.5	10.2	2.8	0.0	10.2	90.2	104
9	0.750	25	3.2	21.7	9.0	4.5	0.0	9.0	79.6	80
10	0.875	25	3.2	19.6	9.0	7.2	0.0	9.0	79.6	80
11	1.000	25	3.2	19.0	10.0	7.0	0.0	10.0	88.5	100
12	1.000	25	3.2	18.0	8.0	8.0	1.0	9.0	79.6	80
13	1.500	25	3.2	16.0	7.0	11.0	0.0	7.0	62.0	40

TABLE II

Experiment.	Moles of the catalyzer (ethylacetate).	Weight of (ethylphenoxy-acetate).	Weight of sodium.	Weight of sodium salt deposited in ether A.	Weight of pyrimidine obtained from salt A.	Weight of sodium salt soluble in ether B.	Weight of pyrimidine obtained from salt B.	Total yield of pyrimidine.	Per cent of theoretical.	Percentage increase.
1	0.000	25	1.6	8.0	3.0	12.0	1.5	4.5	39.8	..
2	0.000	25	1.6	13.0	4.8	8.9	0.0	4.8	42.4	..
3	0.000	25	1.6	11.0	4.8	10.0	0.0	4.8	42.4	..
4	0.000	25	1.6	6.0	1.2	16.0	3.2	4.4	38.9	..
5	0.500	25	1.6	19.5	8.0	..	..	8.0	70.8	78
6	0.500	25	1.6	18.8	7.0	..	..	7.0	62.0	55
7	1.000	25	1.6	17.0	7.5	..	..	7.5	66.3	66
8	2.000	25	1.6	15.2	5.3	..	..	5.3	46.8	18

when no ethyl acetate is used. The yield of pyrimidine was practically constant, or about 45% of the theoretical. The yields in per cent are based on the assumption that if the yield of the sodium salt $C_6H_5OCH_2C(ONa):C(OC_6H_5)COOC_2H_5$ was theoretical, and only the *cis* modification underwent condensation, the theoretical yield of pyrimidine would be 11.3 gm. The catalytic influence of ethyl acetate is apparent by inspection of the results tabulated in the last column—*percentage increase.* So far as the writer is aware, it has not hitherto been observed that the esters employed can affect the course of the Claisen condensation.

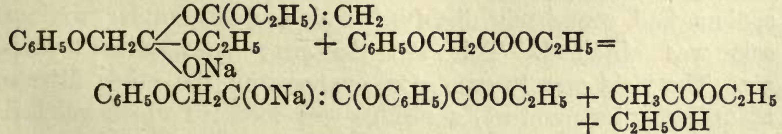
Since this is only a preliminary paper we shall not discuss here the rôle which the ethyl acetate plays in this condensation. The results indicate that it is a catalytic agent, and we are continuing the investigation. The following scheme is offered provisionally, however, to explain the transformations involved. It does not differ materially from Claisen's conception of the rôle of sodium ethylate in the acetoacetic ester condensation. The active agent is the sodium salt[1] $H_2C = C\begin{array}{l} \diagup ONa \\ \diagdown OC_2H_5 \end{array}$. This salt, which contains positive energy, then adds to the ethyl phenoxyacetate forming the addition product XVI. This addition product then unites with



$$C_6H_5OCH_2C\begin{array}{l} \diagup O \\ \diagdown OC_2H_5 \end{array} + CH_2 = C\begin{array}{l} \diagup ONa \\ \diagdown OC_2H_5 \end{array} = C_6H_5OCH_2C\begin{array}{l} \diagup OC(a_2H_5):CH_2 \\ -OC_2H_5 \\ \diagdown ONa \end{array}$$

XVI

another molecule of ethyl phenoxyacetate; ethyl acetate and alcohol are detached, and the sodium salt of the β-ketone ester XVIII is formed



$$C_6H_5OCH_2C\begin{array}{l} \diagup OC(OC_2H_5):CH_2 \\ -OC_2H_5 \\ \diagdown ONa \end{array} + C_6H_5OCH_2COOC_2H_5 = C_6H_5OCH_2C(ONa):C(OC_6H_5)COOC_2H_5 + CH_3COOC_2H_5 + C_2H_5OH$$

XVII

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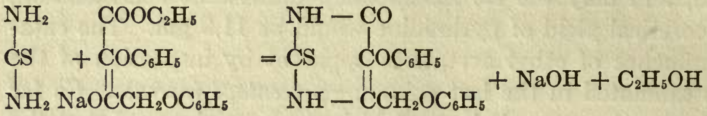
[1] Michael, Ber. d. Chem. Ges., *33*, 3731.

This salt XVII condenses with thiourea to form the pyrimidine —2-thio-4-phenoxymethyl-5-phenoxy-6-oxypyrimidine X. A description of some new pyrimidines which have been prepared from this compound will be given in a future publication.



Experimental Part

Since all our condensations were conducted under the same conditions it will therefore be necessary to describe only one experiment. In this experiment we used ethyl acetate. Kahlbaum's or freshly prepared ethyl phenoxyacetate was always used. The ether was washed with water to remove all alcohol and finally dried over calcium chloride and metallic sodium to remove every trace of water. The condensation was always protected from the air by connecting the flasks with calcium chloride tubes.

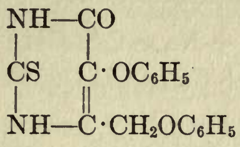
Three and two tenths grams of sodium, which was cut in fine strips, were suspended in 200 c.c. of the dry ether. A mixture of 13 gm. (1 mole) of ethyl acetate and 25 gm. of ethyl phenoxyacetate were then added, and the condensation allowed to proceed at ordinary temperature. There was an immediate reaction, and within a few minutes the ether solution became turbid and the sodium salt began to deposit. Hydrogen was also evolved, and within twenty minutes the reaction became so violent that it was necessary to cool in order to prevent the ether from boiling. The salt deposited slowly and there was no coloration of the ether. After allowing to stand for about 19 hours, the sodium had completely dissolved and a fine granular sodium salt was obtained. This salt darkens on exposure to the air. The yield was 18 gm. On evaporating the ether filtrate at ordinary temperature, a residue was obtained which weighed 8 gm.

Sodium determinations in the salt which deposited from ether:

I 0.9463 gm. of substance gave 0.2820 gm. of Na_2SO_4.
II 0.5813 gm. of substance gave 0.1985 gm. of Na_2SO_4.

Calculated for	Found	
$C_{18}H_{17}O_5Na$	I	II
Na 6.84%	9.66%	11.07%

Condensation of the Sodium Salt with Thiourea 2-thio-4-phenoxymethyl-5-phenoxy-6-oxypyrimidine



Calculating that the sodium salt (18 gm.) was pure

$$C_6H_5OCH_2(ONa):C(OC_6H_5)COOC_2H_5,$$

a molecular proportion of sodium and thiourea were dissolved in absolute alcohol and the salt then suspended in the solution. After digestion on the steam bath for about 10 hours, the condensation was considered complete and the excess of alcohol then evaporated. The residue was then dissolved in a small volume of water, and hydrochloric acid added cautiously, when hydrogen sulphide was evolved and the pyrimidine deposited in a crystalline condition. Sometimes the product was oily and slowly hardened on cooling. It was purified by crystallization from alcohol. The compound is soluble in alcohol and benzene and difficultly soluble in water. It separates from alcohol in slender prisms which melt at 218° to a red oil. The yield was 8 gm. nitrogen determination (Kjeldahl).

Calculated for	Found
$C_{17}H_{14}O_3N_2S$	8.44%
N 8.58%	

The residue, above, soluble in ether, was likewise digested with thiourea in the presence of sodium ethylate, and we obtained here 1 gm. of the pure thiopyrimidine, the total yield, therefore, being

9 gm. of the pure pyrimidine. In practically all our experiments we failed to obtain any pyrimidine by digesting the ether soluble product with thiourea. The material was chiefly phenoxyacetic acid mixed with its ester and other oily impurities which were not identified.

ABSTRACT

Ethyl phenoxyacetate undergoes a Claisen condensation in ether solution and in the presence of metallic sodium, forming the sodium salt of *a*, γ-phenoxyacetoacetate

$$2\ C_6H_5OCH_2COOC_2H_5 + Na = C_2H_5OH + C_6H_5OCH_2C(ONa):C(OC_6H_5)COOC_2H_5$$

This same salt is also formed by condensation of the phenoxyacetate in the presence of ethyl acetate. We obtained no evidence of the formation of ethyl-γ-phenoxyacetoacetate

$$C_6H_5OCH_2COCH_2COOC_2H_5$$

The free ketone ester was not isolated. Its presence was established by digestion of the crude condensation product with thiourea in the presence of sodium ethylate when 2-thio-4-phenoxymethyl-5-phenoxy-6-oxypyrimidine was formed.

The yield of this pyrimidine was found to be much greater in those condensations which were conducted in the presence of ethyl acetate. A quantitative study of the reaction has revealed the interesting fact that this increase in the yield of the ketone ester is due to the catalytic influence of the ethyl acetate. The investigation is being continued.

PHENOLPHTHALEIN AND ITS COLORLESS SALTS.— III. PREPARATION OF MONOBASIC PHENOLPHTHALATES

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Harriman Research Laboratory (Roosevelt Hospital), New York City

Introduction

Recently we described[1] the isolation and purification of the tribasic salts of a carbinol form of phenolphthalein, and it is now our object to describe the preparation and properties of the monobasic salts, and also to discuss certain recent views regarding the "phenolphathlein problem."

Discussion

In our first paper[2] we came to the conclusion that hydration begins with the smallest amount of alkali. We are glad to note that about the same time Thiel[2] came to a similar conclusion independently, as follows: "Schon in ziemlich schwach alkalischer Lösung ist ein grosser Teil des Salzes in Carbinolform vorhanden, wie man aus den Versuchen von Acree und Slagle leicht berechnen kann." We also set up a series of equilibria expressing our views on the behavior of phenolphthalein when dissolving in alkali. Thiel in his paper also gives most of the same equilibria.

We believe the equilibria will help to explain, to a larger extent than the purely chemical theories alone, the various phenomena observed with phenolphthalein and its derivatives. Thiel, however, does not come to any conclusion as to whether the quinoid

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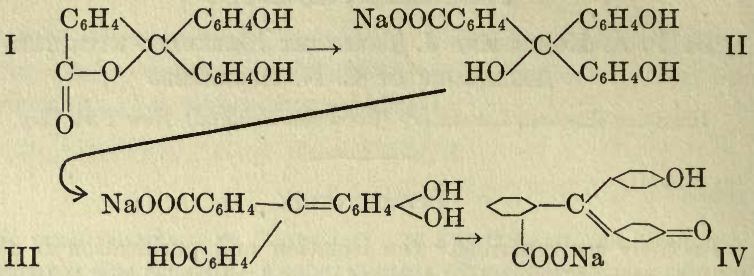
[1] Jour. Amer. Chem. Soc., *33*, 1780.
[2] Jour. Amer. Chem. Soc., *33*, 62.
[3] Sammlung Chemischer und Chem. Technische Vorträge, *16*, 388.

or the carbinol form is primary. We believe we can dispose of that question if the law of mass action is accepted as correct.

Gomberg,[1] who is inclined to assume the formation of the colored dibasic salt through the carbinol form, gives this equation:



This theory, though plausible, does not agree with facts. Disregarding the omission of another atom of sodium in the molecule —for phenolphthalein is dibasic—the equation means practically that when phenolphthalein is dissolved in weak alkali a semi-stable colored quinoid salt is formed. Furthermore it means—and this is its weakest point—that in an excess of alkali the full color of phenolphthalein is never reached; or, in other words, most of the phenolphthalein will remain in the carbinol form (II) because of the fact that the carbinol is the stable form in excess alkali hydroxide. A glance at our former curves and figures[2] will convince that the reverse is true. In making tribasic salts with saturated alkali hydroxide, a very dark, almost black solution, having a bronze metallic luster, is produced, after which hydration and fading take place. We believe that we can safely conclude that *in ordinary phenolphthalein* the quinoid *dibasic salt is essentially primary*, and the carbinol form essentially secondary.

We explain the facts thus, giving an equilibrium from our first paper. (Similar equations are given by Stieglitz, Acree, Wegscheider, McCoy, and Hildebrand.)

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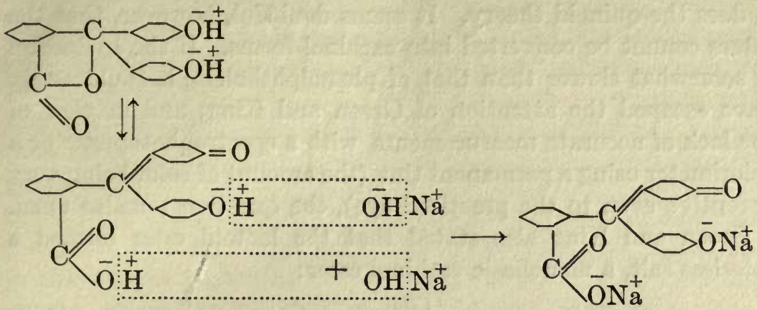
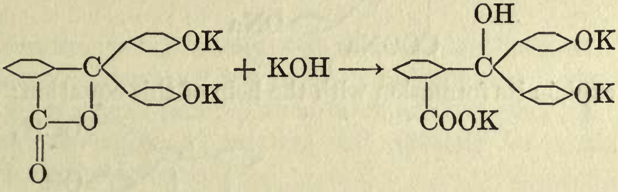
[1] Ber., *40*, 1880.

[2] Jour. Amer. Chem. Soc., *33*, 68.



As may be observed, the only assumption necessary in this equation is that a lactone is in equilibrium with its acid, or an acid with its lactone. Meyer and Spengler[1] believed that the quinoid group is not essential to the color of phenolphthalein; and, like Gomberg, they held that the splitting open of the lactone ring involved the formation of the carbinol group.



(Acree and Slagle believed that the lactoid form can exist as a colorless salt, but our experiments show that very little if any can exist as such.)

The underlying idea seems to be that the hydroxyl ion of the alkali hydroxide satisfies the valence set free when the lactone ring is severed. This assumption is unnecessary, and has been abandoned by Meyer himself.[2]

Why Green and King[3] found much support for the quinone theory in the behavior of the two esters—the methyl ester and the lactoid methyl ester—on treatment with alkali, we fail to understand. The statement that the methyl ester does not fade, or is unattacked by excess hydroxide, seems to us to support the ideas of Gomberg and Meyer and Spengler fully as much as

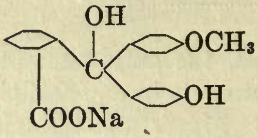
[1] Ber., *38*, 1318.

[2] Ber., *42*, 2832.

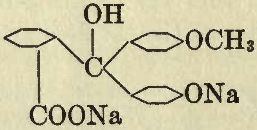
[3] Ber., *39*, 2365.

it does the quinoid theory. It seems doubtful, however, that the esters cannot be converted into carbinol forms. If the hydration is somewhat slower than that of phenolphthalein, it could easily have escaped the attention of Green and King; and in view of the lack of accurate measurements, with a spectrophotometer or a colorimeter using a permanent tint (the amount of color being very deceptive even to the practiced eye), the question remains open.

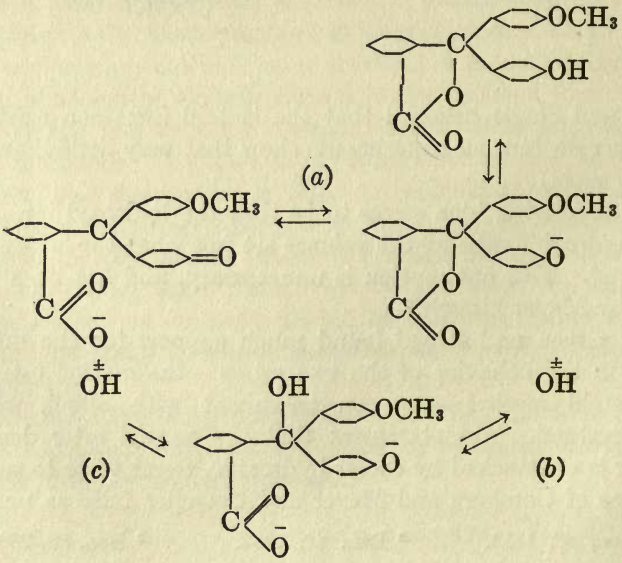
Green and King also stated that the lactoid ester formed a colorless salt, a monobasic carbinol ester:



We believe that this was meant for a dibasic salt:



and we explain its formation with the help of this equation:



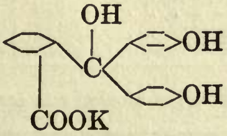
The first equation gives the ionization of the lactoid ester, the equation (*a*) represents the equilibrium between lactone and acid, and (*b*) indicates the carbinol formation directly. As can be seen, the only assumption necessary to explain the behavior of the lactone methyl ester is that the speed of hydration directly (*b*) is greater than the speed of formation of the quinoid acid. For the speed of hydration to be greater than the speed of quinoid acid formation is not unexpected. The formation of a quinoid acid in this case is dependent on the change of position of an electric charge, or on the mobility of the hydrogen atom of a phenol group. Since ordinary phenolphthalein had two phenol groups, both of which probably are active, to one phenol group in the lactoid ester, its speed of quinoid acid formation should be the greater. The dibasicity of phenolphthalein means that the speed of the salt formation of its phenol group is about the same as that of its carboxyl group. Therefore any decrease in the speed of carboxyl formation will result in the increased neutralization of the phenol group.

To sum up, it may be said that the mass-law holds also for intramolecular changes: if the speed of quinoid acid formation depends upon phenol groups, when there are two such groups in a molecule, the speed cf reaction will certainly be greater than when there is only one.

A determination of the basicity of this ester, as well as the quantitative study of the amount of color, would help to clear up the matter. If the salt is monobasic and gradually becomes dibasic, it would indicate a slow action of (*b*). If dibasic, it would indicate rapid action of (*b*).

Preparation of Monobasic Phthalates.—One method consists in using absolute alcohol to dissolve the tribasic salt, while in a second method acetone is used to dissolve the monobasic salt as it is formed. The latter method is suitable for the sodium salt, but not for the potassium.

Potassium salt



C_2H_5OH

H_2O

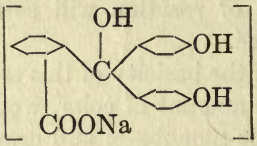
Twenty-five grams of tripotassium phenolphthalate were dissolved in 400 gm. absolute alcohol, and 10 to 15 gm. anhydrous sodium sulphate were added to remove some of the water contained as water of crystallization in the tribasic salt. We are not certain that this purpose was accomplished. After passing carbon dioxide through the solution for 2 hours, it was filtered, concentrated by vacuum distillation, and precipitated with absolute ether. The crystalline precipitate was washed with ether, air dried, and placed in a desiccator.

ANALYSIS

Sample.	0.5152 gm.		0.5002 gm.		0.5087 gm.		Theory.
	gm.	per cent	gm.	per cent	gm.	per cent	per cent
Phenolphthalein	0.3728	72.4	0.3616	72.3	0.3673	72.2	72.6
Potassium . .	0.0470	9.1	0.0456	9.1	0.0456	9.0	8.9
Alcohol[1] . . .	0.0546	10.6	0.0530	10.6	0.0539	10.6	10.5
OH^- and H_2O by difference . .	0.0408	7.9	0.0400	8.0	0.0419	8.2	8.0

[1] Only one quantitative determination of alcohol was made, using 5.00 gm. of the salt.

Sodium salt



C_2H_5OH

H_2O

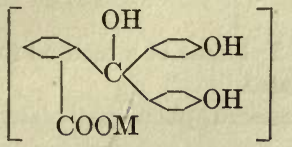
The sodium salt was made in the same way as the potassium salt.

ANALYSIS

Sample.	0.5028 gm.		0.5040 gm.		Theory.
	gm.	per cent	gm.	per cent	
Phenolphthalein	0.3749	74.5	0.3823	75.8	75.4
Sodium	0.0278	5.5	0.0286	5.7	5.4
Alcohol[1]	0.0578	11.6	0.0580	11.6	10.9
OH^- and H_2O by difference . .	0.0423	8.4	0.0351	7.0	8.3

[1] Only one determination of alcohol was made, using 1.476 gm. material.

It seems that acetone, alcohol, and water can be used interchangeably without producing much difference in the crystal form. The monobasic sodium salt was made with acetone, which replaced wholly or in part the alcohol of the salt just described.



CH_3COCH_3

$(H_2O)n$ (For Na, n = 2)

M = K or Na.

The sodium salt, crystallized from acetone only, gave the following analysis:

			Average.	Theory.
	per cent			
Phenolphthalein[1]	72.9	72.7	72.8	70.3
Sodium	5.0	5.3	5.2	5.1
Acetone	14.4	10.1	12.2	12.8
OH- and H_2O by difference	8.7	11.9	10.3	11.8

[1] Phenolphthalein is too high, owing possibly to the presence of a little free phenolphthalein precipitated from the decomposed dibasic salt.

When the salt is precipitated with alcoholic ether (3%) the analysis is slightly different, part of the acetone being replaced by alcohol.

	Theory.		
	per cent		
Phenolphthalein	71.2	69.3	72.0
Sodium	5.1	5.0	5.4
½ molecule acetone, ½ molecule alcohol	11.6	11.6	10.7
OH- and 2 H_2O by difference	12.1	10.4	11.9
Acetone (alone)	6.5	6.3	. . .

SUMMARY

I. The dynamics of phenolphthalein reactions have been discussed, and it is shown that they explain some of the recently observed phenomena.

II. A description is given for the first time of a method for the isolation of monobasic phenolphthalates.

III. Monosodium and monopotassium phenolphthalates are described.

THE COPPER SALTS OF AMINO ACIDS, PEPTIDES, AND PEPTONES

By P. A. Kober and K. Sugiura

Harriman Research Laboratory (Roosevelt Hospital), New York City

Introduction

It is our belief that a quantitative study of the copper salts of proteolytic substances will throw some light on the constitution of protein, and it is therefore our intention to present from time to time our results in this field.

Technique

As part of our results are at variance with some obtained previously by other investigators, our technique and results will be described and discussed before the advancement of any theory.

Fischer,[1] Abderhalden,[2] and others prepared the copper salts of amino acids, peptides, and peptones by boiling. We found that they were formed best at a low temperature, preferably in an ice mixture. Since some heat of neutralization makes the process an exothermal one, it is not unexpected that the reaction will be more complete at a low temperature. A further objection to boiling lies in the fact that a few of these salts have slight tendency to hydrolyze. Where a reaction can be brought about at a freezing temperature the danger of decomposing sensitive and unstable peptides is obviously reduced to a minimum.

The form of the copper hydroxide is very important; on standing it is dehydrated with the formation of cupric oxide. That the oxide is slower in its reaction with these proteolytic substances can readily be seen from the constitution of the copper salts (see page 178).

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[1] Fischer, Untersuchungen über Amino-Säuren, Polypeptide, und Proteine.

[2] Abderhalden, Ber., *40*, 2737.

The best conditions for forming these copper salts quantitatively are as follows:

(*a*) For soluble proteolytic substances:

Five to 10 c.c. of 5% cupric chloride solution are diluted to 150 or 200 c.c. with ice-cold distilled water, and neutralized with alkali. This can be done most suitably by mixing 100 gm. of fine ice with 100 gm. of the cupric chloride solution, and neutralizing with N/5 alkali, using phenolphthalein as an indicator. The neutralized mixture is then filtered, the ice being placed on the filter also, in order to keep the precipitate of cupric hydroxide cool. The hydroxide is washed once or twice with cold distilled water on the filter paper, removed with the ice to the cooled solution of amino acids or peptide, and stirred from 5 to 10 minutes.

On filtering off the excess of cupric hydroxide, the solution will contain the copper salts of all the proteolytic substances. As a rule, the solutions require boiling to decompose the quite appreciable amount of carbamino salts that are formed with CO_2. The amount of carbamino salts formed is increased by the presence of sodium chloride,[1] whereas alcohol, on the contrary, hinders their formation.

(*b*) For insoluble substances with somewhat soluble copper salts:

If the proteolytic substance is insoluble, 10 to 20 c.c. N/10 ammonia are added to the sample, and it is stirred until dissolved. If necessary, the mixture may be heated to hasten solution. After cooling the solution in an ice mixture, cold cupric hydroxide, made as above, is added and stirred for 5 or 10 minutes, 150 c.c. water is then added, and the solution filtered after thorough shaking. After washing the precipitate well with hot water, the filtrate and wash waters are concentrated and titrated in the usual way. Controls on this method, using copper hydroxide and 20 c.c. N/10 ammonia, gave only .0003 to .0005 gm. copper oxide in the filtrate.

(*c*) For insoluble substances with quite insoluble copper salts:

Where the copper salt crystallizes out and is filtered off with the excess copper hydroxide, it is necessary to separate the insoluble copper hydroxide from the insoluble copper salt.

Very satisfactory reagents for this purpose are the bicarbonates

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[1] Experiments on this subject are described in detail in another paper.

MONOBASIC AMINO ACIDS

Substance.		Weight of sample.	CuO in filtrate.	CuO in ppt.	Theoretical weight CuO calc. for this sample.	Per cent total CuO to theory.
		gm.	gm.	gm.	gm.	
Glycin	a	0.1015	0.0000	0.0563	0.0538	99.6
Glycin	a	0.1013	0.0000	0.0533	0.0537	99.3
Alanin	a	0.1008	0.0000	0.0454	0.0451	100.7
Alanin	a	0.1019	0.0000	0.0453	0.0455	99.6
Aminobutyric acid	a	0.1019	0.0005	0.0344	0.0394	87.3
Active valin	a	0.0944	0.0015	0.0301	0.0321	93.8
Isoleucin	a	0.1014	0.0011	0.0307	0.0308	103.2
Active prolin	a	0.1018	0.0078	0.0269	0.0352	98.6
Aminobutyric acid	b	0.1022	0.0004	0.0403	0.0395	102.0
Aminobutyric acid	b	0.1007	0.0007	0.0405	0.0388	104.4
Tyrosin[1]	b	0.1027	0.0007	0.0263	0.0226	116.4
Tyrosin	b	0.1011	0.0007	0.0269	0.0222	121.2
Tryptophan[2]	b	0.1022	0.0000	0.0183	0.0199	92.0
Tryptophan[2]	b	0.1017	0.0000	0.0183	0.0198	92.4
Tryptophan	b	0.0999	0.0000	0.0177	0.0195	90.8
Asparagin	b	0.1003	0.0005	0.0304	0.0302	100.7
Asparagin	b	0.1005	0.0006	0.0310	0.0303	102.3
Asparagin	b	0.1005	0.0005	0.0308	0.0303	101.7
Phenylalanin	b	0.1012	0.0000	0.0247	0.0244	101.2
Phenylalanin	b	0.1001	0.0000	0.0244	0.0242	100.8
Normal amino caproic acid	c	0.1006	0.0009	0.0297	0.0306	100.0
Normal amino caproic acid	c	0.1003	0.0003	0.0315	0.0305	105.7
Phenylglycin	c	0.1011	0.0000	0.0280	0.0266	105.3
Leucin	c	0.1003	0.0051	0.0246	0.0305	97.4
Leucin	c	0.1010	0.0054	0.0261	0.0307	102.6
Sarcosin hydrochloride[3]	a	0.1002	0.0021	0.0299	0.0315	101.6
Sarcosin hydrochloride	b	0.1017	0.0030	0.0308	0.0320	105.6
Arginin di-nitrate	a	0.1010	0.0011	0.0121	0.0134	98.5
Arginin di-nitrate	b	0.1006	0.0008	0.0139	0.0133	110.5
Arginin di-nitrate	a	0.1008	0.0011	0.0113	0.0134	92.5
Arginin di-nitrate	a	0.1022	0.0011	0.0134	0.0136	106.6
Histidin di-hydrochloride[4]	a	0.1000	0.0161	0.0005	0.0175	94.9
Histidin di-hydrochloride	b	0.1001	0.0173	0.0011	0.0175	105.1
Histidin di-hydrochloride	a	0.1014	0.0167	0.0005	0.0177	97.2
Lysin picrate	a	0.1006	0.0006	0.0097	0.0107	96.3
Lysin picrate	a	0.1011	0.0008	0.0109	0.0107	109.3

[1] The tyrosin copper solution has a greenish " complex " color.

[2] If more than 0.1 gm. tryptophan is used, method (c) must be added to this technique.

[3] All acid salts, such as hydrochlorides, nitrates, etc., are neutralized with N/10 alkali, using phenolphthalein as an indicator, before being treated with copper hydroxide as in method (a).

[4] Histidin forms a complex salt, as do the other monobasic amino acids, and on treatment with excess alkali, changes its color but little. Only on boiling the color changes towards a biuret, It is not a clear color, but smoky, and makes the solution look very dark. Characteristic is the deep red color to which the alkaline solution turns on the addition of acid. We expect to make this a basic for the colorimetric quantitative and qualitative estimation of histidin.

of sodium and potassium. Using 10 to 20% solutions of $KHCO_3$, we have obtained the results given below on leucin, tryptophan, cystin, amino-normal-caproic acid, and phenylglycin.

The amino substance is treated as in (*b*), but the excess copper hydroxide, mixed with the insoluble copper salt, is then treated with 20 c.c. of 20% $KHCO_3$, and washed with small lots of 10% $KHCO_3$. until the filtrate shows only traces of copper. The final residue of copper salt is then transferred with filter paper to the first filtrate, and after being dissolved in dilute HCl[1] is titrated as before.

In another paper we give a few experiments on the solubility of the "insoluble" copper salts in various concentrations of $KHCO_3$. In the near future we hope to give the details of more experiments along these lines, especially on the determination of amino acids in the presence of polypeptides.

Boiling directly with copper hydroxide or oxide will result without doubt in the *incomplete* formation of copper salts; this will help to explain the unexpected results obtained by Abderhalden and Hirsch on d-alanyl-l-leucyl-isoleucin and its glycyl derivatives.

SUMMARY OF DATA

Amino Acid Copper Salts

The results with our technique on *a* amino acids confirm the analyses made by previous investigators of isolated copper salts, which have without exception the general formula CuA_2, where A = one molecule of monobasic *a* amino acid.

With other amino acids, whose NH_2 group is not in the *a* position, Fischer found the formula to be CuA_2, where A = a monobasic amino acid; except (as in the case of isoserin) when an oxy group is in the *a* position, where the formula is CuA.

We have obtained the same results with isoserin[2] using the technique above:

Substance.	Weight of sample.	CuO in filtrate.	CuO in ppt.	Theoretical wt. CuO calc. for this sample.	Per cent total CuO to theory.
	gm.	gm.	gm.	gm.	
Isoserin	0.1010	. . .	0.0807	0.0765	105.5
Isoserin	0.1007	0.0121	0.0740	0.0762	113.0
Isoserin	0.1009	0.0299	0.0499	0.0764	104.5

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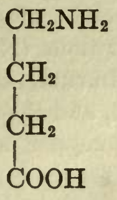
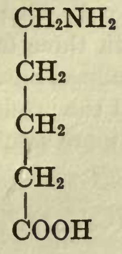
[1] As large amounts of sodium acetate retard the iodimetric titrations of copper, we neutralize with c. p. HCl.

[2] Made according to Fischer's directions from epichlorhydrin, Ber., *35*, 3787.

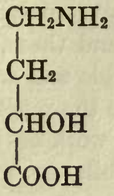
According to Fischer, when the amino group is in the γ, δ, and ε position (regardless of an oxy group in the *a* position) no copper salts are formed. This is shown below.



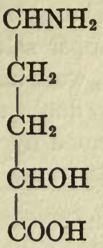
$$\begin{array}{l} CH_2NH_2 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ COOH \end{array}$$



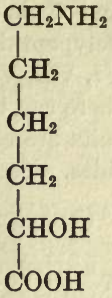
$$\begin{array}{l} CH_2NH_2 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ COOH \end{array}$$



$$\begin{array}{l} CH_2NH_2 \\ | \\ CH_2 \\ | \\ CHOH \\ | \\ COOH \end{array}$$

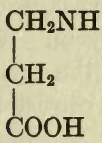


$$\begin{array}{l} CHNH_2 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CHOH \\ | \\ COOH \end{array}$$



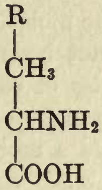
$$\begin{array}{l} CH_2NH_2 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CHOH \\ | \\ COOH \end{array}$$

While the following do form copper salts:



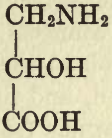
$$\begin{array}{l} CH_2NH \\ | \\ CH_2 \\ | \\ COOH \end{array}$$

(β alanin)$_2$Cu



$$\begin{array}{l} R \\ | \\ CH_3 \\ | \\ CHNH_2 \\ | \\ COOH \end{array}$$

(α amino acid)$_2$Cu



$$\begin{array}{l} CH_2NH_2 \\ | \\ CHOH \\ | \\ COOH \end{array}$$

(isoserin)$_1$Cu

Our results confirm the previous figures on dibasic salts having a general formula CuA, where A = a dibasic acid, such as aspartic, glutaminic, cystinic, etc.

Dibasic Amino Acids

Substance.	Method of prepara-tion.	Weight of sample.	CuO in filtrate	CuO in ppt.	Theoretical wt. CuO calc. for this sample.	Per cent total CuO to theory.
		gm.	gm.	gm.	gm.	
Cystin	c	0.1013	0.0000	0.0320	0.0332	96.4
Cystin	c	0.1000	0.0000	0.0324	0.0331	97.9
Cystin	c	0.1008	0.0000	0.0331	0.0334	99.1
Aspartic acid [1]	a	0.1022	0.0007	0.0575	0.0611	95.3
Aspartic acid	a	0.0997	0.0009	0.0579	0.0596	98.6
Glutaminic acid [1]	a	0.01002	0.0005	0.0500	0.0542	93.5
Glutaminic acid	a	0.01025	0.0004	0.0518	0.0554	94.9

[1] Before boiling, the copper salts are diluted to 150 c.c. with water.

Polypeptide Copper Salts

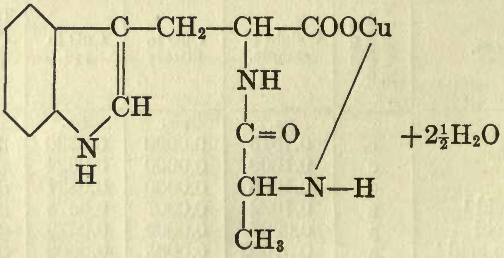
Out of a hundred or more polypeptides, Fischer, Abderhalden, and their collaborators have analyzed only about eight of the polypeptide copper salts; and these, with three exceptions (Nos. VI, VII, VIII), were insoluble and crystallized out. In such cases there can be no doubt as to the purity of the product, and the results are confirmed by our work on the more soluble copper peptides. These cases are as follows:

I (leucyl-glycin copper)$_2$O[1] +H_2O, or $(C_8H_{15}O_3N_2Cu)_2O + H_2O$.

Fischer concluded that one molecule of copper hydroxide combined with one molecule of leucyl-glycin, and that two molecules of the copper leucyl-glycin are connected by an oxygen atom. Although we have found one molecule of copper hydroxide to one of leucyl-glycin, we have not been able to find that an oxygen atom connects two molecules of copper leucyl-glycin. We have determined the molecular weight of this salt by the cryroscopic method, and find it to have a molecular weight consistent with the formula (leucyl-glycin)Cu.

II (phenyl-glycin-glycin)$_1$ copper,[2] $C_{10}H_{10}N_2O_3Cu$.
III (l-leucyl-l-histidin)$_1$ copper,[3] $C_{12}H_{18}O_3N_4Cu$.
IV (alanyl-l-tryptophan)$_1$ copper,[4] $C_{14}H_{15}N_3O_3Cu$.

Abderhalden and Kempe have assumed the following structure for this body (a discussion of this may be found in another paper):



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[1] Fischer, Ann., *340*, 145.
[2] Fischer, Ann., *340*, 195.
[3] Fischer and L. H. Cone, Ann., *363*, 107.
[4] Abderhalden and M. Kempe, Ber., *40*, 2737.

V (l-propyl-l-phenylalanin)$_1$ copper,[1] $C_{14}H_{16}N_2O_3Cu + 3\frac{1}{2}H_2O$.
VI (d-alalyl-l-leucyl-isoleucin)$_2$ copper,[2] $(C_{15}H_{27}O_4N_3)_2Cu$.
VII (glycyl-d-alanyl-l-leucyl-isoserin)$_2$ copper,[3] (peptide)$_2$Cu.
VIII (tri-glycyl-glycin)$_2$ copper,[4] (tetrapeptide)$_2$Cu.

Out of the large number of peptide copper salts examined by Fischer, Abderhalden, and ourselves, the last three form an apparent exception to the rule. There is good reason to believe that the formulas given for VI, VII, and VIII may be incorrect.

Abderhalden and Hirsch boiled their peptides (VI, VII) with cupric hydroxide, and evaporated to dryness. Assuming that the residue contained nothing but the pure copper salt of the peptide, they determined the amount of copper and found it to fit the formula given above. According to our experience, the copper salt could not be formed quantitatively under these conditions, and that the results are consistent with their formula would seem to us to be purely accidental.

Curtius' tri-glycyl-glycin copper (VIII) seems not to be a true copper salt of polypeptide. The ester hydrochloride was boiled with cupric oxide and the salt precipitated by the addition of alcohol. The copper chloride present in the resulting solution, it seems to us, would prevent the formation of a true copper salt. Our results on the tetrapeptides do not support Curtius' formulas.

Using the technique described above, we have formed the copper salts of the following peptides,[5] and have found the results to be consistent with the formula (peptide)$_1$Cu:

[1] Fischer, Ber., *42*, 4752.

[2] Abderhalden and Hirsch, Ber., *43*, 2439.

[3] Ibid.

[4] Curtius, Ber., *37*, 1284.

[5] The majority of the peptides used in this study were prepared or collected by the late Dr. Arthur H. Koelker. A small number (four di-peptides and three tri-peptides) were made according to Fischer's directions by Dr. H. Hager and ourselves in this laboratory. Glycyl tryptophan was obtained in very pure crystalline form through the kindness of Kalle & Co.

DI–PEPTIDES

Specimen.	Substance.	Weight of sample.	CuO in filtrate after adding 3 c.c. N NaOH (CO_2 free) and boiling.	CuO in ppt. after adding 3 c.c. N NaOH (CO_2 free) and boiling.	Total CuO.	Theoretical weight CuO calculated for this sample.	Per cent total CuO found to theory.
		gm.	gm.	gm.	gm.	gm.	
A	Glycyl-l-tyrosin	0.1015	0.0167	0.0073	0.0240	0.0340	70.6
B	Glycyl-l-tyrosin	0.1023	0.0267	0.0042	0.0309	0.0342	90.4
C	Glycyl-l-tyrosin	0.1017	0.0271	0.0016	0.0287	0.0340	84.4
D	Glycyl-l-tyrosin	0.1011	0.0268	0.0021	0.0289	0.0338	85.8
E	Glycyl-tyrosin	0.0545	0.0142	0.0043	0.0185	0.0181	102.2
A	D–leucyl-l-leucin	0.1011	0.0268	0.0003	0.0271	0.0330	82.1
B	D-leucyl-d-leucin	0.1007	0.0294	0.0013	0.0307	0.0328	93.6
C	L-leucyl-d-leucin	0.1016	0.0250	0.0004	0.0254	0.0331	76.7
D	D-leucyl-d-leucin	0.1010	0.0268	0.0037	0.0305	0.0329	92.7
E	R-leucyl-leucin	0.1006	0.0288	0.0014	0.0302	0.0328	92.1
F	L-leucyl-d-leucin	0.1004	0.0266	0.0021	0.0287	0.0327	87.8
A	L-alanyl-d-alanin [1]	0.1014	0.0320	0.0120	0.0440	0.0503	87.5
B	L-alanyl-d-alanin [1]	0.1010	0.0250	0.0217	0.0467	0.0502	93.0
C	D-alanyl-d-alanin	0.1016	0.0454	0.0035	0.0489	0.0454	107.7
D	D-alanyl-d-alanin	0.1018	0.0473	0.0048	0.0521	0.0506	103.0
E	D-alanyl-d-alanin	0.1001	0.0465	0.0041	0.0506	0.0497	101.8
F	D-alanyl-d-alanin [1]	0.1006	0.0282	0.0202	0.0484	0.0500	96.8
A	R-valyl-glycin	0.1005	0.0410	0.0059	0.0469	0.0459	102.2
B	R-valyl-glycin	0.1003	0.0085	0.0008	0.0093	0.0458	20.3
C	R-valyl-glycin	0.1003	0.0212	0.0018	0.0230	0.0458	50.2
D	R-valyl-glycin	0.1001	0.0395	0.0052	0.0447	0.0457	97.8
E	R-valyl-glycin	0.1002	0.0047	0.0004	0.0051	0.0458	11.1
F	R-valyl-glycin	0.0521	0.0093	0.0016	0.0109	0.0238	45.8
A	Glycyl-valin (crude)	0.1012	0.0384	0.0052	0.0436	0.0462	94.4
B	R-glycyl-valin	0.1012	0.0400	0.0062	0.0462	0.0462	100.0
C	R-glycyl-valin	0.1020	0.0422	0.0006	0.0428	0.0466	91.8
D	Glycyl-d-valin	0.1015	0.0390	0.0059	0.0449	0.0464	96.8
E	Glycyl-d-l-valin	0.0654	0.0271	0.0011	0.0282	0.0299	94.3
A	R-glycyl-aminobutyric acid [1]	0.1022	0.0244	0.0263	0.0507	0.0508	99.8
B	R-glycyl-aminobutyric acid	0.1007	0.0437	0.0030	0.0467	0.0500	93.4
A	Amino-normal-caproic-glycin	0.0664	0.0257	0.0015	0.0272	0.0281	96.8
A	R-leucyl-glycin	0.0901	0.0344	0.0041	0.0385	0.0381	101.0
B	R-leucyl-glycin	0.1003	0.0398	0.0037	0.0435	0.0425	102.4
C	R-leucyl-glycin	0.1010	0.0398	0.0045	0.0443	0.0427	103.7
D	R-leucyl-glycin	0.1004	0.0378	0.0044	0.0422	0.0425	99.3
E	R-leucyl-glycin	0.1013	0.0397	0.0047	0.0444	0.0428	103.7
F	R-leucyl-glycin	0.1013	0.0381	0.0047	0.0428	0.0428	100.0

[1] This substance, judging from the heavy precipitate of CuO formed on adding alkali, is very impure; it is probably a mixture containing amino acids.

DI–PEPTIDES, *Continued*

Specimen.	Substance.	Weight of sample.	CuO in filtrate after adding 3 c.c. N NaOH (CO_2 free) and boiling.	CuO in ppt. after adding 3 c.c. N NaOH (CO_2 free) and boiling.	Total CuO.	Theoretical weight CuO calculated for this sample.	Per cent total CuO found to theory.
		gm.	gm.	gm.	gm.	gm.	
	Leucyl-aspartic acid [1]	0.1015	0.0175	0.0106	0.0281	0.0328	85.7
A	Glycyl-tryptophan	0.1016	0.0257	0.0010	0.0267	0.0310	86.1
A	Glycyl-d-alanin	0.1011	0.0524	0.0006	0.0530	0.0550	96.5
B	Glycyl-d-l-alanin	0.1006	0.0501	0.0049	0.0550	0.0548	100.4
C	Glycyl-d-alanin	0.1013	0.0494	0.0043	0.0537	0.0551	97.5
A	L-alanyl-glycin	0.1005	0.0496	0.0054	0.0550	0.0547	100.5
B	R-alanyl-glycin	0.1007	0.0516	0.0032	0.0548	0.0548	100.0
C	D-l-alanyl-glycin	0.0559	0.0285	0.0009	0.0294	0.0304	96.7
D	R-alanyl-glycin	0,1009	0.0512	0.0014	0.0526	0.0549	95.8
E	L-alanyl-glycin	0.1013	0.0492	0.0055	0.0547	0.0552	99.1
A	Glycyl-l-leucin	0.1006	0.0370	0.0036	0.0406	0.0425	95.5
B	Glycyl-d-l-leucin	0.0909	0.0357	0.0013	0.0370	0.0384	94.0
B	Glycyl-d-l-leucin	0.0720	0.0280	0.0010	0.0290	0.0305	95.1
C	Glycyl-leucin	0.1005	0.0380	0.0022	0.0402	0.0425	94.6
A	Glycyl-amino-normal-caproic	0.1004	0.0391	0.0026	0.0417	0.0425	98.1
B	Glycyl-amino-normal-caproic	0.1013	0.0368	0.0049	0.0417	0.0428	97.4
C	Glycyl-amino-normal-caproic	0.0963	0.0377	0.0014	0.0391	0.0407	96.1
A	Glycyl-asparagin	0.1028	0.0397	0.0031	0.0428	0.0433	98.8
A	Glycyl-asparagin	0.1009	0.0379	0.0024	0.0403	0.0425	94.8
A	Alanyl-asparagin [1]	0.0750	0.0026	0.0201	0.0227	0.0294	77.2
A	Alanyl-asparagin [1]	0.0551	0.0019	0.0144	0.0163	0.0215	75.5
A	Leucyl-asparagin	0.1016	0.0209	0.0006	0.0215	0.0330	65.2
A	Leucyl-asparagin	0.1004	0.0205	0.0010	0.0215	0.0326	66.0
A	Leucyl-asparagin	0.1013	0.0205	0.0009	0.0214	0.0329	65.0
A	Glycyl-phenylglycin	0.1021	0.0355	0.0030	0.0385	0.0390	98.7
B	Glycyl-d-phenylglycin	0.1022	0.0358	0.0010	0.0368	0.0391	94.1
A	Aminobutyl-glycin	0.1010	0.0467	0.0045	0.0512	0.0502	102.0
B	Aminobutyl-glycin	0.1005	0.0435	0.0059	0.0494	0.0499	99.0
A	Glycyl-glycin	0.1007	0.0519	0.0069	0.0588	0.0607	96.9
B	Glycyl-glycin	0.0123	0.0536	0.0070	0.0606	0.0616	98.4

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[1] This substance, judging from the heavy precipitate of CuO formed on adding alkali, is very impure; it is probably a mixture containing amino acids.

TRI-PEPTIDES

Speci-men.	Substance.	Weight of sample.	CuO in filtrate.	CuO in ppt.	Total CuO.	Theoretical weight CuO, calc. for this sample.	Per cent CuO in filtrate to theory.	Per cent total CuO to theory.
		gm.	gm.	gm.	gm.	gm.		
A	Glycyl-glycyl-alanin [1]	0.1008	0.0367	0.0163	0.0530	0.0395	92.9	134.2
B	Glycyl-glycyl-alanin	0.1021	0.0356	0.0064	0.0420	0.0400	89.0	105.0
A	Glycyl-glycyl-amino-butyric .	0.1011	0.0382	0.0006	0.0388	0.0371	103.0	104.6
B	Glycyl-glycyl-amino-butyric .	0.0820	0.0286	0.0012	0.0298	0.0333	85.9	89.5
A	R-glycyl-alanyl-glycin [1]	0.1013	0.0376	0.0207	0.0583	0.0397	94.7	146.9
B	R-glycyl-alanyl-glycin [1]	0.1016	0.0381	0.0211	0.0592	0.0398	95.7	148.8
C	Glycyl-d-alanyl-glycin	0.0323	0.0113	0.0009	0.0122	0.0127	89.0	96.1
A	Glycyl-amino-butyl-glycin [1] . .	0.1007	0.0350	0.0229	0.0579	0.0369	94.8	156.9
B	Glycyl-amino-butyl-glycin [1] . .	0.1016	0.0357	0.0197	0.0554	0.0372	96.0	148.9
C	R-glycyl-amino-butyl-glycin [1] .	0.1003	0.0347	0.0209	0.0556	0.0368	94.3	151.1
A	Glycyl-valyl-glycin	0.0519	0.0047	0.0026	0.0073	0.0179	26.3	40.8
B	Glycyl-valyl-glycin	0.0639	0.0077	0.0032	0.0109	0.0220	35.0	49.5
C	Glycyl-valyl-glycin	0.0509	0.0046	0.0026	0.0072	0.0175	26.3	41.1
A	Gylcyl-leucyl-glycin	0.1013	0.0293	0.0004	0.0297	0.0329	88.5	90.3
A	Glycyl-leucyl-glycin	0.1010	0.0282	0.0002	0.0284	0.0328	86.0	86.6
A	Glycyl-leucyl-glycin	0.1005	0.0277	0.0002	0.0279	0.0326	85.0	85.6
B	Glycyl-leucyl-glycin	0.1008	0.0306	0.0052	0.0358	0.0327	93.6	109.5
A	Glycyl-glycyl-l-leucin	0.1020	0.0287	0.0024	0.0311	0.0331	86.7	94.0
B	Glycyl-glycyl-leucin	0.1010	0.0279	0.0044	0.0323	0.0328	86.4	98.5
A	L-leucyl-glycyl-glycin	0.1011	0.0284	0.0043	0.0327	0.0328	86.6	99.7
B	Leucyl-glycyl-glycin	0.1013	0.0283	0.0057	0.0340	0.0329	86.1	103.3
C	R-leucyl-glycyl-glycin	0.1007	0.0173	0.0019	0.0192	0.0327	52.9	58.7

A	Leucyl-alanyl-alanin	0.1017	0.0272	0.0050	0.0322	0.0296	91.9	108.8
B	L-leucyl-d-alanyl-d-alanin . .	0.1014	0.0262	0.0033	0.0295	0.0295	88.8	100.0
A	Glycyl-glycyl-valin	0.0757	0.0225	0.0020	0.0245	0.0261	86.2	93.9
B	Glycyl-glycyl-valin	0.1013	0.0284	0.0023	0.0307	0.0349	80.8	88.0
C	Glycyl-glycyl-valin	0.1007	0.0291	0.0037	0.0328	0.0347	83.9	94.5
D	Glycyl-glycyl-valin	0.0516	0.0155	0.0005	0.0160	0.0178	87.1	89.9
A	R-alanyl-glycyl-glycin[1]	0.1012	0.0370	0.0165	0.0535	0.0396	93.4	135.1
B	Alanyl-glycyl-glycin	0.0987	0.0254	0.0031	0.0285	0.0387	65.6	73.6
C	D-alanyl-glycyl-glycin	0.0492	0.0168	0.0014	0.0182	0.0193	87.0	94.3
A	Alanyl-leucyl-glycin	0.1012	0.0274	0.0037	0.0311	0.0311	88.1	100.0
A	Glycyl-glycyl-glycin	0.1000	0.0378	0.0010	0.0388	0.0421	89.8	92.2
A	Glycyl-glycyl-glycin	0.1003	0.0370	0.0006	0.0376	0.0422	87.7	98.0
A	Glycyl-glycyl-glycin[1]	0.1016	0.0409	0.0000	0.0409	0.0427	95.8	95.8
A	Glycyl-glycyl-glycin[1]	0.1020	0.0405	0.0000	0.0405	0.0429	94.4	94.4
A	L-leucyl-glycyl-d-alanin . . .	0.0569	0.0161	0.0008	0.0169	0.0175	92.0	96.6
A	Leucyl-alanyl-glycin	0.1002	0.0289	0.0040	0.0329	0.0308	93.8	106.8
A	Amino-butyl-glycyl-glycin . .	0.1011	0.0350	0.0028	0.0378	0.0371	94.3	101.9
A	Valyl-glycyl-glycin	0.1023	0.0288	0.0027	0.0315	0.0352	81.8	89.5
A	Amino-normal-capronyl-glycyl-glycin	0.1003	0.0304	0.0035	0.0339	0.0325	93.5	104.3
A	Glycyl-d-alanyl-d-alanin . . .	0.0536	0.0144	0.0001	0.0145	0.0192	75.0	75.5
A	Glycyl-d-alanyl-d-alanin . . .	0.0507	0.0139	0.0001	0.0140	0.0186	74.7	75.3

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[1] The copper salt in this case was formed in cold alkaline solution.

TETRA-PEPTIDES

Specimen.	Substance.	Weight of sample.	CuO in filtrate.	CuO in ppt.	Total CuO.	Theoretical weight CuO, calc. for this sample.	Per cent CuO in filtrate to theory.	Per cent total CuO to theory.
		gm.	gm.	gm.	gm.	gm.		
A	Normal-amino-caproic-di-glycyl-glycin[1]	0.1017	0.0202	0.0005	0.0207	0.0268	75.4	77.2
A	Normal-amino-caproic-di-glycyl-glycin	0.1006	0.0174	0.0004	0.0178	0.0265	65.7	67.2
A	R-aminobutyl-di-glycyl-glycin[1]	0.1050	0.0260	0.0037	0.0297	0.0305	85.2	94.1
A	R-aminobutyl-di-glycyl-glycin .	0.1006	0.0241	0.0022	0.0263	0.0292	82.5	90.1
A	R-alanyl-di-glycyl-glycin[1] . .	0.1012	0.0270	0.0040	0.0310	0.0309	87.4	100.3
A	R-alanyl-di-glycyl-glycin . . .	0.1008	0.0267	0.0017	0.0284	0.0308	86.7	92.2
A	Leucyl-di-glycyl-glycin[1] . . .	0.1008	0.0239	0.0030	0.0269	0.0265	90.2	101.5
A	Leucyl-di-glycyl-glycin	0.1015	0.0234	0.0024	0.0258	0.0267	87.6	96.6

[1] Filtered without boiling to decompose carbamino salts.

PEPTONES, ETC.

Substance.	Weight of sample.	CuO in filtrate.	CuO in ppt.	Molecular weight,[1] calc. from total CuO.
	gm.	gm.	gm.	
"Witte's" peptone . . .	0.1025	0.0041	0.0000	1990
"Witte's" peptone . . .	0.1046	0.0042	0.0000	1982
"Witte's" peptone . . .	0.1014	0.0039	0.0000	2070
"Roche" peptone	0.1110	0.0302	0.0173	186
"Merck" peptone	0.1020	0.0044	0.0002	1765
Meat peptone	0.1067	0.0000	0.0000	. . .
"Ereptone"	0.1005	0.0064	0.0133	406

[1] This calculation is based on the assumption that one molecule of peptone, as in the case of the peptides, combined with only one molecule of copper hydroxide.

The results on the above substances, within experimental error, and so far as the purity[1] of the peptides permitted, show unmistakably that one molecule of peptide, whatever number of amino acids it may contain, combines with only one molecule of copper hydroxide. This interesting fact will no doubt give us an easy method of determining the molecular weights of proteolytic substances, provided the copper salts can be separated from the excess copper hydroxide. (See also the other paper on this subject.)

The question that remains to be solved is: How are these copper salts formed and what is their structure? Taking glycyl-glycin for an example, it is interesting to attempt to picture the structure of this peptide, keeping in mind the latest work of Werner on the valency of nitrogen.

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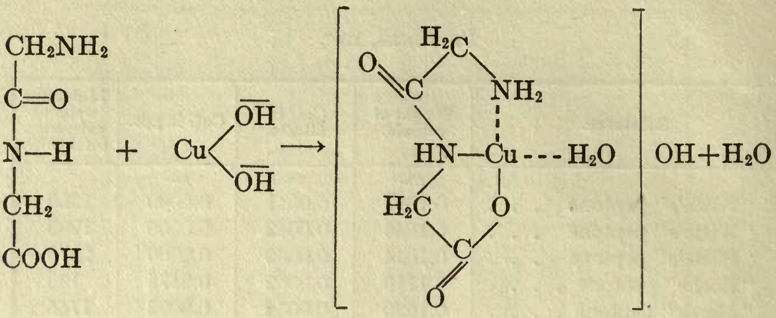
[1] Although we have not yet been able to account for all the discrepancies, yet a few qualitative tests revealed Cl and Br bodies, mixed with some of the peptides. And indeed, some of the peptides were labeled as crude and unpurified. Part of the discrepancies are due, too, to the hydrolysis of the copper salt on five minutes' boiling, The results represent, therefore, the minimum purity.



As our other experimental work and our discussions would take us far beyond the limits of this paper, we conclude simply by indicating the directions in which our experiments have led us.

We are not ready to offer a theory of the biuret reaction, as we wish to check spectrographically our macroscopic observations on color. The following, therefore, is only tentative.

For the present we shall use the following terms: (*a*) *Biuret color*, a purple red, resembling an alkaline phenolphthalein solution in color. Colors having a bluer tinge we shall term (*b*) *partial biuret*, or *semi-biuret*, as some are probably mixtures of pure *biuret* and ordinary complex-blue. Another term we should like to fix: (*c*) *biuret reaction* of a peptide; the color reaction obtained on adding a large excess of alkali to the peptide when it is *completely combined* with the copper, that is, the color reaction of the *alkaline copper salt.*

If the peptides are to be classified according to these terms we find that:

I. *All simple di-peptides* made from mono-amino acids, excluding their amide derivatives, give about the same color with copper in alkaline solution—a deep blue color like that of the ammonia-copper complex.

II. The neutral copper salts of all *tri-peptides,* made from mono-amino acids, excluding their amide derivatives, and of all *amides* of *di-peptides* change color on the addition of excess alkali. They give shades of the "semi-biuret" color, the shade varying with the constituent amino acids and the temperature.[1]

[1] The amount of biuret color seems to increase with rise of temperature, which fact would suggest that an equilibrium exists between the blue and red substances.

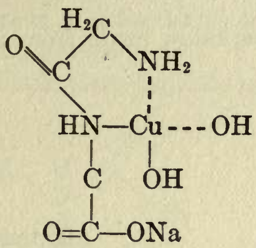
III. The color of the neutral copper salts of all *tetra-peptides* of mono-amino acids, and of *amides of tri-peptides,* changes color on addition of excess alkali from the deep blue of their neutral copper complex, to the purple-red biuret color.

To summarize:

I. When a substance is so combined with copper that only *two nitrogen atoms* are connected with the copper in a ring formation,[1] stable in excess alkali, the result is a *deep blue* color, like that of the copper-ammonia complex.

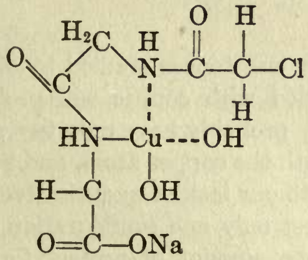
For example:

(*a*) All simple di-peptides made from mono-amino acids, like



Alkaline
Cu(glycyl-glycin)

(*b*) All carboxyl derivatives of simple di-peptides, made from mono-amino acids; such as



Alkaline
Cu(chloracetyl-glycyl-glycin)

II. When *three nitrogen* atoms are connected with the copper in a ring formation that is stable in excess alkali, a "*semi-biuret*" color is produced.

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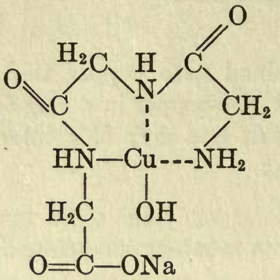
[1] By ring formation we mean formations of not more than six members.

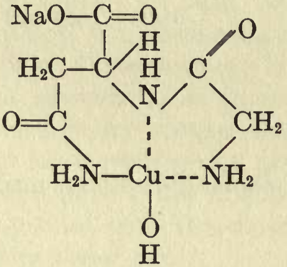
For example:

(*a*) All simple tri-peptides made from mono-amino acids, such as



Alkaline
Cu(glycyl-glycyl-glycin)

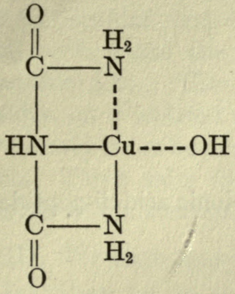
(*b*) All amides of simple di-peptides, made from mono-amino acids, such as

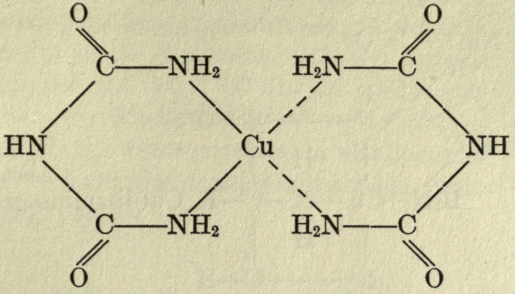


Alkaline
Cu(glycyl-asparagin)

(*c*) Various di-amides and other substances studied by Schiff. Some of these when fully combined with copper will probably give a blue complex-color, and they probably have only two nitrogen atoms connected in the ring with the copper atom, and belong to the first class of salts. (Owing to our lack of quantitative data on the subject, however, we suggest only one configuration, that of biuret.) Furthermore, when the amount of proteolytic substance is in large excess, as is usually the case when the biuret test is made, two or more molecules of the substance may combine to form a mixture of nitrogen complexes. Thus:

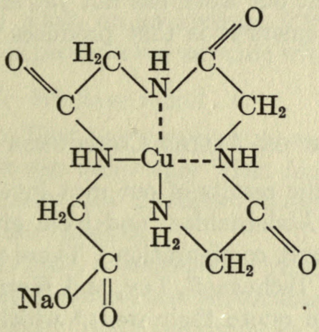
A "semi-biuret" complex, and a "true biuret" complex[1]





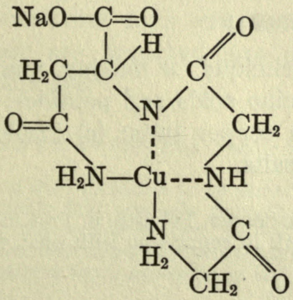
III. When four nitrogen atoms, as in the case of biuret copper just shown, are connected with the copper in a ring formation that is stable in excess alkali, a purple-red color, like that of phenolphthalein in alkaline solution, is produced. This is the true biuret color. For example:

(*a*) All simple tetra-peptides made from mono-amino acids, as



Alkaline
Cu(tri-glycyl-glycin)

(*b*) All amides of simple tri-peptides made from mono-amino acids, as



Alkaline
Cu(di-glycyl-asparagin)

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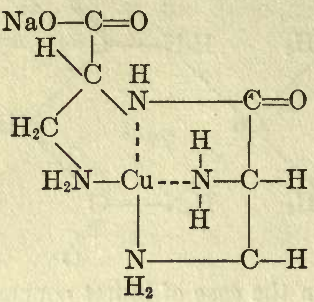
[1] Schiff's compound; with our ideas of structure, which accord with his analyses. Ber., *29*, I, 298 (1896).

(*c*) Some di-amino di-peptides, as



Alkaline Cu(di-amino-propionic acid di-peptide)

Fischer [1] found that this substance was the only di-peptide giving a strong biuret reaction, and was inclined to doubt the identity and purity of the substance. If our suppositions are correct, there can be no question as to the identity of this body, as our results support Fischer's work. But our work has not yet made clear which of the two possible isomers it is that produces the biuret configuration.

A REVIEW OF PREVIOUS WORK ON ALLIED COMPOUNDS

So far we have given a part of the results of our own investigations and those of Fischer and Abderhalden, and have given a chemical picture of a possible biuret configuration. There was much pioneer work done by Schiff, Tschugaeff, Ley, and Werner, and we regret that we cannot here quote their work,[2] which is supported to a large extent by the results just given.

SUMMARY

I. We have developed a technique for making, quantitatively, copper salts of (*a*) soluble amino acids and peptides; (*b*) insoluble amino acids with soluble copper salts; (*c*) insoluble amino acids having insoluble copper salts.

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[1] Fischer, Untersuch. über Amino-Säuren, Polypep. u. Proteine, 50.

[2] A short discussion of their work in connection with what we have done will be given in our next paper.

II. (*a*) We have formed the copper salts of 33 di-peptides, 26 tri-peptides, and 4 tetra-peptides, quantitatively, in solution, and have found the results to be consistent with the formula $(\text{peptide})_1\text{Cu}_1$. This supports the work of Fischer and Abderhalden on 5 isolated salts. (*b*) We have formed copper salts of brom and chlor bodies of tri- and tetra-peptides, in alkaline solution. These salts seem to have the same configuration, practically, as the corresponding peptide salts.

III. We have found

(*a*) That, on an average, 99% of the copper of all amino acid salts (except that of histidin) is precipitated as oxide when treated with a certain excess of alkali.[1]

(*b*) That, on an average, 6.4% of the copper of di-peptide salts is precipitated as oxide with the same excess of alkali.

(*c*) That, on an average, 6.3% of the copper of tri-peptide[2] salts is precipitated as oxide with the same excess of alkali.

(*d*) That, on an average, 7.3% of the copper of tetra-peptide[2] salts is precipitated as oxide with the same excess of alkali.

IV. We have found

(*a*) That our experiments seem to show that a *true biuret reaction* can occur only when four nitrogen atoms are so arranged that they can combine "co-ordinately" with the copper in an alkaline solution.

(*b*) That a semi-biuret reaction can occur only when three nitrogen atoms are so arranged that they can combine "co-ordinately" with the copper in alkaline solution.

V. We have concluded that most proteins probably are not one long catenary chain of amino acids. On account of their yielding a semi-biuret color with excess alkali and excess copper, we think they are branched into chains, in which tri-peptide chains predominate.[3]

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[1] Using 3 to 5 c.c. $\text{N}\cdot\text{CO}_2$ free NaOH for every 0.1 gm. substance, and boiling.

[2] Assuming all the substances to be perfectly pure, which of course they are not. It is probable that perfectly pure tri- and tetra-peptides will not precipitate any of the copper of their salts under the conditions given above. We are convinced that impurities will account for most of the precipitation.

[3] This will receive more attention in the near future.

Our thanks are due to Dr. Wm. G. Lyle for his encouragement in this work, and for placing at our disposal the excellent collection of proteolytic substances belonging to the late Dr. A. H. Koelker; and to Miss Calm M. Hoke for much assistance in preparing this article for publication.

OF THE PREPARATION OF OXAN AND OF THE EXISTENCE OF A HIGHER GRADE OF ITS OXIDATION, PEROXAN

By A. P. Lidoff

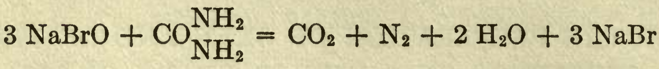
Technological Institute, Charkov, Russia

In the year 1909 I published a paper in Russian entitled "Of the Existence of Other Gaseous Compounds of Carbon and Nitrogen besides Cyanogen," and I submitted to the Seventh International Congress of Applied Chemistry the basis of this work. In it I came to the conclusion that alongside with the carbon dioxide and carbon monoxide there exist also similar gases, oxymonocyan or oxan and monocyan or cyanil. The last-named gas is obtained by the stilling of cyanogen with red-hot powdered iron and by burning a carbon lamp in nitrogen. Oxan is obtained by combustion of a gas mixture containing monocyan, by warming a mixture of nickel cyanide with phosphorous pentoxide, and, the easiest of all, by heating up to 160° a mixture of cyanogen bromide and cyanogen iodide with silver oxide.

The last researches in this direction, partly published in the "Journal of the Russian Chemical Society" and partly unpublished, led to the seeking of an easy manner of obtaining oxan and of oxan salts in the purest state possible.

I. *Of the Reciprocal Action of a Solution of Sodium Hypobromite with Urea*

As, on account of the reciprocal action of urea with hypobromite solution which is confirmed by numerous analytical data, a certain quantity of nitrogen is always lost, it was interesting to find out whether this loss is not due to the formation of oxan, and whether it would not be possible to make use of this reciprocal action in order to obtain pure salt of bariumoxanate. Many experiments made in this direction confirm that the reaction does not take place in conformity with the equation



$$3\ NaBrO + CO\begin{matrix}NH_2\\NH_2\end{matrix} = CO_2 + N_2 + 2\ H_2O + 3\ NaBr$$

as the proportionate quantities of nitrogen and carbon dioxide do not remain the same. With the changes of the concentration of the solutions the quantity of carbon dioxide formed is always superior, and the weight of this carbon dioxide from the precipitated barium salt is always less than the weight of pure carbon dioxide, and constantly changes and always tends to decrease in weight, while the concentration of the solution diminishes. By oxidation of the solution of urea always diminishing in strength with an hypobromite solution (100 gm., 50 gm., 25 gm., 20 gm., 10 gm., in 1000 c.c. water and 5 c.c. brom on 50 c.c. of strong solution of sodium hydroxide free from carbon dioxide) the weight of the gas obtained from this barium carbonate salt, freed from admixture of the second treatment of sodium hydroxide, was found to be gradually and regularly diminishing (1.974, 1.945, 1.925, 1.921, 1.911). The further dilution however does not bring near the weight of the gas to the weight of a liter of the pure oxan — 1.875 gm.

II. *The Oxidation of Sodium Cyanamide with Hypobromite Solution and Hydrogen Peroxide*

Much better results in obtaining a weight nearer to the weight of pure oxan were obtained by the oxidation of a solution of sodium cyanamide with hypobromite solution. The weight of the gas from the average of three determinations was found to equal 1.896.

By the oxidation with a 5% solution of sodium cyanamide with perhydrol solution first in the cold and afterwards by warming it till the lead acetate solution does not give any yellow precipitate of lead cyanamide (the nitrogen of cyanamide is expelled in very small quantities) a solution is formed in which the lead acetate gives a white precipitate and the gas expelled like carbon dioxide is of much lesser weight.

III. *Oxidation of Potassium Cyanate with Hypobromite Solution and Hydrogen Peroxide*

Working potassium cyanate in the same conditions, it was found that in this case also nitrogen does not get expelled but remains connected with potassium in the form of potassium oxanate salt. Working in a neutral solution, perhydrol oxidizes the potassium cyanate solution to all appearance in conformity with the equation

$$2\ KCNO + H_2O_2 = K_2CNO_2 + CNO + H_2O$$

but alongside with this reaction there is also hydrolysis of potassium cyanate and at the same time there is always more or less potassium carbonate and ammonium carbonate formed.

By the oxidation of an alkali solution containing strictly necessary and sufficient quantities of alkali to be able to bind the expelled oxan in conformity with the equation

$$2\ KCNO + 2\ NaHO + 2H_2O_2 = K_2CNO_2 + Na_2CNO_2 + 2\ H_2O$$

the conditions for the reaction with regard to the formation of a greater quantity of this gas are greatly ameliorated.

Still better results for the reaction are obtained by oxidizing powdered potassium cyanate in alcohol with an equivalent quantity of sodium hydroxide alcohol solution and alcohol peroxide solution (the latter solution has to be added in small quantities) in a hermetically closed vessel which is for a certain time energetically shaken.

In this case nitrogen is not at all expelled and at the end of the reaction, in dependence with the quantity of alcohol used, 15 to 20% more salt is filtered than there was taken potassium cyanate, while if the oxidation went with the formation of potassium carbonate, out of each 162 parts of potassium cyanate there ought to be formed only 138 parts of potassium carbonate.

IV. *Further Oxidation of Salts of Oxan*

If we submit the mixture of potassium and sodium salt thus obtained, the greater part of which consists in oxan salts, to the further oxidation of an alcohol solution of perhydrol, a further ozidation of the salts will take place, and there will probably be formed salts of peroxan: the characteristic individuality of these salts being, besides hydroscopity, their tendency under the influence of acids to very different decompositions, either, *first,* to expel gases much heavier than carbon dioxide and oxan, or, *secondly,* to expel oxygen only, or, *thirdly,* to expel oxan and hydrogen peroxide.

V. *Of the Formation of Oxan Salts by the Combustion of Potassium Cyanate with Cupric Oxide in Dry Nitrogen*

By heating a mixture of dry potassium cyanate with cupric oxide in dry nitrogen in a temperature of not higher than 375°, a potassium oxanate is principally formed and free oxan is expelled in conformity with the equation

$$2\,KCNO + CuO = K_2CNO_2 + CNO + Cu$$

That the reaction is really so, is confirmed as well by the weight of the gas expelled by the heating, as by the weight of the gas produced from the remaining salts.

The weight of the last-named gas is found to be, from numerous determinations, very near to that of oxan and is nearly always lower than 1.900.

It seems that by this process of oxidation temperature is the principal factor; even a great abundance of cupric oxide does not change the reaction in what concerns the formation of a considerable quantity of carbon dioxide. If only the salt had had time to react in the above-shown way, the further heating up to a high temperature with abundance of cupric oxide does not change the reaction.

VI. *Heating of Potassium Cyanate or Mixture of that Salt with Cupric Oxide in Dry Oxygen*

The reaction, however, changes very greatly if potassium cyanate or its mixture with cupric oxide is heated in dry oxygen.

In this case, alongside with oxan, a great quantity of carbon dioxide is formed, and also very often, though not always, heavier gas than carbon dioxide and oxan, which gives an in water insoluble barium salt.

This heavier gas very probably is the product of the oxidation of oxan, peroxan, the weight of which is equal to 2.590. On account of its easy disintegration, it is difficult to determine it.

If we consider the weight of the gas which fluctuated between 2.060 to 2.359 under these conditions, a gas is obtained which represents a mixture of all the three gases. That the potassium cyanate alone, as well as with cupric oxide by heating in oxygen, takes in the latter and expels it in ignition (oxan salts act in this as transmitter of oxygen) is proved by this, that several times considerable increase of weight of the salt (up to 8%) has been observed; this would of course have been impossible if the reaction only led to the formation from potassium cyanate to potassium carbonate.

VII. *Of the Formation of Oxan by the Reciprocal Action of Nitrogen Dioxide with Charcoal*

The simplest way of obtaining oxan and oxan salts consists in the reciprocal action of dry nitrogen dioxide with dry charcoal, broken into small pieces at a low temperature. In the aforementioned paper, published three years ago, I indicated that by the reciprocal action of nitrogen oxides with charcoal at a high temperature, a diminution of the initial quantity of nitrogen is observed, although the weight of the carbon dioxide thus formed is always equal to the normal weight of carbon dioxide.

As all the above-mentioned facts establish without doubt that oxan is principally formed at a low temperature, experiments were made of the reciprocal action of nitrogen dioxide with charcoal at a temperature not exceeding 300°. It was then found out that oxan is more energetically formed at a temperature of about 300°, but, judging by the weight, the gas is less pure than when the temperature of the charcoal is not higher than 150°. When a fixed volume of nitrogen dioxide is passed backward and forward through dry charcoal heated up to the above-mentioned temperature, and in one of the vessels (best of all in the decomposition flask of nitrometer) a small quantity of a strong solution of sodium hydroxide free from carbon dioxide is poured in, one can observe that at 300° the whole quantity of nitrogen dioxide is completely and rapidly absorbed, at 150° slowly, but also completely. If the solution of sodium hydroxide, which has absorbed the gas, is immediately decomposed by phosphoric acid, in most cases pure oxan, if we judge by weight, is obtained. But if this solution is not decomposed for a certain length of time, less gas is obtained and the gas has more weight.

VIII. *Polymerization of Oxan*

An original particularity of oxan is its tendency to polymerize, as well in free state (this is comparatively more difficult: the greatest diminution of volume observed during three days was from $44\frac{1}{2}$ c.c. $\frac{746}{19.2}$ to $40\frac{4}{10}$ c.c. $\frac{752}{19.2}$, while the weight of the gas increased to $7\frac{1}{10}$ mgr.), as in salts (comparatively easily). In this manner the weight of gas in the salts just obtained is generally much less than the weight of gas from the same salts which have lain several days in closed tubes, consequently without access of air. Alongside with gaslike polymer of oxan there seemed to be also a solid polymer of it, as from barium, potassium, or sodium salts which have conserved a long time, the gas obtained is not only heavier than originally, that is, immediately after the salts have been prepared, but there is also a lesser quantity and sometimes the salts do not expel any gas at all. In this way the difficulty of obtaining oxan in a pure state is owing to the fact that alongside with oxan very often carbon dioxide is formed and also that oxan can readily polymerize and oxidize.

ABOUT SOME PROPERTIES OF THE OXAN SALTS

By A. P. Lidoff

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On account of the before-stated property of oxan to relatively easily oxidize and polemerize, it is very difficult to obtain oxan salts in a pure state, and I have not been able to obtain them in an absolutely pure state.

Sodium, potassium, lithium, calcium, barium, lead, and copper salts were obtained. For the identification of the purity of the salts, the quantity of metal, the quantity of gas and its weight were determined. Nearest to the theoretical data concerning sodium oxanate were those obtained by the examination of the crystalline salt which was separated from a strong alcohol solution of sodium hydroxide after reaction with a gas mixture formed by the reciprocal action of nitrogen dioxide on charcoal at 90°–100°.

	Obtained.	Theory for Na_2CNO_2	Theory for Na_2CO_3
Found Na in the form of NaCl	112.7%	112.5%	110.3%
Quantity of gas in 1 gm.		215.9 c.c. $\frac{760}{0°}$	210.1 $\frac{760}{0°}$
Weight of 1 l. of gas	1.894	1.875	1.975

Solubility of the Oxan Salts in Water.—The characteristic property of oxan salts is their better solubility in water compared with carbonate salts; this is especially to be noticed in lithium and calcium salts. Lithium carbonate is soluble in 100 parts of water according to the data of various authors who do not agree with each other, at an ordinary temperature in the quantity of 0.769—1.4787 [1] and the solubility of lithium oxanate was found to exceed three or four times the maximum of the above data. For calcium salts a still greater difference is observed, and it is much

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[1] Comey, A. M., A Dictionary of Chemical Solubilities Inorganic.

better soluble in water than calcium carbonate. The solubility of other oxanate salts, barium, lead, and copper, especially the last-named, although not in such a measure, is greater than that of the corresponding carbonate salts.

Hydrolysis of Oxanate Salts.—Alkali oxanate salts in a prolonged boiling in water and still better in a solution of sodium hydroxide with zinc powder partly hydrolyze, and in this way a more or less large quantity of ammonium can be separated. The quantity obtained, however, has never been found to correspond to the theoretical quantity of nitrogen, mostly fluctuates in very small quantities, and the maximum found was only 50% of the theoretical amount. Potassium salts seem to hydrolyze easier than sodium salts.

Condensation of Oxan Salts.—A very important and characteristic property of oxan salts is their above-mentioned one of condensing in the course of time, and on this account the quantity of gas from the salts is diminished and its weight is increased. In some salts this property is more developed than in others; so calcium and barium salts are condensed easier than alkali salts. As a characteristic example can be given the following: in one case the weight of the gas from the barium salts which had just been prepared was found to be 1.878, and the same salt after a lapse of only 6 days gave already less gas and the weight of the gas increased to 1.932.

Oxidation of Oxan Salts.—Oxan salts, especially the alkali salts, in warming them in oxygen at 300° absorb the latter. This can be remarked on account of the weight increasing, notwithstanding that a small quantity of gas is separated, which brings about a precipitate in the barium hydroxide solution. The weight of the gas from the salt after the reciprocal action with oxygen is always greater than the weight of the gas from the same salt before the reaction.

Reduction of the Peroxan Salts. — If oxan salts can oxidize with the formation of peroxan salts, it is clear that the contrary reaction can also take place, Experience quite confirms this. In leading dry hydrogen through a glass tube in which there is a combustion boat with a determined quantity of a mixture of oxan and peroxan salts, the diminution of the weight of the combustion boat and the augmentation of the weight of the calcium chloride tube is always observed. Although at the same time the weight of the control calcium chloride tube remains unchanged. At the same time a diminution of the weight of the gas of this salt after the reaction with hydrogen is remarked and, which is also characteristic, the gas frequently receives a very pronounced smell of cyan. The reduction can also be produced in a water solution by cooling with ice and aluminium prepared with mercury salts.

The Solubility of Peroxan Salts in Alcohol and Ether.—Washing with alcohol and ether the crude crystalline salt which is separated from an alcohol solution of sodium hydroxide in leading through this solution the gas mixture which is formed by the reciprocal action of nitrogen dioxide on charcoal at 300°, a comparatively great quantity of salt is extracted which does not at all correspond to the solubility in these liquids of carbonate salts. After the evaporation at an ordinary temperature in the open air or in the exsiccator *in vacuo*, hydroscopic salts remain. Of these, the sodium salt left in the open air little by little is decomposed, loses its hydroscopity, and, to judge by the weight of the gas from it, is changed in oxanate salt. In the decomposition with acid, these hydroscopical salts are decomposed and, together with the gas which is soluble in a solution of sodium hydroxide, is separated a more or less large quantity of gas insoluble in sodium hydroxide, which in the principal part consists of oxygen.

The determination of sodium in these sodium salts (in the form of sodium sulphate, Na_2SO_4) always gives a lesser quantity of sulphate (up to 105%) than is needed for soda (133.9%) and sodium oxanate (135.4%).

Peroxan Salts as Oxidizer. — In drying on filtering paper peroxan salts, the paper loses its strength, and after a few days easily turns into powder and is therefore clearly changed in oxycellulose. In the same manner, if a mixture of oxan and peroxan salts is treated with a small quantity of alcohol and that mixture is left standing in a close vessel, very soon aldehyde is smelled.

OF THE EXISTENCE OF AN ISOMER OF OXAN, BETA-OXAN

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If we let through a long tube with charcoal (length, 2000 mm., diameter, 25 mm.) dry nitrogen dioxide at an ordinary temperature and direct the gas mixture which is formed through an alcohol solution of sodium hydroxide, after a certain length of time (30–40 hours) a crystalline precipitate is formed (lamellar crystals of rhombical system or needles). This crystalline salt, if decomposed without access of air with phosphoric acid, expels gas, contrary to the salt formed under the same conditions but at a higher temperature (200°–300° C.) *very slowly*, and this gas, in its greater part, is not more soluble, neither in an alkali solution nor in an alkali solution of pyrogallol. At the same time it has a strong smell of cyan, a great weight (the average weight of 1 liter at $\frac{760 \text{ mm.}}{0^\circ}$ is 1.848), and is comparatively easily soluble in an acid solution of cuprous chloride.

Contrary to oxan, in this gas the quantity of nitrogen, almost exactly corresponding to the quantity of nitrogen in oxan, can be easily determined by the ignition of this gas with metallic magnesium powder. This gas by the ignition with platinasbest increases in volume and diminishes in weight. Basing ourselves on these data, sufficiently characterizing the nature of this gas, we can presume that it is an isomer of alpha-oxan, α–OCN, beta-oxan, β–ONC, a product of the oxidation of beta-moncyan, or beta-cyanil—$N\equiv C$.

ABSTRACT

ETHYL ISOBUTYL- AND ISOAMYL-ISOUREA

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The paper includes an improvement, when applied to monoalkyl cyanamides, of a previously described method for making alkylcyanamides from the amine, bromine, and potassium cyanide. It describes the preparation from isobutylcyanamide and isoamylcyanamide of the corresponding isoureas by the addition of alcohol to the nitril group of the cyanamides. This addition of alcohol is found to take place in the presence of hydrogen chloride or, even more rapidly, in the presence of sodium alcoholate.

The isoureas of this series, the oxygen ethers of the monoalkylureas, are basic oils which in their properties closely resemble the oxygen ethers of the dialkylureas previously described by the senior author. For example, heated with water they give only the urea and alcohol and with dilute hydrochloric acid the urea and ethyl chloride. In neither case is there any urethane (or cyanamide) formation, as would be expected to be formed, from analogy to the products given under similar conditions by the related imidoethers.

The hydrochloride, chlorplatinate, picrate, and ferrocyanide of the new isoureas are described. The acid ferrocyanides, as in the earlier-known isoureas, are quite insoluble and are useful for detecting small amounts of the isoureas, but in this series the picrate is but slightly soluble and is by far the best derivative for identification purposes.

INFLUENCE DES SUBSTITUANTS SUR L'ACTION DU BENZÈNE ET DE QUELQUES BENZÈNES SUBSTITUÉS SUR LE CHLORURE DE BENZOYLE EN PRÉSENCE DU TRICHLORURE D'ANTIMOINE

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Après avoir investigué l'influence des substituants sur le pouvoir des corps aromatiques de fixer le trihalogénure d'antimoine,[1] j'entrepris l'étude de cette influence dans une réaction plus compléxe, à savoir—dans le synthèse des cétones par l'action du hydrocarbure ou autre dérivée benzénique sur le chlorure de benzoyle en présence du trichlorure d'antimoine. Le choix de cette réaction était déterminé par le fait qu'elle procède avec une vitesse appréciable,[2] accompagnée d'une élimination de l'acide chlorhydrique, permettant de mesurer facilement cette vitesse; en outre les combinaisons moléculaires du trichlorure d'antimoine avec les substances aromatiques, préparées et étudiées dans mes travaux mentionnés ci-dessus, devaient prendre part dans le synthèse des cétones—ce qui facilitait l'étude de ses phases successives.

Le synthèse des cétones en présence du trichlorure d'antimoine ne s'accomplit pas à une température voisine de l'ordinaire, comme c'est le cas pour ce même synthèse en présence du chlorure d'aluminium, mais demande une température supérieure à 100°. Après beaucoup d'expériences préalables je me suis arrêté à la température de 155°, où la vitesse de la réaction du benzène avec le chlorure de benzoyle en présence du $SbCl_3$ est assez grande pour pouvoir être mesurée. Mais avant d'aborder ces déterminations j'ai jugé nécessaire d'investiguer, si les hydrocarbures aromatiques et le chlorure de benzoyle ne réagissent pas entre eux à 155° sans

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[1] Journal de Chimie Physique, *10* (année 1912).

[2] W. Comstock, Amer. Chem. Journal, *18*, 547 (1896).

l'intermédiaire d'un sel minéral, car sur ce point je n'ai pu trouver aucun renseignement précis. Je chauffais donc à 155° de un à vingt jours en tubes scellés des mélanges équimoléculaires d'un hydrocarbure aromatique et du chlorure de benzoyle soigneusement déssechés. Quelques dizaines des expériences démontrèrent que le benzène, le toluène, l'éthylbenzène, les trois xylènes isomères ne se combinent pas appréciablement pour former un cétone; seul le mésithylène entre en combinaison avec le chlorure de benzoyle avec dégagement du chlorure d'hydrogène. En admettant que la réaction $C_6H_3(CH_3)_3 + C_6H_5COCl = C_6H_2(CH_3)_3COC_6H_5 + HCl$ est bimoléculaire, nous obtenons les valeurs suivantes pour les constantes K_2 $\left(K_2 = \frac{1}{t} \cdot \frac{x}{a(a - x)}\right.$, où x est la quantité du C_6H_5COCl, entrée en réaction, exprimée en pourcentages de la quantité prise a):

TABLE I

Temps en minutes. t	Quantité du C_6H_5COCl prise.	Quantité du C_6H_5COCl entrée en réaction.	x	$K_2 \times 10\ g$
	gr.	gr.		
1200	1.1434	0.0074	0.65	55
5040	0.9419	0.0200	2.12	43
10800	1.1565	0.0810	7.0	62
			moyenne	5

En outre je me suis assuré en investiguant au moyen de l'analyse thermique quelques systèmes binaires formeés par les hydrocarbures aromatiques et le chlorure de benzoyle[1] que ces composants n'entrent pas en combinaison.

Voyons maintenant comment le synthèse des cétones procéde en présence du trichlorure d'antimoine.

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[1] Annales de l'Institut Polytechnique Pierre le Grand à St. Petersbourg, *16*, 73 (1911).

Je ne parlerai pas ici des appareils employés, parce qu'ils ne présentent rien de nouveau; la constante de vitesse de la réaction fut déduite de la quantité du chlorure d'hydrogène éliminée, absorbée dans une solution acqueuse de potasse caustique et déterminée par titration avec le nitrate d'argent. Un courant d'air soigneusement séché passait par tous les appareils; ce courant maintenait en mélange parfaitement homogène les corps réagissants, enlevait en même temps le chlorure d'hydrogène et le transportait au appareils absorbants. Plus la vitesse de ce courant d'air est grande, plus grande est la quantité du HCl absorbée par la potasse; mais à partir d'une certaine vitesse—variable pour chaque appareil employé—la quantité du HCl absorbée reste sensiblement la même pour une même réaction: la vitesse du courant d'air fut toujours maintenue au dessus de cette limite. Comme il était nécessaire d'intercaler entre l'appareil à réaction et les appareils absorbants un condenseur à eau pour empêcher le transport des substances réagissantes aux barboteurs absorbants, les indications de ces derniers étaient en retard relativement à la marche actuelle de la réaction, et la correction nécessaire (calculée en partant du volume connu du condenseur et du volume d'air passant en une minute à travers les appareils) fut introduite dans les indications du temps.

Il faut en outre remarquer que la température élevée des expériences mettait obstacle à l'emploi d'un dissolvant usuel: les valeurs des constantes ne sont en conséquence qu'approximatives, mais, comme tous les synthèses ont été étudiés dans les conditions identiques, les nombres obtenues sont comparables entre eux. Dans tous les cas où la vitesse de la réaction est assez grande, cette dernière, comme le montre l'expérience, a lieu jusqu'au transformation presque complète (99–99.8%) du mélange du hydrocarbure et du chlorure en cétone. Pour plus de détails je renvoi à l'article russe qui doit paraître prochainement dans les Annales de l'Institut Polytechnique de St. Petersbourg.

Les valeurs des constantes furent calculées d'après la formule $K_2 = \frac{1}{t} \cdot \frac{x}{a(a-x)}$, parce que les quantités des corps réagissants—chlorure de benzoyle et hydrocarbure aromatique—furent prises toujours équimoléculaires et les quantités du trichlorure d'antimoine seules variaient. Pour calculer la constante j'ai posé *a* égale à 100 et *x* égale à la quantité du HCl absorbée pendant le temps *t* (en minutes), exprimée en pourcentages de la quantité totale qui peut se dégager du chlorure de benzoyle employé. Je ne donne ici que les valeurs moyennes des constantes.

Passons maintenant aux résultats des expériences. La réaction fondamentale entre une molécule du benzène et une molécule du chlorure de benzoyle en présence de 2.01 molécules du trichlorure d'antimoine marche à 155° assez lentement: dans 2.5 heures il ne se dégage que 76.4% de la quantité théorique du HCl, pour elle la constante K_2 est égale à 0.000227. Si on me prend que 0.99 de molécule du $SbCl_3$, la vitesse est plus petite et $K_2 = 0.000054$. Les quantités du $SbCl_3$ dans les deux réactions sont dans le rapport $2.01 : 0.99 = 2.03$; les constantes $0.000227 : 0.000054$ dans le rapport 4.2. Il est évident que les constantes de vitesse diminuent proportionellement aux carrés des concentrations du trichlorure d'antimoine. C'est d'ailleurs le cas pour toutes les réactions investiguées où furent employées les quantités différentes du $SbCl_3$. Comme il est difficile, à cause de la hygroscopicité du trichlorure d'antimoine, d'en peser une quantité repondant exactement à une ou deux molécules, on peut, en se servant du rapport observé, calculer la valeur de la constante K_2 exactement pour deux, une . . . molécules du $SbCl_3$. Nous obtenons ainsi pour la réaction $2.0SbCl_3 + C_6H_6 + C_6H_5COCl = 2.0SbCl_3 + C_6H_5COC_6H_5 + HCl$, $K_2 = 0.000224$ et pour la réaction $1.0SbCl_3 + C_6H_6 + C_6H_5COCl = 1.0SbCl_3 + C_6H_5COC_6H_5 + HCl$, $K_2 = 0.0000546$. Cela permet d'obtenir les constantes comparables entre eux pour les différents benzènes substitués, rapportées à 1.0 ou 2.0 molécules du $SbCl_3$.

La substitution d'un atome d'hydrogène benzénique par un alkyle a une influence prononcée: le toluène réagit sur le chlorure de benzoyle avec une vitesse bien supérieure à celle montrée par le benzène; le même phénomène est constaté pour l'ethyl-, propyl-, isoamylbenzène: pour les deux derniers hydrocarbures la constante de vitesse possède la valeur la plus considérable entre les benzènes monoalkylés. Les valeurs des constantes sont rapporteés dans la table II. suivante:

TABLE II. — CONSTANTES DE VITESSE DE L'ACTION DES BENZÈNES MONOALKYLÉS SUR LE CHLORURE DE BENZOYLE À 155°

Hydrocarbure.	Réaction en présence de 2 $SbCl_3$, K_2.	Relation.	Réaction en présence de 1 $SbCl_3$, K_2.	Relation.
C_6H_6	0.000224	1	0.0000546	1
$C_6H_5CH_3$	0.00272	12	0.00067	12
$C_6H_5C_2H_5$	0.00466	21	0.00111	20
$C_6H_5C_3H_7$	0.0051	23	0.0012	22
$C_6H_5C_5H_{11}$	0.0052	23	. . .	. .

La constante pour le benzène étant posée égale à 1, on apperçoit dans cette table la grande influence des substituants alkyles: la substitution d'un hydrogène par un méthyle augmente la valeur de cette constante 12 fois, par un propyle—même 23 fois. Le mélange réagissant contenant l'isoamylbenzène devient tout noir dans quelques instants pendant la réaction; c'est peut-être à cause de cette décomposition que la valeur de la constante pour l'isoamylbenzène est la même que pour le propylbenzène. Les relations entre les constantes de vitesse, comme nous le voyons, sont les mêmes, indépendamment du nombre des molécules (une ou deux) du trichlorure d'antimoine.

TABLE III. — CONSTANTES DE VITESSE DE L'ACTION DES BENZÈNES BIALKYLÉS SUR LE CHLORURE DE BENZOYLE À 155°

Hydrocarbure.	Réaction en présence de 2 $SbCl_3$, K_2.	Relation.	Réaction en présence de 1 $SbCl_3$, K_2.	Relation.
C_6H_6	0.000224	1	0.0000546	1
$C_6H_5CH_3$	0.00272	12	0.00067	12
$C_6H_5C_2H_5$	0.00466	21	0.0011	20
$C_6H_4(CH_3)_2$ para	0.00476	21	0.00112	20
" ortho	0.00725	32	0.00176	32
" méta	0.0178	80	0.00446	81
$C_6H_4CH_3C_3H_7$ para	0.0089	40	0.0022	40

L'influence de deux substituants peut être observée dans les benzènes bisubstitués, dont furent investigués les trois xylènes et le cymène. Les valeurs des constantes de vitesse pour les réactions de ces quatre hydrocarbures avec le trichlorure de benzoyle, ainsi que les mêmes données pour le benzène, le toluène et l'éthylbenzène se trouvent dans la table III.

En comparant les constantes pour le toluène et les xylènes il est évident, que le seconde méthyle comme substituant produit une grande augmentation de vitesse de la réaction; de même que pour les hydrocarbures benzéniques monoalkylés l'augmentation du poids moléculaire du substituant produit une accélération de la réaction, ici la valeur de la constante pour le cymène (qu'on peut envisager comme le paraxylène où un méthyle est remplacé par un isopropyle) est presque double de celle du paraxylène. L'influence de l'isomérie est très prononcée, comme le montrent les constantes de l'éthylbenzène et des trois xylènes: la vitesse maximale est observée pour le métaxylène, tandisque les réactions des xylènes ortho et para ne diffèrent pas beaucoup entre elles.

L'introduction d'un troisième substituant alkyle dans le benzène produit une nouvelle accéleration, comme il s'ensuit de la table IV.

TABLE IV. — CONSTANTES DE VITESSE DE LA RÉACTION DES BENZÈNES TRIALKYLÉS AVEC LE CHLORURE DE BENZOYLE À 155°

Hydrocarbure.	Réaction en présence de 2 $SbCl_3$, K_2.	Relation.	Réaction en présence de $SbCl_3$, K_2.	Relation.
C_6H_6	0.000224	1	0.0000546	1
$C_6H_5CH_3$	0.00272	12	0.00067	12
$C_6H_4(CH_3)_2$ méta	0.0178	80	0.00446	81
$C_6H_3(CH_3)_3$1.3.5	0.107	478	0.0269	493
$C_6H_3(CH_3)_3$1.2.4	0.0316	141	0.0076	139

La constante de vitesse pour le mesithylène est si grande, qu'en présence de deux molécules du $SbCl_3$ la réaction à 155° produit déja en 4 minutes 98% du cétone. Ainsi l'augmentation du nombre des alkyles tend à accélerer énormement la réaction. En même temps l'effet de l'isomerie des triméthylbenzènes est très prononcé, et la vitesse maximale est observée dans le cas du mésithylène, où tous les méthyls sont en méta: le même phénomène fut observé pour les xylènes, dont le mètaisomère donnait la plus grande vitesse. La relation entre la constante K_2 pour le mésithylène et K_2 pour le pseudocymène reste à peu près la même si on fait réagir ces hydrocarbures avec le chlorure de benzoyle en présence de deux, une, ou une demi molécule du $SbCl_3$:

Quantité du $SbCl_3$ employée	$2SbCl_3$	$1SbCl_3$	$0.5SbCl_3$
Relation des constantes K_2 pour le mésithylène et le pseudocymène	$\frac{0.107}{0.0316} = 3.4$	$\frac{0.0269}{0.0076} = 3.5$	$\frac{0.00674}{0.00188} = 3.6$

Outre les hydrocarbures nommés j'ai investigué encore l'action du chlorure de benzoyle sur d'autres hydrocarbures aromatiques, à savoir sur le diphényle, diphényl- et triphénylméthane. La constante de vitesse de ces réactions est assez grande, notamment en présence de deux molécules du trichlorure d'antimoine K_2 = 0.0175 pour le diphénylméthane, 0.0035 pour le diphényle et 0.0030 pour le triphénylméthane. Mais ces réactions sont accompagneés à 155° par une forte décomposition, et ces données n'ont pas par conséquent grande valeur.

Quant aux autres benzènes substitués beaucoup d'entre eux ne peuvent être employés par suite de la grande réactivité du chlorure de benzoyle; c'est un petit nombre seulement que j'ai pu investiguer dans leur réaction avec le chlorure de benzoyle en présence du trichlorure d'antimoine. Les halogènes retardent beaucoup la marche de la réaction, comme le montre la table suivante:

TABLE V.—CONSTANTES DE VITESSE DE LA RÉACTION DES BENZÈNES HALOGÉNÉS SUR LE CHLORURE DE BENZOYLE EN PRÉSENCE DE DEUX MOLÉCULES DU $SbCl_3$:

Benzène substitué.	K_2.	Relation.
C_6H_6	0.000224	1
C_6H_5Cl	0.000022	0.1
C_6H_5Br	0.0000049	0.022

L'introduction du chlore diminue la valeur de la constante de 10 fois, l'introduction du brome—de 50 fois. Deux halogènes agissent encore plus énergiquement et ni le dichloro-, ni le dibromobenzène ne réagissent pas avec le C_6H_5COCl.

Le même effet est produit par le nitrogroupe: le nitrobenzène agit en présence de deux molécules du $SbCl_3$ sur le chlorure de benzoyle avec la même vitesse à peu près que le bromobenzène. Le groupe du sulfoxyle SO_3H semble suspendre tout à fait l'action dans les conditions employées ici.

Nous pouvons donc conclure de cette étude que les alkyles et peut-être les autres restes des hydrocarbures comme les groupes phènyle, $CH_2C_6H_5$ accèlerent beaucoup la réaction en question et probablement d'autant plus, que leur nombre est plus considérable (c'est ce que fut observé pour les méthyles); l'influence de l'isomérie se traduit par une variation considérable de la vitesse. Les substituants halogènes, les groupes nitro retardent la réaction avec le chlorure de benzoyle et même l'empêchent complètement s'ils substituent plus d'un atome d'hydrogène benzénique. J'ai mesuré aussi la vitesse des réactions des mêmes hydrocarbures avec le chlorure de benzoyle en présence du tribromure d'antimoine; mais comme toutes les réactions avec le $SbBr_3$ sont accompagnées d'une forte décomposition, je ne reproduis pas ici les valeurs obtenues à cause de leur incertitude et me bornerai á noter, qu'elles ont la même relation aux substituants que celles obtenues pour le trichlorure d'antimoine.

La réaction examinée—synthèse des cétones aromatiques par l'action du hydrocarbure aromatique sur le chlorure de benzoyle—est analogue à la réaction de Friedel et Crafts, où le chlorure d'aluminium est employé comme agent condenseur. Cette dernière réaction a été l'objet de beaucoup des études, et les recherches de MM. G. Perrier,[1] J. Boëseken,[2] B. Steele [3] et les miennes [4] ont démontrés, que cette réaction s'accomplit par les phases suivantes: il se forme d'abord une combinaison du chlorure acide avec le

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[1] Combinaisons du chlorure d'aluminium anhydre avec un certain nombre de composés chimiques, Caen, 1896.

[2] Recueil Pays-Bas, 19, *19* (1900); *24*, 6 (1905) et ailleurs.

[3] Journ. Chem. Soc., *83*, 1470 (1903).

[4] Annales de l'Institut Polytechnique de St. Petersbourg, *12*, 1 (1909); *13*, 1, 553 (1910).

chlorure d'aluminium, p. e. $AlCl_3, C_6H_5COCl$; sur cette combinaison agit le hydrocarbure aromatique, il y a dégagement de l'acide chlorhydrique et formation d'une combinaison du cétone avec le $AlCl_3$, p. e. $AlCl_3, C_6H_5COC_6H_5$.

La même réaction en présence du trichlorure d'antimoine ne peut avoir les mêmes phases itermédiaires: comme je l'ai montré au moyen de l'analyse thermique,[1] le chlorure de benzoyle ne se combine pas au $SbCl_3$. Par contre tous les hydrocarbures aromatiques fixent le trichlorure antimonique avec formation pour la plus part de deux combinaisons, dont la combinaison $2SbCl_3$. ArH est stable aux températures plus élevées.[2] Il faut admettre que c'est cette combinaison qui se forme d'abord dans le synthèse des cétones. Ce point de vue est d'ailleurs confirmé par l'expérience: c'est que dans tous les cas, où j'ai pris des quantités variables du trichlorure d'antimoine sur une molécule du hydrocarbure et une molécule du chlorure de benzoyle, les valeurs de la constante de vitesse sont proportionnelles aux carrés des concentrations du $SbCl_3$. La table suivante, où la concentration du $SbCl_3$ est exprimée en nombres de ses molécules sur une molécule du hydrocarbure ou du C_6H_5COCl, et K_2I et K_2II désignent les constantes vitesse observées pour les deux concentrations du $SbCl_3$, le montre bien.

De cette relation entre la concentration du trichlorure d'antimoine et la valeur de la constante de vitesse nous pouvons tirer la conclusion que deux molécules du $SbCl_3$ prennent part à la réaction et sont nécessaires pour former la combinaison $2SbCl_3 \cdot ArH$. Cette première phase s'accomplit avec une très grande vitesse sinon momentanément.

Sur la combinaison $2SbCl_3 \cdot ArH$ agit le chlorure de benzoyle, avec dégagement de l'acide chlorhydrique et formation d'un cétone qui entre en combinaison avec le $SbCl_3$: $2SbCl_3 \cdot ArH + C_6H_5COCl = SbCl_3 \cdot C_6H_5COC_6H_5 + SbCl_3 + HCl$. C'est cette réaction dont nous observons la vitesse en mesurant la quantité du HCl éliminée. Les combinaisons du trichlorure antimonique avec les cétones, comme je l'ai montré,[3] ne contiennent qu'une

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[1] Annales de l'Institut Polytechnique de St. Petersbourg, *15*, 75 (1911).
[2] Ibid., *13*, 266, 565; *14*, 251, 292; *15*, 95 (1910 et 1911).
[3] Annales de l'Institut Polytechnique de St. Petersbourg, *15*, 67 (1911).

molécule de $SbCl_3$; de puis elles se décomposent très vite à 155°, en donnant des cétones, le $SbCl_3$ et en formant quelques produits noirâtres résineux. Nous voyons donc qu'à la fin de la réaction il y a dégagement du trichlorure d'antimoine libre; ce dernier peut faire entrer en réaction une nouvelle quantité du hydrocarbure aromatique et du chlorure de benzoyle et ainsi de suite. Mais la réaction ne peut aller indéfiniment, car une partie du $SbCl_3$ reste toujours dans le produit résineux et chaque nouvelle portion du mélange $ArH + C_6H_5COCl$ réagit de plus en plus lentement. C'est ce dégagement du $SbCl_3$ accompagnant la formation du cétone qui explique comment la réaction d'une molécule de ArH et d'une molécule du C_6H_5COCl va jusqu'à la fin en présence d'une quantité du $SbCl_3$ beaucoup moindre que deux molécules (dans le cas du mésithylène la réaction s'accomplit même en présence de 0.05 mol. du $SbCl_3$).

TABLE VI

C_6H_5COCl. +	Concentrations du $SbCl_3$.		K_2I.	K_2II.	Relation des concent. du $SbCl_3$, I:II.	Carré de cette relation.	Relation des constantes K_2I: K_2II.
	I.	II.					
C_6H_6	2	1	0.000224	0.000055	2	4	4.1
$C_6H_5CH_3$ . . .	2	1	0.00272	0.00067	2	4	4.06
$C_6H_5C_2H_5$ . . .	2	1	0.00466	0.00111	2	4	4.2
$C_6H_5C_3H_7$ . . .	2	1	0.0051	0.0012	2	4	4.2
$C_6H_4(CH_3)_2$ p. .	2	1	0.00476	0.00112	2	4	4.2
$C_6H_4(CH_3)_2$ o. .	2	1	0.00725	0.00176	2	4	4.1
$C_6H_4(CH_3)_2$ m. .	2	1	0.0178	0.00446	2	4	3.98
$C_6H_4CH_3C_3H_7$ p.	2	1	0.089	0.0022	2	4	4.04
$C_6H_3(CH_3)_3$ 1.2.4	2	1	0.0316	0.0076	2	4	4.1
$C_6H_3(CH_3)_3$ 1.2.4	2	0.5	0.0316	0.00188	4	16	16.8
$C_6H_3(CH_3)_3$ 1.2.4	1	0.5	0.0076	0.00188	2	4	4.04
$C_6H_3(CH_3)_3$ 1.3.5	2	1	0.107	0.0269	2	4	3.97
$C_6H_3(CH_3)_3$ 1.3.5	2	0.5	0.107	0.00674	4	16	15.87
$C_6H_3(CH_3)_3$ 1.3.5	2	0.05	0.107	0.000064	40	1600	1664

Comme j'ai remarqué au commencement de cet article, seul de tous les hydrocarbures aromatiques le mésithylène entre en réaction appréciable avec le chlorure de benzoyle à 155°, et la constante de vitesse est exprimée par la valeur $K_2 = 0.00000005$; la même constante est 0.107 présence de deux molécules du $SbCl_3$; elle est 2.140000 fois plus grande. Il est donc évident que le trichlorure d'antimoine est une accélérateur énergique de la réaction examinée, cependant cédant beaucoup au chlorure d'aluminium, puisqu'en présence de ce dernier l'action s'accomplit à la température ordinaire. Mais tandisque pour transformer une molécule du hydrocarbure aromatique et une molécule du chlorure de benzoyle en une molécule du cétone, la présence d'une mol. du $AlCl_3$ au moins est nécessaire (parce que la conbinaison $AlCl_3 \cdot C_6H_5COAr$[1]) est très stable et ne se décompose pas), la même réaction peut s'effectuer avec une quantité beaucoup plus petite du $SbCl_3$.

La réaction de Friedel et Crafts est ordinairement désignée comme une réaction catalytique et le chlorure d'aluminium comme un catalyseur. Cette désignation est évidemment incorrecte pour le synthèse des cétones, si on accepte la définition précise de la catalyse donnée par Ostwald (la catalyse est une accélération d'une réaction à marche lente par une substance étrangère qui reste à la fin de la réaction sans changement et peut en conséquent accélérer la transformation d'une quantité illimitée des corps réagissants), car une molécule du $AlCl_3$ ne peut transformer qu'une mol. du benzène et une mol. du chlorure. Cette réaction rentre dans la catégorie des réactions dites accouplées,[2] où la réaction lente de deux substances est accélérée quand l'une réagit en même temps avec une troisième substance; selon la nomenclature usuelle on peut nommer le chlorure d'aluminium acteur, le C_6H_5COCl inducteur et le benzène récepteur.

Le même synthèse en présence du trichlorure d'antimoine, comme nous avons vu, a d'autres phases intermédiaires et se termine par le dégagement d'une grande partie du $SbCl_3$, lequel peut accélérer la réaction des nouvelles quantités du mélange du C_6H_5COCl et ArH. Il est évident que si la combinaison double finale est complêtement décomposée en ses composants, nous avons la catalyse typique d'Ostwald; le synthèse des cétones au moyen du $SbCl_3$ doit donc être considéré comme réaction intermédiaire entre la vraie catalyse et la réaction accouplée dont le pro-

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[1] Annales de l'Institut Polytechnique de St. Petersbourg, *13*, 1 (1910).
[2] N. Schilow, Zeit. phys. Chemie, *42*, 641 (1903).

duit final présente une combinaison moléculaire stable dans les conditions de l'expérience.

Je poursuis maintenant l'étude de la réaction entre les hydrocarbures aromatiques et le chlorure de benzoyle dans plusieures directions, notamment pour étudier l'accéleration produite par quelques autres sels minérales comparativement au $SbCl_3$ et l'influence des substituants du benzène sur le synthèse des cétones en présence de ces sels.

A STUDY OF THE LASSAIGNÉ REACTION

By S. P. Mulliken and C. L. Gabriel

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The production of alkali cyanide from the nitrogen of organic compounds by ignition with alkali metal and its subsequent precipitation as Prussian blue, when carried out in the manner originally described by Lassaigné,[1] constitutes a qualitative test of considerable delicacy, its author being able to state that he had used it successfully with as little as half a milligram of several difficultly volatile substances. As applied in ordinary practice to volatile or explosive substances and to certain groups of non-volatile, stable compounds, it has not, however, proved as universally reliable as might be desired, and its failures have been made the occasion for various published suggestions for its improvement.[2] The fundamental importance of the sodium fusion in the scheme of systematic organic quantitative analysis as the first step in the search for non-metallic elements has impelled us to return to the study of its undetermined limitations and possibilities.

The method of ignition used in connection with all experiments to be mentioned in this paper was an improvement on earlier modifications of the Lassaigné procedure devised and described elsewhere [3] by one of us.

The apparatus for the ignition is a cast-iron tube 9 cm. in length, 1.3 cm. in internal diameter, having walls 1.6 mm. thick, with a flange-like lip and a rounded closed bottom. It is hung by the flange through a circular perforation in an asbestos board 4 inches in

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[1] Comptes rend., *16*, 387 (1843).

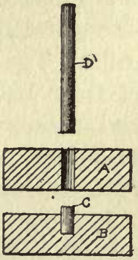
[2] Kronbach, Cent. Platt, *1856*, 912; Jacobson, Ber., *1879*, 2318; Graebe, Ber., *1884*, 1178; Täuber, Ber., *1899*, 3150; Kehrer, Ber., *1902*, 2523; Castellana, Cent. Blatt., *1905*, 45; Ellis, Chem. News, *1910*, 102, 187.

[3] Noyes and Mulliken, Class Reactions of Organic Substances (1896). Mulliken, A Method for the Identification of Pure Organic Compounds, *1*, 13 (1904).

diameter supported on a ring-stand. The lower half of the tube is first brought to full redness by a powerful Bunsen flame. A cylindrical piece of sodium freshly cut from a clean slab of the metal by a quarter-inch cork borer, and weighing a quarter of a gram, is then dropped in. After allowing half a minute for the vaporization of the sodium, the organic substance is dropped down the axis of the tube without being allowed to touch the sides.

In order to ensure the greatest possible uniformity of conditions in comparative experiments, the substance was always introduced in three successive pellets, each weighing 3 cgm. The pellets were prepared by placing a little of the powdered material in the cylindrical cavity of the steel block *A*, which was first laid on the block *B* with its short vertical spindle *C*, and then compressing the powder by a hammer blow on the steel plunger *D*.

The use of compressed pellets greatly diminished the risk of premature volatilization, and is an improvement that may be strongly recommended for general adoption. The use of pellets made from pure naphthalene or sugar powder moistened with dilute solutions of the substances to be tested also made it easily possible to work with single milligram portions—a proceeding otherwise impracticable. After cooling, which was usually hastened by external application of cold water to the warm tube, the excess of sodium was destroyed by adding 3 c.c. of alcohol, and the alkaline tube contents cautiously dissolved in water, filtered and tested. The same tube when cleaned with concentrated hydrochloric acid, water, and a test-tube brush may be used for a great many ignitions.



To throw light on the quantitative efficiency of this treatment with nitrogen compounds of different types, the cyanide formed from a series of representative compounds was determined by titration. A glance at the results will suffice to show the influence of constitution and the advantage sometimes gained by the addition of diluents. The pellets for each experiment weighed a decigram. The percentages of total nitrogen fixed as cyanide were in the several cases as follows: Carbazole, 61.9; p-Toluidine, 61.7; β-Naphthylamine, 61.6; Pyrrole, 52.9; Acetanilide, 52.4; Diphenylamine, 51.4; Pyridine, 48.6; Acetamide, 46.9; m-Dinitrobenzene, 42.6; Azobenzene, 39.5; Picric acid, 35.5; Picric acid (50% in sugar pellets), 49.2; Benzamide, 38.3; p-Nitrotoluene, 41.1; Isopropylamine (boiling point 32°–35°), 17.4; the same (dissolved in an equal volume of benzene), 28.9; Urea, 14; the same (in 50% pellets to supply carbon deficiency), 49.4. The above percentages are all means from two or more concordant independent ignitions. Diazo compounds gave no determinable cyanide.

The suitability of the naphthalene pellet method for testing highly explosive or volatile compounds, or minute quantities of alkaloids, was strikingly shown by the good nitrogen tests obtained from single milligrams of nitroglycerine, nitrated cotton, ethyl nitrate, morphine, strychnine, quinine, and sparteine. These pellets contained 1 mgm. of nitrogen compound in each decigram of pellet. The nitroglycerine was applied to the naphthalene in alcoholic solution and the damp mass gently compressed. The nitrated cotton was placed in solid form in the interior of the pellet. The result with the alkaloids is the more interesting because of their low nitrogen content (morphine contains only 4.91%) and because they have sometimes been said to respond to the Lassaigné test with difficulty. Even the metallic nitrates give cyanide when made into pellets with much naphthalene.

It is important to note that in tests with single milligrams of substance no distinct precipitate of Prussian blue is apparent in the solution, and that the following procedure, which is the safest in all cases, must be adopted. Five drops of a slightly oxidized and nearly neutral ferrous sulphate solution are added to the clear alkaline filtrate from the fusion, and the mixture boiled for at least 2 minutes. The precipitate of iron hydroxides is dissolved by addition of a very slight excess of hydrochloric acid and allowed to stand at least 15 minutes. The solution, which may not be noticeably blue or green in color, is then filtered through a wet filter 1 inch in diameter and the filter well washed, first, with hot dilute HCl of 1.08 specific gravity, and then with water. After drying a pale bluish stain will be clearly seen if 0.1 mgm. of nitrogen is present. Repeated blank experiments with pure naphthalene have shown that atmospheric nitrogen is *not* fixed by the sodium in sufficient quantity to give more than a faint grayish stain to the paper, despite the presence of the cast iron of the tube.

The high efficiency of the sodium fusion in the iron tube in fixing halogen from undiluted decigram portions of organic compounds was shown by experiments with chloral hydrate, dibrombenzene, and phenyl iodid. The percentage of the chlorin fixed was found to be 93; of the bromin, 90.9; and of the iodin, 99. One milligram of fluorbenzene in a naphthalene pellet gave a fusion residue rich enough in fluorine to give a distinct etching on glass when treated with sulphuric acid in the apparatus of Woodman and Talbot.[1]

Sugar pellets containing only 0.1% of sulphur in the form of potassium benzene sulphonate were found to still yield enough alkaline sulphide to the fusion to give a faint color reaction for sulphur with sodium nitroprusside. Experiments on the detection of other elements than have been mentioned above are in progress and may be published later.

[1] Jour. Am. Chem. Soc., *1906*, 1437.

THE ELECTRON CONCEPTION OF VALENCE.—III. OXYGEN COMPOUNDS

By J. M. Nelson and K. George Falk

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Some of the possible applications of the electron conception of valence were considered in the first two papers.[1] It may be recalled here that this view of valence differs from the ordinary one in that the linking or bond between two atoms is considered to be formed by the transfer of a (negatively charged) corpuscle or electron, and the bond therefore is assumed to possess "direction," the atom from which the electron is removed having a unit positive charge, that to which it is transferred a unit negative charge. In graphic formulas the bonds are represented by arrows instead of by lines, the heads of the arrows indicating the directions in which the electrons are transferred. Since an indiscriminate application of this view of valence, especially to compounds of carbon, results in an almost unlimited number of possibilities of imaginary structures, in order to apply these ideas to experimental results rationally it is necessary to select some general guiding principles based upon compounds whose structures are definitely known and upon the relations of the elements to each other. An attempt was made to formulate some of these principles in the first two papers, to which reference may be made instead of repeating the views expressed there, and the relations which followed are given in some detail there for a number of classes of compounds containing single, double, and triple bonds. In this paper some of the relations which result when this view of valence is applied to oxygen compounds will be discussed briefly.

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[1] Jour. Amer. Chem. Soc., *32,* 1637–54 (1910); *33,* 1140–52 (1911). A preliminary paper treating of the same subject was published in the School of Mines Quarterly, *30,* 179–98 (1909).

When oxygen is combined with other elements, the direction of the valences between the atoms of oxygen and the atoms of the combined elements can in most cases be readily ascertained owing to the pronounced electro-chemical character of oxygen. This makes the consideration of the oxygen compounds simpler than those in which carbon atoms are combined with each other, and where the direction of the valences cannot be readily determined because of the equal readiness with which the carbon atom takes up and loses electrons to form bonds. Furthermore, the "inertia" of carbon[1] under ordinary conditions makes possible the existence of isomeric substances differing from each other in stability to a greater extent than has been observed with any other element. A corresponding inertia is not so evident with oxygen, and therefore isomeric substances are not known to the same extent here as with carbon.

In most of its compounds oxygen is electronegative as compared with the elements with which it is combined. This fixes the directions of the valences when the oxygen atom is united to other atoms by two single bonds. A few examples may be given:

Water	Ammonium Hydroxide	Methyl Alcohol
$H\rightarrow O\leftarrow H$	$H_4\substack{\rightarrow\\\rightarrow\\\rightarrow\\\rightarrow}N\rightarrow O\leftarrow H$	$H_3\substack{\rightarrow\\\rightarrow\\\rightarrow}C\rightarrow O\leftarrow H$

For substances containing a double-bonded oxygen atom, the direction of the two valences forming the double bond cannot be settled so satisfactorily. Since the union takes place between unlike atoms, the two valences may be assumed to have the same direction for substances under ordinary conditions. This assumption is not contradictory to the conclusion reached for the double bond between two carbon atoms,[2] where the experimental evidence indicated that for substances under ordinary conditions and for the stable form of isomeric substances the directions of the valences are opposite and that for the isomeric less stable forms of these substances the directions of the valences are the same. In the present case the double bond between unlike atoms is considered.

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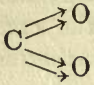
[1] Cf. van't Hoff, Lectures on Theoretical and Physical Chemistry, Part III, 96 (1899).

[2] Falk and Nelson, first paper, 1643.

It is also readily conceivable that the double bond between two carbon atoms in a molecule, the two parts of which differ greatly in electro-chemical properties, may have the same direction for the two valences. A few examples of the oxygen compounds may be given:

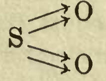
Carbon Dioxide



Nitric Oxide

$N \rightrightarrows O$

Sulphur Dioxide

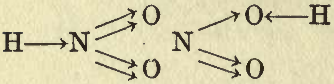


Formaldehyde

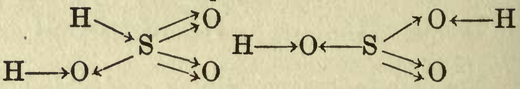
$H_2 \rightrightarrows C \rightrightarrows O$

Substances which contain a hydroxyl group show tautomerism in a number of cases, the reactions indicating that the substance in question may be represented by two formulas (depending upon the reagents used and the conditions of the reaction) which differ in that in the one case the hydrogen is in combination with the oxygen, and in the other the hydrogen is combined with some other atom in the molecule. The graphic formulas for these tautomeric substances are given by the two classes just considered for which a number of examples follow:

Nitrous Acid



Sulphurous Acid



Hypochlorous Acid

$H \longrightarrow Cl \rightrightarrows O \quad Cl \longrightarrow O \longleftarrow H$

Cyanic Acid

$H \longrightarrow N \leftleftarrows C \rightrightarrows O \quad N \Lleftarrow C \longrightarrow O \longleftarrow H$

The general formulation of the four important types [1] of tautomerism with the hydroxyl group in compounds of carbon and nitrogen is as follows:

1. $\begin{matrix}H\searrow\\H\nearrow\end{matrix}\overset{|}{C}-\overset{|}{C}\rightrightarrows O \quad H\rightarrow\overset{|}{C}=\overset{|}{C}\rightarrow O\leftarrow H$ β-keto esters, diketones.
2. $H\rightarrow\overset{|}{N}-\overset{|}{C}\rightrightarrows O \quad \overset{|}{N}=\overset{|}{C}\rightarrow O\leftarrow H$ Amides, isatine, etc.
3. $\begin{matrix}H\searrow\\H\nearrow\end{matrix}\overset{|}{C}-N\rightrightarrows O \quad H\rightarrow\overset{|}{C}=N\rightarrow O\leftarrow H$ Nitroparaffins, oximes, etc.
4. $H\rightarrow\overset{|}{N}-N\rightrightarrows O \quad \overset{|}{N}=N\rightarrow O\leftarrow H$ Nitrosamines.

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[1] Sidgwick, The Organic Chemistry of Nitrogen, 279 (1910).

In all of these compounds it is important to note that the hydrogen atom has parted with one electron and that the oxygen atom has gained two electrons. In nitrous, sulphurous, and hypochlorous[1] acids the hydrogen atom is in direct combination with the central atom (nitrogen, sulphur, or chlorine) in the one form, and shifts its position to the oxygen combined with the central atom for the other form. In this change there is a change in the state of the valence of the central atom. With nitrogen, in the one case, four electrons are removed and one gained, in the other three are removed; with sulphur, five removed, one gained, and four removed; with chlorine, two removed, one gained, and one removed. The algebraic sum of the electrons removed and gained is constant for the central atom, but the distribution is evidently different. With the tautomeric carbon compounds the conditions are somewhat different. If the first action of a hydrogen atom of the group $H_2\rightrightarrows\overset{|}{C}-\overset{|}{C}\rightrightarrows O$ is to shift to the adjacent atom (carbon in this case), the group $H\longrightarrow C{=}\overset{\swarrow H}{C}\rightrightarrows O$ is obtained. This group, containing a hexavalent carbon atom, is not capable of existence and rearranges to $H\longrightarrow\overset{|}{C}{=}\overset{|}{C}\longrightarrow O\longleftarrow H$. The hydrogen atom, therefore, is transferred to the atom which is once farther removed than with the change in nitrous, sulphurous, and hypochlorous acids, but in considering the intermediate grouping, which is unstable and can be converted to either of the more stable forms, a satisfactory analogy

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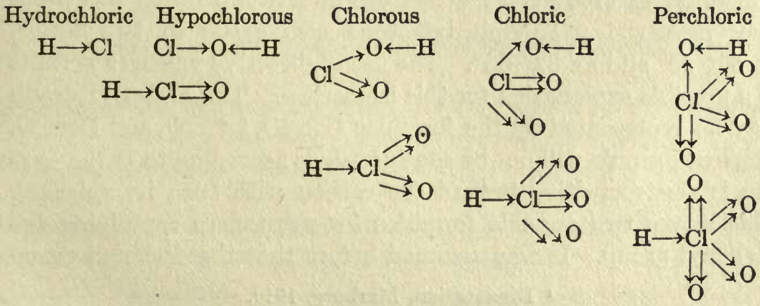
[1] The relations holding for hypochlorous acid also hold true for the other acids of chlorine with hydrogen and oxygen. The complete list of these acids with the two possible tautomeric forms of the oxygen acids are as follows:



is obtained. Similar explanations may be applied to the carbon-nitrogen and nitrogen-nitrogen tautomeric compounds where the unstable grouping contains a hexavalent carbon atom (as in cyanic acid), a nitrogen atom with two double bonds and hydrogen (similar to the one form of nitrous acid, but apparently unstable in these compounds), or a heptavalent nitrogen atom (as in the nitroparaffins). The algebraic sums of the electrons gained and lost by the atoms in the production of bonds remain constant for each of the atoms involved in the tautomeric change.

In the compounds of oxygen which have been considered so far, the oxygen atom in every case was assumed to have taken up two electrons either from the same atom or from two atoms of some other element or elements, and the cases of isomerism are due to the position of a hydrogen atom and the distribution of the valences for the other atoms in tautomerism. It was not necessary to assume a difference in the direction of the valences for the oxygen atom.

A number of ketones are known to exist in two forms, one form stable under ordinary conditions. There has been no satisfactory explanation to account for the difference in behavior of these forms by means of the usual structural formulas. The two forms of benzophenone — stable form, m. 48°, unstable form, m. 26.5° — were shown by Schaeling [1] to be chemical isomers. He studied the conditions for converting them into each other and determined the viscosities and refractive indices at a number of temperatures for the two forms in the liquid state. The low melting form was found to be the more stable at high temperatures, the high melting form at low temperatures, while for intermediate temperatures (100°–230°) a mixture of the two forms was probably present. p-Tolylphenylketone also exists in two forms, m. 55°–56° and m. 52°–53°. The use of directive valences permits of a possible explanation for this isomerism. The carbonyl group may be represented by the formulas $C\rightrightarrows O$, $C\leftleftarrows O$, and $C\leftleftarrows O$. The last formula will not be considered, as according to it the oxygen is electropositive toward the carbon with both its valences. This leaves two possible formulas for substances containing the carbonyl group. It was assumed before that the carbonyl group

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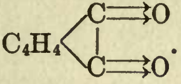
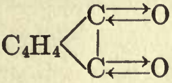
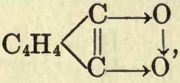
[1] Dissertation, Marburg, 1910.

is to be represented by the formula $C \rightrightarrows O$ when only one form of the substance is known. When two forms are known, as with benzophenone and p-tolylphenylketone, there is at present no evidence to determine which of the two structures is to be assigned to each form. To bring the formulas into line with those previously considered, the grouping $C \rightrightarrows O$ will be assigned to the more stable form under ordinary conditions, and the grouping $C \leftrightarrows O$ to the less stable form under ordinary conditions. The cause of the isomerism then is referred to the directions of the two valences of the double bond. This classes the isomerism of benzophenone (and of p-tolylphenylketone) with the "cis-trans" isomerism of the oximes, etc., as illustrated in the first paper,[1] and refers it to the same cause as the isomerism of the compounds containing a double bond between two carbon atoms with the difference, as stated above, that to the stable forms ordinarily are assigned the structures containing the two valences acting in opposite directions for $>C=C<$ compounds and in the same direction for $>C=O$ compounds.

o-Quinone was shown by Willstätter and Müller[2] to exist in two modifications, one of which forms colorless prisms and is readily converted (on standing at ordinary temperatures, more rapidly on warming) into the red form. The diketone structure is assigned by them to the colored form, the peroxide structure to the colorless. On the basis of directive valences, the stable o-quinone, or in this case the diketone form, would possess the structure  $C_4H_4\left\langle\begin{array}{l} C \rightrightarrows O \\ | \\ C \rightrightarrows O \end{array}\right.$. If the direction of one of the valences of the double bond in one of the ketone groups is reversed to represent the less stable form in the same way that the two modifications of benzophenone were represented, the structure  $C_4H_4\left\langle\begin{array}{l} C \leftrightarrows O \\ | \\ C \leftrightarrows O \end{array}\right.$ is obtained for the colorless form. If this structure is compared with the "peroxide" structure  $C_4H_4\left\langle\begin{array}{ll} C \longrightarrow & O \\ \| & \downarrow \\ C \longrightarrow & O \end{array}\right.$, it is seen that in these two formulas the oxygen atoms are in the same valence condition, one having gained two electrons, the other having gained

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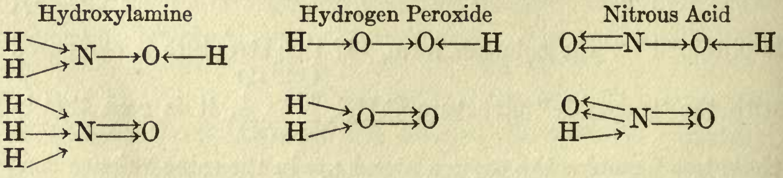
[1] Page 1648.

[2] Ber., *41*, 2580 (1908).

one and lost one. In other words, the two formulas represent the same facts as far as the loss and gain of electrons in the valences of the oxygen atoms are concerned. The arrangement of the valences in the rest of the molecule will not be considered here, — the isomerism being assumed to be due primarily to the oxygen atoms, or carbonyl groups. The main point to which it is desired to direct attention in this case is that the isomerism of the ketones may be classed together and referred to the same underlying principles as the isomerism of all double-bond compounds (which are generally grouped under geometrical isomerism), that it leads to the same explanation for the two forms for o-quinone and for benzophenone, and that at the same time it agrees with the diketone and peroxide structures for the two forms of o-quinone.

Haakh[1] considers that two modifications of p-benzoquinone may be assumed to exist, the benzoid (peroxide structure) and the quinoid (diketone structure). He assumes that at ordinary temperatures p-benzoquinone is present mainly in the peroxide form which can rearrange to the diketone form from which the intensely colored substances are derived. It is pointed out further that, on the basis of Thiele's formulation, partial valences are only present on the oxygen atoms in the diketone form, which would tend to form molecular compounds.

The formulation of hydrogen peroxide when directive valences are employed is somewhat confusing. The usual representation of the tautomeric forms is $H{-}O{-}O{-}H$ and $\genfrac{}{}{0pt}{}{H}{H}\!\!>\!O{=}O$. With directive valences, the simplest method of arriving at a conclusion appears to be by a comparison with the tautomeric formulas of hydroxylamine and nitrous acid containing directive valences. When this is done, the following formulas are obtained:



Here, as in the previous cases of tautomerism, the hydrogen atom of the negative hydroxyl group (of which the oxygen has gained

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[1] J. pr. Chem., *82*, 546 (1910).

two electrons) is assumed to be transferred, although it is possible to formulate the relations so as to involve the shifting of the other hydrogen atom. At present the former is to be preferred on account of the analogy to the other cases of tautomerism considered.

The question of the structures of α-and β-pinacolin may be considered in the same way as the compounds already discussed. The benzpinacolins will be taken up specifically, as more work has been done with these than with the other pinacolins. In view of its reactions, the ketone structure $(C_6H_5)_3C\cdot\overset{\overset{O}{\uparrow\uparrow}}{C}\cdot C_6H_5$ has been generally assigned to β-benzpinacolin. At first sight it would appear that the structure of an isomer should be represented in the same way as the isomeric form of benzophenone, namely, that the isomerism is to be ascribed to the directions of the valences of the carbonyl double bond. In view, however, of the reactions of β-benzpinacolin, its reduction by hydriodic acid and phosphorus to tetraphenyl ethane as well as the series of reactions pinacone-α-pinacolin-β-pinacolin, showing the migration of a phenyl group from one carbon atom to the adjoining carbon atom, and furthermore, the conclusion of Delacre[1] that it is impossible to assign to each of the pinacolins a simple structure, but that their reactions may be expressed by the ketone and oxide formulas with a preponderance of the former for the β form and of the latter for the α form, the conclusion is probable that the isomerism of these two substances may better be classed with tautomerism, and represented by the formulas $(C_6H_5)_3C\cdot\overset{\overset{O}{\uparrow\uparrow}}{C}\cdot C_6H_5$ and $(C_6H_5)_2C\overset{\nearrow O\nwarrow}{\quad\cdot\quad}C(C_6H_5)_2$ the hypothetical intermediate compound in analogy with the hypothetical intermediate compounds described previously with tautomeric substances, being formulated $(C_6H_5)_2C:\overset{\overset{O}{\uparrow\uparrow}}{C}(C_6H_5)_2$. As before, a substance having this formula with a hexavalent carbon atom is evidently unstable and rearranges to the oxide form shown above; this is the formula generally ascribed to α-benzpinacolin. The shifting of a phenyl

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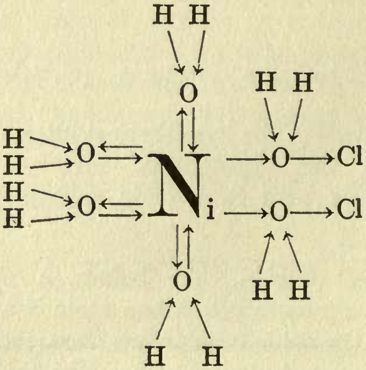
[1] Bull. Soc. Chim. de France, (4), 7, 167 (1910).

group (or methyl group in the analogous tert.-butyl methyl ketone, etc.) differentiates these compounds from the compounds considered previously under tautomerism, in which a hydrogen atom changed position, but aside from the fact that the presence of the hydrocarbon group makes the two forms of the substance more stable and easier to isolate than with the hydrogen compounds, there is a satisfactory analogy to the tautomeric substances to permit of the classification of the pinacolins with them.

Not much space need be devoted to oxonium salts here. They are derived from compounds of oxygen in which the oxygen atom has gained two electrons, by the further gain of an electron at the same time that an electron is given up to an "electro-negative" element. This is in strict analogy with the view of the formation of ammonium salts from ammonia. Baeyer and Billiger[1] showed that the formation of oxonium salts was a fairly general property of oxygen compounds.

The formulation of hydrates may be attempted in several different ways. The method indicated by Sir William Ramsay[2] for the ammonia groups in the cobaltammine nitrites, in his address on "The Electron as an Element" will be given here. According to this formulation, the water molecules are combined with the metallic element, by the oxygen atom and the metallic element each giving off and taking up an electron, leaving the algebraic sum of the electrons gained and lost the same as before the union. Thus the graphic formula for $NiCl_2 \cdot 6H_2O$ would be



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[1] Ber., *34*, 2679 (1901).

[1] J. Chem. Soc., *93*, 774 (1908).

in which the chlorine atoms are ionizable, following Ramsay's suggestions. It may be noted that the oxygen of the water molecule is in the oxonium state, but that ionization as oxonium salt does not take place when the two valences are directly combined with the metal.

ABSTRACT OF A PAPER ENTITLED

TETRACHLORFLUORESCEIN AND SOME OF ITS DERIVATIVES

By W. R. Orndorff and E. F. Hitch

Ithaca, N. Y.

Tetrachlorfluorescein has been prepared in two modifications—a colored quinoid and a colorless lactoid form.

A colorless diacetate, a colorless dibenzoate and monobenzoate of tetrachlorfluorescein, and colorless compounds of tetrachlorfluorescein with ether and with ethyl acetate have been prepared. These are all derivatives of the lactoid form of tetrachlorfluorescein.

The dipotassium, disodium, diammonium, monopotassium, and monosodium salts, the hydrate and the methyl ester of tetrachlorfluorescein have been prepared. All of these compounds are colored and are therefore derivatives of the quinoid form of tetrachlorfluorescein.

A colorless carbinol carboxylic acid of tetrachlorfluorescein has been prepared. This substance is isomeric with the yellow hydrate, but forms the same colored salts with alkalies, and the same colorless diacetate as is obtained from this hydrate and from the anhydrous modifications of tetrachlorfluorescein.

The introduction of the four chlorine atoms into the fluorescein molecule increases its acid and decreases its basic properties. This is shown by the conduct of tetrachlorfluorescein toward hydrochloric acid and toward gaseous ammonia, as compared with that of fluorescein itself.

Tetrachloreosin, which is the tetrabrom derivative of tetrachlorfluorescein, its compound with acetic acid, and its diacetate have been made. These are all colorless compounds and therefore have the lactoid structure. Tetrachloreosin itself has only been obtained in the colorless lactoid modification.

As examples of the derivatives of the colored quinoid form of tetrachloreosin, the hydrate and the dipotassium salt have been prepared.

The introduction of four bromine atoms into the molecule of tetrachlorfluorescein increases the acidity of the compound, as is shown by the behavior of tetrachloreosin toward gaseous ammonia and toward strong solutions of the alkalies.

Indications of the existence of the two possible isomeric tetrachlorfluoresceins have been obtained.

The absorption and fluorescence spectra of solutions of fluorescein, tetrachlorfluorescein, eosin, and tetrachloreosin have been studied. The theory of Stark and Meyer, that the benzene nucleus is the seat of fluorescence, is apparently confirmed.

SYNTHESES IN THE TERPENE GROUP

By William Henry Perkin, Jr.
Manchester, England

In that remarkable section of chemistry which deals with the terpenes and their derivatives, there are probably few substances of greater importance than the closely related group, *terpin*, *terpineol*, and *dipentene*, and this is due, not only to the great scientific interest attaching to these substances, but also to their industrial importance. Terpin, which, as is well known, is readily obtained from oil of turpentine by oxidation with nitric acid, combines with water to form the highly characteristic compound, terpin hydrate, $C_{10}H_{18}(OH)_2,H_2O$, and from the first this hydrate has been specially selected by chemists for investigation, partly because it is so readily available and partly because there was reason to suppose that the determination of its constitution would afford a valuable clue to the nature of the terpene group as a whole.

The fact that the constitution of terpin and its derivatives is now well understood is due in the first place to the laborious analytical researches of Baeyer, Tilden, Tiemann and Schmidt and Wallach and to the brilliant theoretical deductions of Wagner.

The difficulties which early investigators of terpin and its derivatives had to encounter were of a quite unusual kind, not only owing to the fact that the chemical behavior of the many partially unsaturated closed carbon chain compounds belonging to this class was at that time not at all understood, but also because of the unexpected fundamental intramolecular changes which were frequently met with and which gave rise to false deductions and the suggestion of many formulæ now known to be incorrect.

That a close relationship exists between terpin, terpineol, and dipentene was long ago evident from the work of Tilden[1] and of Wallach,[2] who showed that when terpin is digested with dilute

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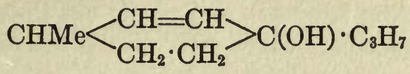
[1] Ber., *12*, 848 (1879).

[2] Annalen, *230*, 258 (1885).

acids it yields terpineol, and that the latter is converted by heating with potassium hydrogen sulphate into dipentene, changes which are due simply to the successive elimination of water

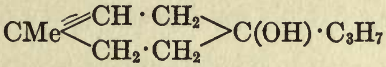
$C_{10}H_{18}(OH)_2$	$C_{10}H_{17}\cdot OH$	$C_{10}H_{16}$
Terpin	Terpineol	Dipentene

The first to represent terpineol as a derivative of *p*-cymene appears to have been Kanonnikoff,[1] who, mainly from physical considerations, proposed the formula



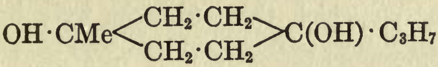
$$CHMe<\begin{matrix}CH{=}CH\\ CH_2\cdot CH_2\end{matrix}>C(OH)\cdot C_3H_7$$

for this substance. In a remarkable paper[2] which contains a careful investigation of terpineol, Wallach suggested the following modification of this formula:



$$CMe<\begin{matrix}{=}CH\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>C(OH)\cdot C_3H_7$$

and shortly afterwards Baeyer[3] published a research on the same subject in which he expresses his agreement with Wallach's view of the constitution of terpineol and at the same time suggests the formula



$$OH\cdot CMe<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>C(OH)\cdot C_3H_7$$

for terpin.

The strongest argument against the acceptance of these views was the fact that in whichever way water is eliminated from Wallach's terpineol formula, a constitution for dipentene is arrived at which does not contain an asymmetric carbon atom, whereas it is well known that dipentene is an externally compensated mixture of the two active *d*- and *l*-limonenes. In order to

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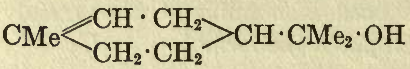
[1] J. Russ. Phys. Chem. Soc., *15*, 472 (1883).
[2] Annalen, *277*, 105 (1893).
[3] Ber., *26*, 2558 (1893).

get over this difficulty, Baeyer[1] suggested that the activity of the limonenes may be due to the asymmetry of the whole molecule and not to the presence of an asymmetric carbon atom.

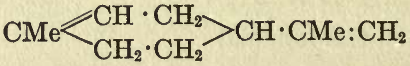
In 1894 Wagner published his classical paper "On the Oxidation of Cyclic Compounds,"[2] in which he discusses the constitutions of some of the more important members of the terpene group.

From a careful consideration of the relationship of terpineol to pinene, pinol, and sobrerol, he deduces the expression



$$\mathrm{CMe}\Big<\begin{matrix}\mathrm{CH\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}\Big>\mathrm{CH\cdot CMe_2\cdot OH}$$

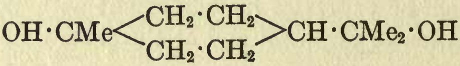
as best representing terpineol, and points out that if this formula is accepted the difficulty with regard to the activity of the limonenes disappears, since the constitution of limonene (dipentene) would then be represented thus:



$$\mathrm{CMe}\Big<\begin{matrix}\mathrm{CH\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}\Big>\mathrm{CH\cdot CMe{:}CH_2}$$

that is to say, by a formula which contains an asymmetric carbon atom.

The constitution of terpin itself, deduced from the above formula for terpineol, would then be



$$\mathrm{OH\cdot CMe}\Big<\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}\Big>\mathrm{CH\cdot CMe_2\cdot OH}$$

The evidence on which these formulæ were based is almost entirely of an analytical nature, and it is well known that, mainly owing to molecular changes, often of a far-reaching kind, which have been repeatedly observed during the course of analytical operations in this group, such evidence cannot be accepted as conclusive.

In difficult cases such as this, there is only one really satisfactory way of establishing constitutional formulæ, and that is to synthesize the substances in question by methods which are straightforward and leave no doubt as to the nature of each of the steps in the synthesis.

[1] Ber., *27*, 454 (1894). [2] Ber., *27*, 1636.

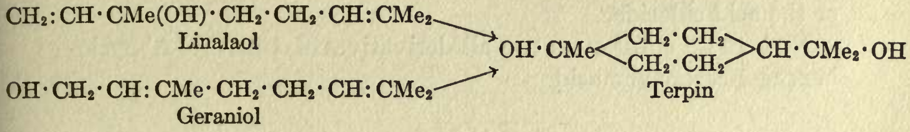
The first synthesis of dipentene (*dl*-limonene) appears to have been carried out in 1879 by Bouchardat, who showed that isoprene is polymerized by heating at 270°, and that one of the products is dipentene:

$$2\ \mathrm{CH_2{:}CMe\cdot CH{:}CH_2} \longrightarrow \mathrm{CMe}\left<\begin{matrix}\mathrm{CH\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}\right>\mathrm{CH\cdot CMe{:}CH_2}$$

Isoprene

Dipentene

but a process of this kind, difficult to understand and involving, as it does, a high temperature, cannot be accepted as valid evidence of the constitution of dipentene. In 1892 Bertram and Wahlbaum showed that linalaol, and Tiemann and Schmidt in 1895 that geraniol, are converted into terpin by the action of formic acid or 5% sulphuric acid



$$\begin{matrix}\mathrm{CH_2{:}CH\cdot CMe(OH)\cdot CH_2\cdot CH_2\cdot CH{:}CMe_2} \searrow \\ \mathrm{OH\cdot CH_2\cdot CH{:}CMe\cdot CH_2\cdot CH_2\cdot CH{:}CMe_2} \nearrow\end{matrix}\ \mathrm{OH\cdot CMe}\left<\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}\right>\mathrm{CH\cdot CMe_2\cdot OH}$$

Linalaol

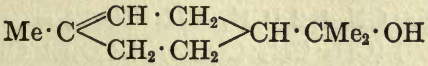
Geraniol

Terpin

processes involving in each case addition of water and ring formation, but these interesting transformations are again too complicated to be of real value in establishing the constitution of terpin.

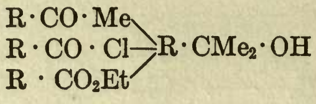
During a series of experiments on the constitution and synthesis of camphor and its derivatives it occurred to the author that it would be interesting to attempt to devise methods for the synthesis of some of the members of the terpene group of such a direct nature that there could be no doubt as to the constitution of the substances synthesized.

The series of researches on the synthesis of the terpenes which was commenced in the laboratories of the University of Manchester in 1900, and the first of which was published in 1904, had for its starting point the following idea. If the formula



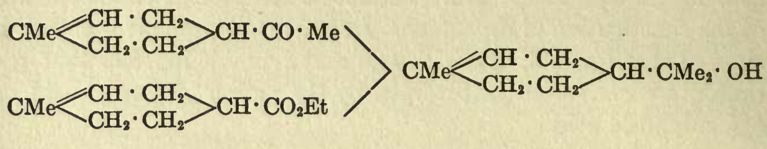
$$\mathrm{Me\cdot C}\left<\begin{matrix}\mathrm{CH\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}\right>\mathrm{CH\cdot CMe_2\cdot OH}$$

supposed to represent terpineol is examined, it will be observed that it contains the grouping $-\mathrm{CMe_2\cdot OH}$. Now this group is known to be produced when zinc methyl or magnesium methyl iodide acts on methyl ketones, acid chlorides, or esters



$$\left.\begin{array}{l}\mathrm{R\cdot CO\cdot Me}\\ \mathrm{R\cdot CO\cdot Cl}\\ \mathrm{R\cdot CO_2Et}\end{array}\right\rangle \mathrm{R\cdot CMe_2\cdot OH}$$

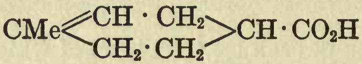
If then the suggested formula for terpineol is correct, this substance should be produced by the action of zinc methyl or magnesium methyl iodide on the following



$$\left.\begin{array}{l}\mathrm{CMe}\Big\langle\begin{array}{l}\mathrm{CH\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{array}\Big\rangle\mathrm{CH\cdot CO\cdot Me}\\ \mathrm{CMe}\Big\langle\begin{array}{l}\mathrm{CH\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{array}\Big\rangle\mathrm{CH\cdot CO_2Et}\end{array}\right\rangle \mathrm{CMe}\Big\langle\begin{array}{l}\mathrm{CH\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{array}\Big\rangle\mathrm{CH\cdot CMe_2\cdot OH}$$

or the acid chloride.

Now these substances are all derivatives of 1-methyl-Δ^1-cyclohexene-4-carboxylic acid



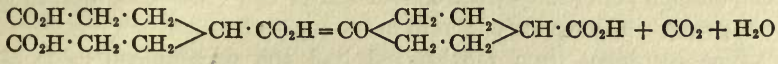
$$\mathrm{CMe}\Big\langle\begin{array}{l}\mathrm{CH\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{array}\Big\rangle\mathrm{CH\cdot CO_2H}$$

and as this acid was at that time unknown, the first problem was to discover some means by which its synthesis could be accomplished.

It was the difficulty of synthesizing this acid which postponed the synthesis of terpineol for four years, but ultimately the acid was prepared in considerable quantities by the following rather complicated series of reactions. When ethyl β-iodopropionate and the sodium derivative of ethyl cyanacetate are allowed to interact in molecular proportions at the ordinary temperature, a curious action takes place which results in the formation of ethyl γ-cyanopentane-$\alpha\gamma\epsilon$-tricarboxylate and regeneration of half of the ethyl cyanoacetate:

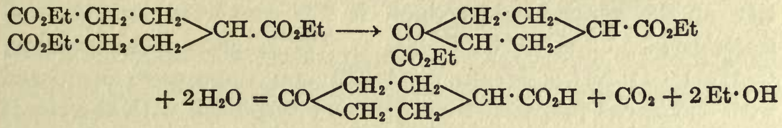
$$\begin{array}{l}2\,\mathrm{CO_2Et\cdot CHNa\cdot CN} + 2\,\mathrm{ICH_2\cdot CH_2\cdot CO_2Et} = \\ \quad \mathrm{CO_2Et\cdot C(CN)\,(CH_2\cdot CH_2\cdot CO_2Et)_2} + \mathrm{CO_2Et\cdot CH_2\cdot CN} + 2\mathrm{NaI}\end{array}$$

This cyano-ester is hydrolyzed by boiling with concentrated hydrochloric acid with the formation of pentane-$\alpha\gamma\epsilon$-tricarboxylic acid, $CO_2H\cdot CH(CH_2\cdot CH_2\cdot CO_2H)_2$, and when the sodium salt of this acid is heated with acetic anhydride and then distilled, a remarkable decomposition takes place with elimination of carbon dioxide and water and formation of δ-ketohexahydrobenzoic acid or *cyclo*hexanone-4-carboxylic acid



$$\begin{matrix} CO_2H\cdot CH_2\cdot CH_2 \\ CO_2H\cdot CH_2\cdot CH_2 \end{matrix}\!>CH\cdot CO_2H = CO<\begin{matrix} CH_2\cdot CH_2 \\ CH_2\cdot CH_2 \end{matrix}\!>CH\cdot CO_2H + CO_2 + H_2O$$

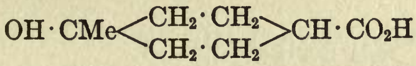
Subsequently, in a research carried out in conjunction with F. W. Kay, it was found that a better yield of the keto-acid is obtained when the ester of pentane-$\alpha\gamma\epsilon$-tricarboxylic acid is digested with sodium and the ethyl *cyclo*hexanone-2:4-dicarboxylate thus formed is then boiled with dilute hydrochloric acid



$$\begin{matrix} CO_2Et\cdot CH_2\cdot CH_2 \\ CO_2Et\cdot CH_2\cdot CH_2 \end{matrix}\!>CH.CO_2Et \longrightarrow CO<\begin{matrix} CH_2\cdot CH_2 \\ \underset{CO_2Et}{CH}\cdot CH_2 \end{matrix}\!>CH\cdot CO_2Et$$

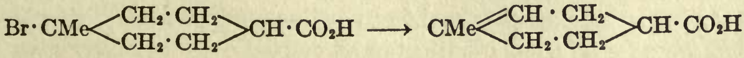
$$+\,2\,H_2O = CO<\begin{matrix} CH_2\cdot CH_2 \\ CH_2\cdot CH_2 \end{matrix}\!>CH\cdot CO_2H + CO_2 + 2\,Et\cdot OH$$

The next step was to convert *cyclo*hexanone-4-carboxylic acid into 1-methyl*cyclo*hexanol-4-carboxylic acid, and this is readily accomplished by treating the ester of the ketonic acid with magnesium methyliodide in the usual manner



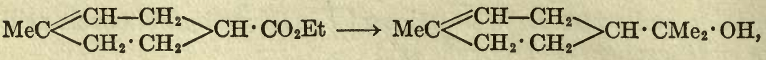
$$OH\cdot CMe<\begin{matrix} CH_2\cdot CH_2 \\ CH_2\cdot CH_2 \end{matrix}\!>CH\cdot CO_2H$$

When the hydroxy-acid is heated with hydrobromic acid, it is converted into 1-methyl-1-bromocyclohexane-4-carboxylic acid, and this, when digested with sodium carbonate, loses hydrogen bromide with formation of 1-methyl-Δ^1-cyclohexene-4-carboxylic acid



$$Br\cdot CMe<\begin{matrix} CH_2\cdot CH_2 \\ CH_2\cdot CH_2 \end{matrix}\!>CH\cdot CO_2H \longrightarrow CMe\begin{matrix} {=}CH\cdot CH_2 \\ <CH_2\cdot CH_2 \end{matrix}\!>CH\cdot CO_2H$$

The last step was to convert the unsaturated acid into its ester and to act on this with an ethereal solution of magnesium methyl iodide, when an almost quantitative yield of an oil was obtained which, on examination, proved to be *terpineol.* This synthesis is readily understood with the aid of the formulæ



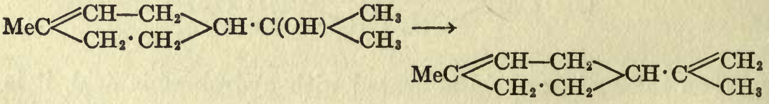
$$\mathrm{MeC}{<}\begin{matrix}\mathrm{CH{-}CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}{>}\mathrm{CH\cdot CO_2Et} \longrightarrow \mathrm{MeC}{<}\begin{matrix}\mathrm{CH{-}CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}{>}\mathrm{CH\cdot CMe_2\cdot OH},$$

the change being simply the conversion of the $-\mathrm{CO_2Et}$ group into the group $-\mathrm{CMe_2\cdot OH}$.

The terpineol thus synthesized had the pronounced odor of lilac which is so characteristic of this substance, and distilled constantly at 135° under 60 mm. pressure, and this was found to be exactly the temperature at which a sample of pure terpineol, from Schimmel & Co., distilled in the same apparatus and under the same conditions.

In order that there might be no room for doubt as to the identity of the synthetical product, it was converted into the *nitrosochloride,* $\mathrm{C_{10}H_{18}O,NOCl}$ (m. p. 122°), and *phenylurethane,* $\mathrm{C_{10}H_{17}O\cdot CO\cdot NH\cdot C_6H_5}$ (m. p. 113°), and these were compared with specimens prepared from ordinary terpineol, with the result that the preparations obtained from both sources were found to be absolutely identical.

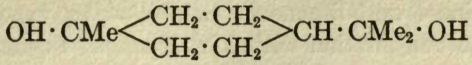
The next step was to convert the synthetical terpineol into dipentene, which was readily accomplished by heating with potassium hydrogen sulphate, when water was eliminated according to the scheme,



$$\mathrm{MeC}{<}\begin{matrix}\mathrm{CH{-}CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}{>}\mathrm{CH\cdot C(OH)}{<}\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{matrix} \longrightarrow \mathrm{MeC}{<}\begin{matrix}\mathrm{CH{-}CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}{>}\mathrm{CH\cdot C}{<}\begin{matrix}\mathrm{CH_2}\\ \mathrm{CH_3}\end{matrix}$$

The *dipentene* produced in this way was converted into the *tetrabromide,* $\mathrm{C_{10}H_{16}Br_4}$ (m. p. 125°), the *dihydrochloride,* $\mathrm{C_{10}H_{16}}$, 2 HCl (m. p. 48°–50°), and the *nitrosochloride,* $\mathrm{C_{10}H_{16},NOCl}$ (m. p. 106°), and these derivatives were compared with the corresponding specimens obtained from ordinary dipentène, with which they were found to be identical in all respects.

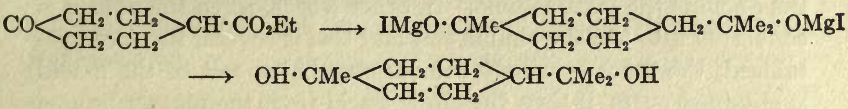
Lastly, the synthetical terpineol was agitated with dilute sulphuric acid until the oil had become converted into a mass of crystals; these, on examination, were found to consist of pure terpin hydrate



$$OH\cdot CMe<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>CH\cdot CMe_2\cdot OH$$

and thus the synthesis of the three substances, terpin, terpineol, and dipentene, which have played so prominent a part in the history of the terpene group, was accomplished, and in a way which can leave no further doubt as to their constitutions.

Subsequently it was found, also in conjunction with Kay, that terpin is directly obtained when ethyl *cyclo*hexanone-4-carboxylate is treated with a large excess of magnesium methyl iodide



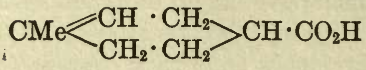
$$CO<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>CH\cdot CO_2Et \longrightarrow IMgO\cdot CMe<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>CH_2\cdot CMe_2\cdot OMgI$$
$$\longrightarrow OH\cdot CMe<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>CH\cdot CMe_2\cdot OH$$

In this synthesis the magnesium methyl iodide reacts not only on the carbonyl group of ethyl *cyclo*hexanone-4-carboxylate, converting that into $-CMe\cdot OH$, but also on the $-CO_2Et$ group, converting that into $-CMe_2\cdot OH$, and this observation has very much simplified the synthesis of terpin, since it is now no longer necessary, in carrying out this synthesis, to first prepare terpineol and then to hydrate it by the action of dilute sulphuric acid. This synthesis is also valuable because it conclusively proves the positions of the two hydroxy-groups in terpin.

The terpineol and dipentene (*dl*-limonene), obtained by synthesis in the manner I have been describing, are of necessity optically inactive. Ordinary commercial terpineol, which is made by the dehydration of terpin, is also inactive, but active terpineols of varying rotations have been isolated from essential oils. Thus *l*-terpineol from niaouli oil has α_D $-2.10°$, whereas Schimmel & Co., the well-known dealers in essential oils, obtained a *d*-terpineol from cardamon oil which had the high rotation $\alpha_D + 83.31°$. Ertscikikowsky describes an *l*-terpineol prepared from pinene with the still higher rotation $\alpha_D - 117.5°$. Since most of the naturally occurring substances belonging to the terpene group are optically active, it was thought that it would be interesting to endeavor to obtain optically active terpineols and terpenes by synthetical processes.

With a view to solving this problem, in the first instance in the case of terpineol and limonene, the following experiments were carried out in conjunction with Mr. Kenneth Fisher.

A considerable quantity of *dl*-1-methyl-Δ^1-cyclohexene-4-carboxylic acid



$$\mathrm{CMe}{\ll}\begin{matrix}\mathrm{CH}\cdot\mathrm{CH_2}\\ \mathrm{CH_2}\cdot\mathrm{CH_2}\end{matrix}{>}\mathrm{CH}\cdot\mathrm{CO_2H}$$

was prepared by the methods already described, and this was resolved by the fractional crystallization of the strychnine and brucine salt, when it was found that the strychnine salt of the *d*-acid is the less soluble, whereas, on the other hand, the brucine salt of the *l*-acid is the least soluble. In other words, when the *dl*-acid is converted into the strychnine salt and this is several times recrystallized, the more sparingly soluble strychnine salt of the *d*-acid is obtained pure; if then the crude *l*-acid from the mother liquors is converted into the brucine salt and this is recrystallized, the sparingly soluble salt of the *l*-acid separates in a pure condition. In this way it was possible to separate the *dl*-acid into its *d*- and *l*-modifications, and these were found to have the rotations $\alpha_D + 55°$ and $- 58°$ respectively. The esters of these acids were prepared and yielded, on treatment with magnesium methyl iodide, the corresponding *d*- and *l*-terpineols which had $\alpha_D + 44.2°$ and $-46.6°$ respectively, and thus the synthesis of optically active terpineols was accomplished.

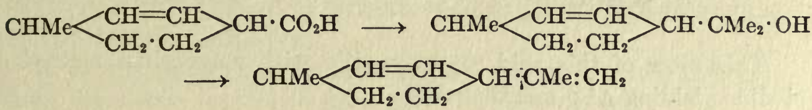
Attempts to convert these active terpineols into the corresponding active limonenes were, however, unsuccessful. When, for example, *l*-terpineol of rotation $- 46.6°$ was dehydrated by magnesium methyl iodide in the cold, racemization was almost complete, since the hydrocarbon, which was obtained in an almost quantitative yield, had a rotation of only $- 5°$ and consisted essentially of dipentene.

In the case of the *d*-terpineol of rotation $+ 44.2°$ the dehydration agent employed was anhydrous oxalic acid at 100°, but racemization was then even more complete, since the hydrocarbon obtained was practically inactive. This behavior is remarkable, because in other analogous cases, as will be shown presently, no difficulty was experienced in obtaining active terpenes from other synthetical active menthenols by dehydration.

The process used in the synthesis of terpineol from ethyl 1-methyl-Δ^1-*cyclo*hexene-4-carboxylate by the action of magnesium methyl iodide, that is to say, the process

$$\mathrm{CMe}\left<\begin{matrix}\mathrm{CH\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}\right>\mathrm{CH\cdot CO_2H} \longrightarrow \mathrm{CMe}\left<\begin{matrix}\mathrm{CH\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}\right>\mathrm{CH\cdot CMe_2\cdot OH}$$

is capable of wide general application, for it is obvious, if the necessary unsaturated acids are available, that it should always be possible with the aid of this process to prepare the corresponding menthenols and from these the menthadienes. Thus, for example, if 1-methyl-Δ^2-*cyclo*hexene-4-carboxylic acid were available, its ester should react with magnesium methyl iodide to yield Δ^2-*p*-menthenol(8), and this on dehydration should yield $\Delta^{2\cdot 8(9)}$-*p*-menthadiene

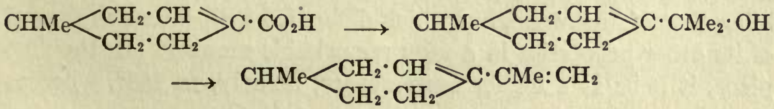


$$\mathrm{CHMe}\left<\begin{matrix}\mathrm{CH{=}CH}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}\right>\mathrm{CH\cdot CO_2H} \longrightarrow \mathrm{CHMe}\left<\begin{matrix}\mathrm{CH{=}CH}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}\right>\mathrm{CH\cdot CMe_2\cdot OH}$$
$$\longrightarrow \mathrm{CHMe}\left<\begin{matrix}\mathrm{CH{=}CH}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}\right>\mathrm{CH\cdot CMe{:}CH_2}$$

I have selected this example because it is a synthesis which has not so far been accomplished, and the reason for this lies in the fact that no method for the synthesis of 1-methyl-Δ^2-*cyclo*hexene-4-carboxylic acid has, so far as I am aware, yet been discovered.

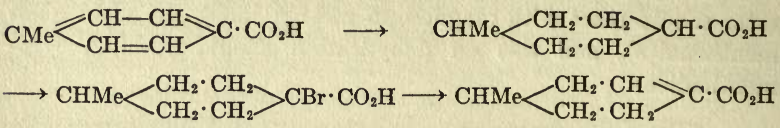
But, with one other exception, all the substances belonging to this type, not only in the *p*- but also in the *m*- and *o*-series, have been synthesized and carefully investigated, and in discussing these developments of the original synthesis of terpineol and dipentene, I propose only to select those examples which seem to me to be the most interesting and characteristic and to discuss these in some detail.

The synthesis which I propose to take next is the synthesis of Δ^3-*p*-menthenol(8) and $\Delta^{3\cdot 8(9)}$-*p*-menthadiene from the ester of 1-methyl-Δ^3-*cyclo*hexene-4-carboxylic acid by the action of magnesium methyl iodide, that is to say, the synthesis represented thus:



$$\mathrm{CHMe}\left<\begin{matrix}\mathrm{CH_2\cdot CH}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}\right>\mathrm{C\cdot CO_2H} \longrightarrow \mathrm{CHMe}\left<\begin{matrix}\mathrm{CH_2\cdot CH}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}\right>\mathrm{C\cdot CMe_2\cdot OH}$$
$$\longrightarrow \mathrm{CHMe}\left<\begin{matrix}\mathrm{CH_2\cdot CH}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}\right>\mathrm{C\cdot CMe{:}CH_2}$$

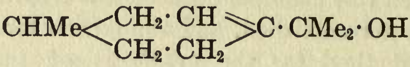
and this investigation was carried out in the first instance in conjunction with Dr. S. S. Pickles. The 1-methyl-Δ^3-*cyclo*hexene-4-carboxylic acid required for this synthesis was prepared in large quantities by the following process: *p*-toluic acid was reduced by sodium and isoamyl alcohol to 1-methyl*cyclo*hexane-4-carboxylic acid; this, on bromination in the usual manner, yielded 1-methyl-4-bromo-*cyclo*hexane-4-carboxylic acid, from which, by the action of boiling sodium carbonate or quinoline, 1-methyl-Δ^3-*cyclo*hexene-4-carboxylic acid is readily obtained as a crystalline substance melting at 134°.



$$\mathrm{CMe}{<}\begin{matrix}\mathrm{CH{-}CH}\\ \mathrm{CH{=}CH}\end{matrix}{>}\mathrm{C\cdot CO_2H} \longrightarrow \mathrm{CHMe}{<}\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}{>}\mathrm{CH\cdot CO_2H}$$

$$\longrightarrow \mathrm{CHMe}{<}\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}{>}\mathrm{CBr\cdot CO_2H} \longrightarrow \mathrm{CHMe}{<}\begin{matrix}\mathrm{CH_2\cdot CH}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}{>}\mathrm{C\cdot CO_2H}$$

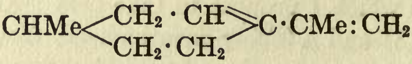
This ester of this acid reacts readily with magnesium methyl iodide yielding Δ^3-*p*-menthenol(8)



$$\mathrm{CHMe}{<}\begin{matrix}\mathrm{CH_2\cdot CH}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}{>}\mathrm{C\cdot CMe_2\cdot OH}$$

a crystalline substance melting at 41°, which has a pleasant but penetrating odor resembling, but much more pronounced than, that of terpineol. It differs from terpineol in the fact that it does not yield a terpin on treatment with dilute sulphuric acid, that is to say, it is not hydrated by this process.

When Δ^3-*p*-menthenol (8) is digested with potassium hydrogen sulphate, it readily loses water with formation of $\Delta^{3\cdot 8(9)}$-*p*-menthadiene



$$\mathrm{CHMe}{<}\begin{matrix}\mathrm{CH_2\cdot CH}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}{>}\mathrm{C\cdot CMe{:}CH_2}$$

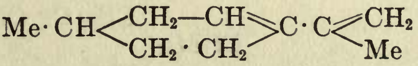
a terpene which has a pronounced odor of lemons closely resembling that of dipentene, but which differs from dipentene in several of its other properties in a very remarkable manner. In the first place, it boils at a higher temperature, namely, at 185°, whereas dipentene distills at 176°, and it has also a much higher refractive index, namely, n_D 1.4924, corresponding to the molecular refraction M 46.02, whereas dipentene has n_D 1.4746 or M 45.23. The value of M for $C_{10}H_{16}|\!\!=^{2}$, calculated in the usual manner, is 45.24, or exactly that found in the case of dipentene. In several other respects the new terpene has properties which are very different from those of dipentene.

The latter hydrocarbon yields a crystalline nitrosochloride, $C_{10}H_{16}$, NOCl, and hydrochloride, $C_{10}H_{16}$,2 HCl, and is especially characterized by its behavior towards bromine, with which it combines to form a crystalline *tetra*bromide, $C_{10}H_{16}Br_4$. The new terpene reacts with nitrosochloride and with hydrogen chloride, yielding oily products which were not further investigated, but the most striking property which it exhibits is that it is capable of combining with only two atoms of bromine to form an unstable *di*bromide of the formula $C_{10}H_{16}Br_2$.

In this respect, then, the new terpene differs in a marked way from dipentene, and since both hydrocarbons are represented by formulæ containing two double linkings, this difference in behavior appeared, at first, difficult to understand.

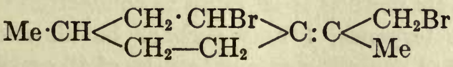
If, however, the formula of

$\Delta^{3.8(9)}$-*p*-menthadiene,



$$\mathrm{Me\cdot CH}<\begin{matrix}\mathrm{CH_2{-}CH}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{C\cdot C}<\begin{matrix}\mathrm{CH_2}\\ \mathrm{Me}\end{matrix}$$

is examined, it will be seen that the two double linkings are in the position –C : C · C : C–, and it has long been known that substances containing this grouping are only capable of uniting with two atoms of bromine to form derivatives in which that grouping becomes –CBr · C : C · CBr–.[1] There can be no doubt that, in combining with two atoms of bromine, $\Delta^{3.8(9)}$-*p*-menthadiene yields a dibromo-additive product of the formula



$$\mathrm{Me\cdot CH}<\begin{matrix}\mathrm{CH_2\cdot CHBr}\\ \mathrm{CH_2{-}CH_2}\end{matrix}>\mathrm{C:C}<\begin{matrix}\mathrm{CH_2Br}\\ \mathrm{Me}\end{matrix}$$

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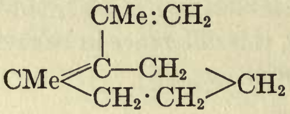
[1] Cf. especially Baeyer and Herb, Annalen, *258*, 2 (1890); Thiele, Annalen, *306*, 87 (1898); *319*, 129 (1901).

(3:9-dibromo-$\Delta^{4(8)}$-*p*-menthene), and that this substance is incapable of combining further with bromine without elimination of hydrogen bromide.

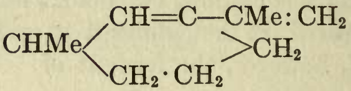
Similar results to the above were obtained in our experiments on the action of halogen acids on $\Delta^{3\cdot8(9)}$-*p*-menthadiene. It is well known that dipentene, $C_{10}H_{16}$, combines readily with *two* molecules of both hydrogen chloride and hydrogen bromide to yield the well-characterized crystalline derivatives $C_{10}H_{16},2\ HCl$ and $C_{10}H_{16},2\ HBr$.

When $\Delta^{3\cdot8(9)}$-*p*-menthadiene is subjected to the action even of a very large excess of either of these reagents, it is only capable of combining with *one* molecule of each, yielding the liquid additive compounds $C_{10}H_{16},HCl$ and $C_{10}H_{16},HBr$.

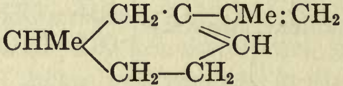
Subsequent experiments showed that this apparently abnormal behavior is exhibited by all menthadienes which contain the grouping, –C : C–C : C–, such as, for example, the terpenes



$\Delta^{1\cdot8(9)}$-*o*-Menthadiene

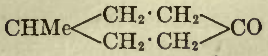


$\Delta^{2\cdot8(9)}$-*m*-Menthadiene

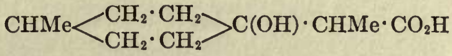


$\Delta^{3\cdot8(9)}$-*m*-Menthadiene

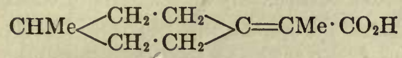
All such terpenes combine with one molecule of bromine or of HCl or HBr only. Owing to the special interest which attaches to these conjugated terpenes, they have received considerable attention, and $\Delta^{3\cdot8(9)}$-*p*-menthadiene, in particular, has been very carefully investigated. In 1910, in conjunction with Professor Wallach of Göttingen, a second method for its synthesis was devised, and as this method is of value in connection with the synthesis of other terpenes, I may perhaps be allowed to rapidly sketch the rather complicated mechanism of the process. In the first place 1–methyl*cyclo*hexan-4-one is condensed with ethyl *a*-bromopropionic ester in the presence of zinc and thus converted into the ester of 1-methyl*cyclo*hexan-4-ol-4- *a*-propionic acid, and this acid, when digested with acetic anhydride, loses a molecule of water and yields 1-methyl*cyclo*hexene-4-propionic acid, which, on distillation, is decomposed into 1-methyl-4-ethylidene*cyclo*hexane and carbon dioxide.


$\mathrm{CHMe}<\begin{array}{l}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{array}>\mathrm{CO}$

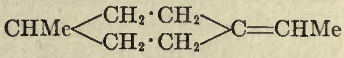
1-Methyl*cyclo*hexane-4-one


$\mathrm{CHMe}<\begin{array}{l}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{array}>\mathrm{C(OH)\cdot CHMe\cdot CO_2H}$

1-Methyl*cyclo*hexane-4-ol-4-*a*-propionic acid

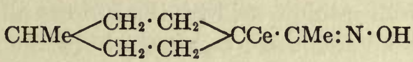

$\mathrm{CHMe}<\begin{array}{l}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{array}>\mathrm{C{=}CMe\cdot CO_2H}$

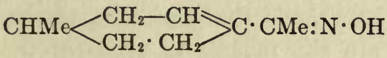
1-Methyl*cyclo*hexene-4-propionic acid

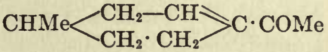

$\mathrm{CHMe}<\begin{array}{l}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{array}>\mathrm{C{=}CHMe}$

1-Methyl-4-ethylidene*cyclo*hexane

This semicyclic hydrocarbon is now converted into the nitrosochloride, and this, by elimination of hydrogen chloride, into the oxime of 4-acetyl-1-methyl-Δ^3-*cyclo*hexene from which this ketone is obtained on hydrolysis.

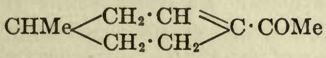

$\mathrm{CHMe}<\begin{array}{l}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{array}>\mathrm{CCe\cdot CMe{:}N\cdot OH}$

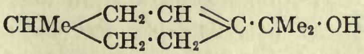

$\mathrm{CHMe}<\begin{array}{l}\mathrm{CH_2{-}CH}\\ \mathrm{CH_2\cdot CH_2}\end{array}>\mathrm{C\cdot CMe{:}N\cdot OH}$

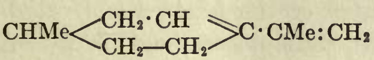

$\mathrm{CHMe}<\begin{array}{l}\mathrm{CH_2{-}CH}\\ \mathrm{CH_2\cdot CH_2}\end{array}>\mathrm{C\cdot COMe}$

4-Acetyl-1-methyl-Δ^3-*cyclo*hexene

Although this process appears to be a long and complicated one, the yields throughout are good, and it was thus found possible to use it with advantage in the preparation of considerable quantities of acetylmethyl*cyclo*hexene. The next step was to cause this ketone to react with magnesium methyl iodide when it was converted quantitatively into Δ^3-*p*-menthenol(8), and this, on dehydration, yielded $\Delta^{3\cdot 8(9)}$-*p*-menthadiene in the usual manner

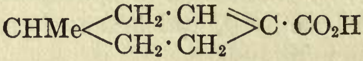

$\mathrm{CHMe}<\begin{array}{l}\mathrm{CH_2\cdot CH}\\ \mathrm{CH_2\cdot CH_2}\end{array}>\mathrm{C\cdot COMe}$


$\mathrm{CHMe}<\begin{array}{l}\mathrm{CH_2\cdot CH}\\ \mathrm{CH_2\cdot CH_2}\end{array}>\mathrm{C\cdot CMe_2\cdot OH}$


$\mathrm{CHMe}<\begin{array}{l}\mathrm{CH_2\cdot CH}\\ \mathrm{CH_2{-}CH_2}\end{array}>\mathrm{C\cdot CMe{:}CH_2}$

The $\Delta^{3\cdot 8(9)}$-*p*-menthadiene obtained in this way was carefully compared with the terpene prepared from *p*-toluic acid by the method just described and the two specimens were found to be identical in all respects. Both had the same high boiling point and refractive index, and both were only able to combine with one molecule of bromine, hydrogen chloride, or hydrogen bromide.

Δ^3-*p*-Menthenol(8) and $\Delta^{3 \cdot 8(9)}$-*p*-menthadiene, prepared by either of these synthetical methods, are of necessity optically inactive, but, owing to their special properties which have repeatedly been referred to, it was thought that it would be interesting to obtain them also in their active modifications. As this particular case has been more exhaustively and completely investigated than any other similar case in the terpene series, I may perhaps be allowed to describe the work in some detail. In the first experiments, carried out with the assistance of F. W. Kay, a large quantity of 1-methyl-Δ^3-*cyclo*hexene-4-carboxylic acid

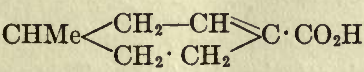


$$CHMe\left\langle\begin{matrix}CH_2\cdot CH\\ CH_2\cdot CH_2\end{matrix}\right\rangle C\cdot CO_2H$$

was prepared from *p*-toluic acid by the process already described. This acid was then resolved by means of brucine and strychnine, because the fortunate discovery was made that the comparative solubilities of the brucine salts are the reverse of those of the strychnine salts. In other words, while the salt 1A, 1B (brucine) is the more sparingly soluble, in the case of the strychnine salts, it is the salt dA, 1B (strychnine) which is the more sparingly soluble. Nevertheless, for reasons which will be stated later, the separation necessitated a very large number of fractional crystallizations and proved to be very tedious, but ultimately the *d*-acid was isolated with the high rotation $\alpha_D + 101.1°$, and the *l*-acid with the corresponding rotation $-100.8°$, and at that time, largely owing to the close agreement in the two values, it was thought that complete separation had been achieved. As the amount of these active acids was small, the following course was then adopted. The ester of the *l*-acid was treated with magnesium methyl iodide in the usual manner and yielded *l*-Δ^3-*p*-menthenol(8) with the rotation $[\alpha]_D -67.3°$, and this, when digested with potassium hydrogen sulphate, gave an *l*-$\Delta^{3 \cdot 8(9)}$-*p*-menthadiene with a rotation of only $-10°$. Obviously partial racemization had taken place, but to a less extent than in the conversion of *l*-terpineol into *l*-limonene, which was mentioned a short time since, in which case racemization was nearly complete. In order to avoid this racemization, the ester of *d*-acid was treated in the cold with a large excess of magnesium methyl iodide and thus directly converted into $\Delta^{3.8(9)}$-*p*-menthadiene, which was then actually obtained with the high rotation +98.2°. It seemed, therefore, probable that the rotation of the menthenols was about $\alpha_D \pm 67.3°$ and that of the menthadienes about $\alpha_D \pm 98.2$. Still there was a suspicion that these values were not entirely satisfactory. In the case of all the cyclohexene carboxylic acids which have so far been investigated, separation of the optically active acids from the externally compensated modifications has always been a long and tedious process, and there appears to be no doubt that this is largely, if not wholly, due to the isomeric salts separating from solvents as isomorphous mixtures or mixed crystals, which are only very gradually resolvable by further fractional crystallization. This difficulty might conceivably be got over if the active base employed for the separation could be varied, but the *cyclo*hexenecarboxylic acids are, unfortunately, so feebly acidic that very few of their salts with active bases are sufficiently stable or well characterized to make them suitable for fractional crystallization.

When the available data are carefully considered, it is difficult to avoid the conclusion that, in the cases detailed above, separation may have, after all, been incomplete. The salts of the active acids were probably still partly racemic, and in the form of mixed crystals, and for these reasons separation by further fractional crystallization was practically impossible, at all events with the comparatively small amounts of material which were available.

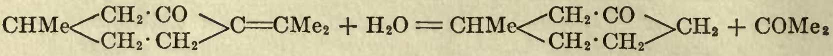
Considerations such as these made it desirable that the actual extent of the resolution effected by the fractional crystallization of the salts of the *cyclo*hexene acids with active bases should, at least in one instance, be experimentally tested, and we have therefore carried out an interesting series of experiments in connection with the optical activity of 1-methyl-Δ^3-*cyclo*hexene-4-carboxylic acid



$$\mathrm{CHMe}<\begin{matrix}\mathrm{CH_2{-}CH}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}\geqslant\mathrm{C\cdot CO_2H}$$

which have a direct bearing on this problem.

In 1896 Wallach showed that pulegone, which occurs in the essential oil of Mentha pulegium, is hydrolyzed by heating with dilute acids according to the scheme

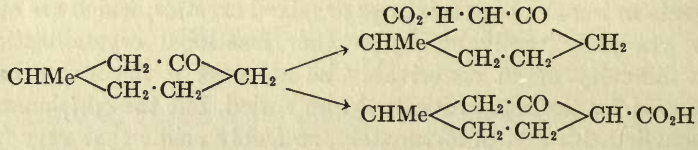


$$\mathrm{CHMe}<\begin{matrix}\mathrm{CH_2\cdot CO}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{C{=}CMe_2} + \mathrm{H_2O} = \mathrm{CHMe}<\begin{matrix}\mathrm{CH_2\cdot CO}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{CH_2} + \mathrm{COMe_2}$$

Pulegone 1-Methyl*cyclo*hexane-3-one

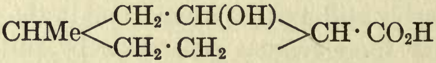
and the 1-methyl*cyclo*hexan-3-one which is formed in this way is the *d*-modification with the rotation $a_D + 8°$.

In conjunction with Messrs. Gardner and Watson, and afterwards with Mr. Chou, this ketone was subjected to the action of sodamide and carbon dioxide, when it yielded a ketonic acid which might have either of the following constitutional formulæ



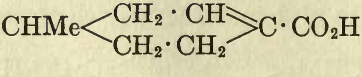
$$\mathrm{CHMe}<\begin{matrix}\mathrm{CH_2\cdot CO}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{CH_2} \begin{matrix}\nearrow \mathrm{CHMe}<\begin{matrix}\mathrm{CO_2\cdot H\cdot CH\cdot CO}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{CH_2}\\ \searrow \mathrm{CHMe}<\begin{matrix}\mathrm{CH_2\cdot CO}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{CH\cdot CO_2H}\end{matrix}$$

That the latter formula represents the acid and that it is therefore 1-methyl*cyclo*hexane-3-one-4-carboxylic acid was proved by the fact that the corresponding hydroxy-acid



$$\mathrm{CHMe}<\begin{matrix}\mathrm{CH_2\cdot CH(OH)}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{CH\cdot CO_2H}$$

obtained by reduction, yields, on oxidation with sulphuric acid, *p*-toluic acid — a proof that the methyl and carboxyl groups occupy the *p*-position. This hydroxy-acid — 1-methyl*cyclo*hexane-3-ol-4-carboxylic acid — has the rotation $-31.8°$ and, when heated with phosphorus trichloride, it yields *d*-1-methyl-Δ^3-*cyclo*hexene-4-carboxylic acid



$$\mathrm{CHMe}<\begin{matrix}\mathrm{CH_2\cdot CH}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{C\cdot CO_2H}$$

which has the high rotation $+150.1°$. This acid was converted into the corresponding *d*-Δ^3-*p*-menthenol(8) and *d*-$\Delta^{3.8(9)}$-*p*-menthadiene by the usual methods, and the α_D values observed (I) may be conveniently tabulated in comparison with those observed by Kay and Perkin (II), as the result of the separation they carried out with brucine λ strychnine in the way already described.

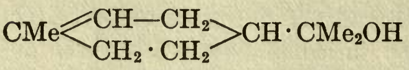
	I	II
d-1-Methyl-Δ^3-*cyclo*hexene-4-carboxylic acid . . .	+150.1°	+101.1°
Ethyl *d*-1-methyl*cyclo*hexenecarboxylate	122.3	86.5
d-Δ^3-*p*-Menthenol(8)	83.2	67.3
d-$\Delta^{3\cdot8(9)}$-*p*-Menthadiene	100.0	98.2

This table shows quite clearly that the substances obtained by Kay and Perkin had rotations which were only about two thirds of the maximum value. There is, however, one curious exception to this, and that is the case of the menthadienes, which, although derived from menthenols of the widely different values as $[\alpha]_D$ + 83.2° and +67.3°, had in both cases practically the same rotations, namely, +100.0° and +98.2°. This seems to indicate quite clearly that some racemization must have taken place in any case during the formation of the menthadiene from the menthenol of rotation $[\alpha]_D$ + 83.2°.

That racemization does undoubtedly take place under certain conditions, to some extent at least, is proved by the following experiment.

Pure *d*-Δ^3-*p*-menthenol(8) of rotation $[\alpha]_D$ + 83.2° was converted into *d*-$\Delta^{3\cdot8(9)}$ -*p*-menthadiene by two different processes, namely, (i) by digesting with 5% oxalic acid, and (ii) by the action of magnesium methyl iodide in the cold. The menthadiene obtained in (i) had $[\alpha]_D$ + 100.0°, whereas the preparation resulting from (ii) had a rotation of $[\alpha]_D$ +90.4° only. Racemization in unsaturated compounds is usually assumed to be due to the reversible migration of the double linking, with consequent loss of optical activity, and seems to have been observed previously only in cases where the double linking is closely associated with the asymmetric carbon atom.

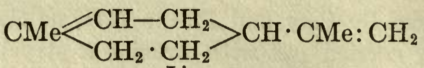
Thus, for example, Wallach has shown that terpineol yields, on treatment with dehydrating agents, not only limonene, but also terpinolene and *α*-terpinene:



$\mathrm{CMe}\Big\langle\begin{array}{l}\mathrm{CH{-}CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{array}\Big\rangle\mathrm{CH\cdot CMe_2OH}$

Terpineol

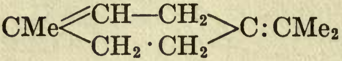
yields



$\mathrm{CMe}\Big\langle\begin{array}{l}\mathrm{CH{-}CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{array}\Big\rangle\mathrm{CH\cdot CMe{:}CH_2}$

Limonene

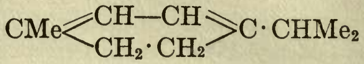
and



$\mathrm{CMe}\Big\langle\begin{array}{l}\mathrm{CH{-}CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{array}\Big\rangle\mathrm{C{:}CMe_2}$

Terpinolene

and

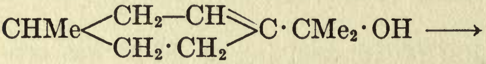


$\mathrm{CMe}\Big\langle\begin{array}{l}\mathrm{CH{-}CH}\\ \mathrm{CH_2\cdot CH_2}\end{array}\Big\rangle\mathrm{C\cdot CHMe_2}$

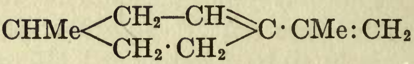
α-Terpinene

This group of terpenes probably represents an equilibrium mixture, but, however that may be, it is quite clear that, if the terpineol in the first instance is optically active, the reversible change into terpinolene alone must ultimately result in the inactivity of the whole. This migration of the double linking with consequent loss of optical activity accounts therefore in a satisfactory manner for the fact that Fisher and Perkin[1] were unable to obtain an active limonene with a rotation of more than 5° (*d*-limonene has $[\alpha]_D + 105°$) from active terpineol by the elimination of water.

It is, however, difficult to understand how this explanation of loss of activity can be applied to the case of racemization during the elimination of water from *d*-Δ^3-*p*-menthenol(8)



$\mathrm{CHMe}\Big\langle\begin{array}{l}\mathrm{CH_2{-}CH}\\ \mathrm{CH_2\cdot CH_2}\end{array}\Big\rangle\mathrm{C\cdot CMe_2\cdot OH}\longrightarrow$



$\mathrm{CHMe}\Big\langle\begin{array}{l}\mathrm{CH_2{-}CH}\\ \mathrm{CH_2\cdot CH_2}\end{array}\Big\rangle\mathrm{C\cdot CMe{:}CH_2}$

since migration of the double linking could hardly affect the asymmetric grouping >CHMe to which optical activity is due, unless, indeed, some profound change in constitution is assumed to take place.

Moreover, it is clear that a profound change in constitution does not take place, because the menthadiene obtained is found to exhibit all those physical properties which are known to be associated with the presence of the conjugated double linking.

The section of the terpenes to which I have so far directed

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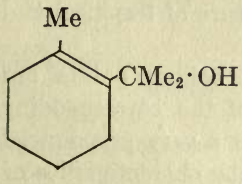
[1] Loc. cit.

special attention has been confined to the derivatives of *p*-cymene, namely, the *p*-menthenols and *p*-menthadienes, but corresponding derivatives of *o*-cymene have also been synthesized by methods which are somewhat similar to those employed in the *p*-series, and to many of these substances considerable interest attaches.

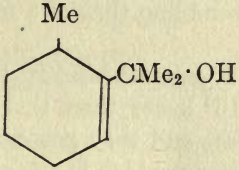
It is remarkable that menthenols and menthadienes of the *o*-series do not appear so far to have been met with as constituents of the natural essential oils; apart from bicyclic terpenes such as pinene and the bicyclic ketones such as tujone and tanacetone, the members of the terpene group which occur naturally are almost all derived from *p*-cymene, but a striking exception is sylvestrene, which belongs to the *m*-series and to this substance reference will presently be made in some detail. It has therefore been necessary to prepare the terpenes of the *o*-series synthetically, and, in order to give a rapid survey of this part of the subject, I have made a table of the possible menthenols and menthadienes of the *o*-series, and of these all have been actually synthesized with the exception of the Δ^2-isomerides in each case, which are as yet unknown.

o-MENTHENOLS

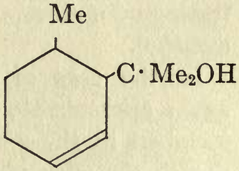
(With boiling points under 30 mm. pressure)



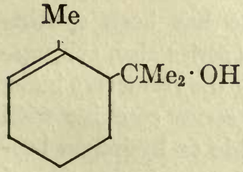
Δ^1- 112°



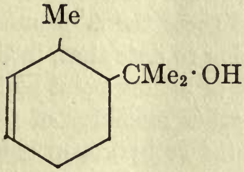
Δ^2- unknown



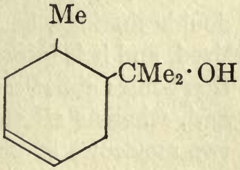
Δ^3- 110°



Δ^6- 110°



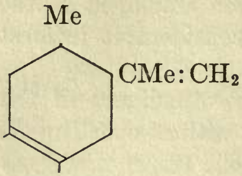
Δ^5- 110°



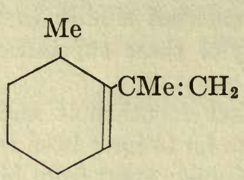
Δ^4- 108°

o-MENTHADIENES

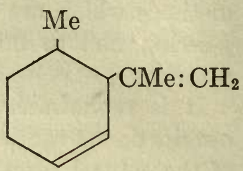
(With boiling points at N. P. and molecular refraction)



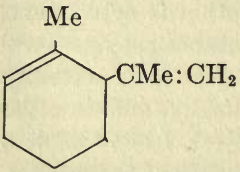
Δ^1- 177°
M 46.0



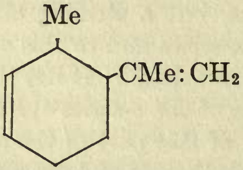
Δ^2- unknown



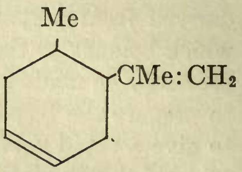
Δ^3- 170°
M 45.4



Δ^6- 171°
M 45.2



Δ^5- 171°
M 45.2



Δ^4- 171°
M 45.2

The *o*-menthenols do not call for special comment; they are colorless viscid oils and distill all approximately at the same temperature, which is about 10° lower than the boiling points of the corresponding substances in the *p*-series. They all have a penetrating odor closely resembling that of a mixture of terpineol and menthol.

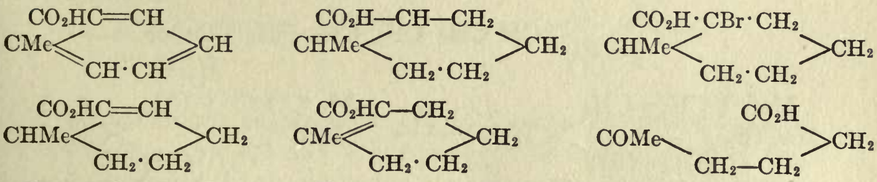
In the case of the *o*-menthadienes the boiling points are again approximately 10° lower than those of the corresponding members in the *p*-series, and they possess in a very pronounced degree the odor of lemons, which is one of the characteristics of dipentene.

Only two of the possible *o*-menthadienes contain conjugated double linkings, and of these the Δ^1-isomeride has been synthesized, and it is interesting to note that, in this series also, conjugation brings about a rise of boiling point and in the refractive index and, whereas all the other members of the series combine with two molecules of bromine or hydrogen chloride or hydrogen bromide, this particular conjugated terpene is again only capable of absorbing one molecule of halogen or of halogen acid.

All the menthenols and menthadienes of the *o*-series which have so far been prepared are inactive, and experiments have not yet been made with the object of obtaining the corresponding active modifications.

In a long and complicated series such as this it is obviously impossible to attempt to describe the preparation and properties of each member in detail. I therefore propose to select three examples which seem to me to be the most instructive, and shall confine my remarks to the synthesis of the Δ^1-, Δ^5-, and Δ^6-isomerides.

Δ^1-*o*-Menthenol(8) and $\Delta^{1\cdot 8(9)}$-*o*-menthadiene were synthesized by two processes, which in many respects were similar to those which had previously been employed in the *p*-series. The first synthesis had for its starting point *o*-toluic acid, which was converted, by reduction with sodium and isoamyl alcohol, into 1-methyl*cyclo*hexane-2-carboxylic acid, and this, on bromination in the usual manner, yielded 2-bromo-1-methyl*cyclo*hexane-2-carboxylic acid. When this bromo acid was treated with alkalies, elimination of hydrogen bromide took place, and an unsaturated acid was formed which obviously might be either the Δ^1- or the Δ^2- unsaturated acid

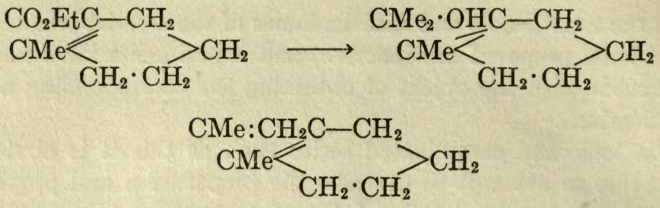


1-Methyl-Δ^2-*cyclo*hexene-2-carboxylic acid

1-Methyl-Δ^1-*cyclo*hexene-2-carboxylic acid

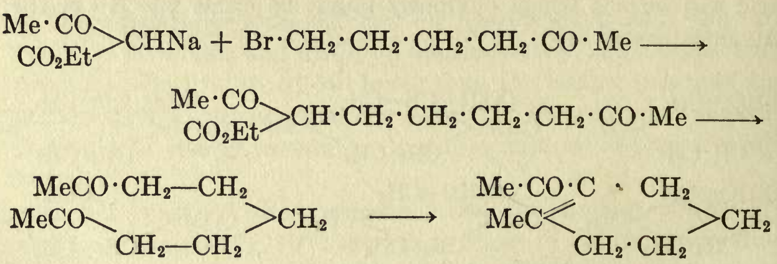
γ-Acetobutyric acid

That the acid was 1-methyl-Δ^1-*cyclo*hexene-2-carboxylic acid was proved by the fact that, on oxidation with permanganate, it yielded γ-acetobutyric acid. Lastly, the unsaturated acid was converted into its ester, and this, on treatment with magnesium methyl iodide, yielded Δ^1-*o*-menthenol(8), from which $\Delta^{18\cdot(9)}$-*o*-menthadiene was obtained by dehydration.

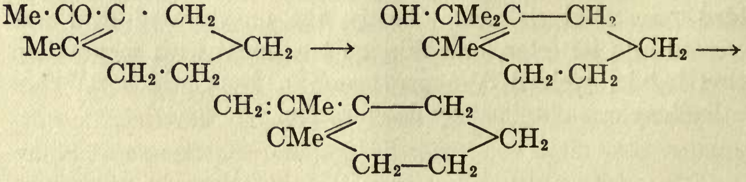


As has already been stated, this menthadiene contains a conjugated double linking and therefore is only capable of combining with one molecule of a halogen or halogen acid.

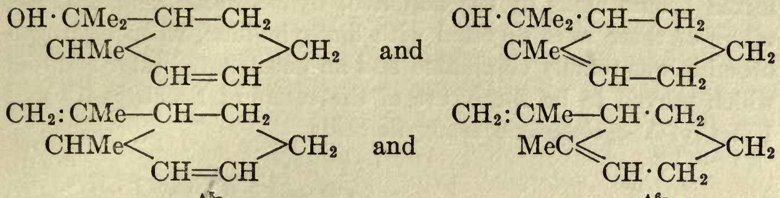
The second method which was employed in the synthesis of this Δ^{1}-*o*-menthenol and $\Delta^{1\cdot 8(9)}$-*o*-menthadiene was of an entirely different nature. The starting point was the sodium derivative of ethyl acetoacetate, which, when treated with δ-acetobutyl bromide, yielded diacetylpentanecarboxylic ester, and this on hydrolysis lost carbon dioxide with the formation of diacetylpentane, a diketone which, on treatment with sulphuric acid, undergoes internal condensation with the formation of 1-methyl-Δ^{1}-*cyclo*hexene methylketone.



This ketone reacts with magnesium methyl iodide to yield Δ^{1}-*o*-menthenol(8), from which $\Delta^{1\cdot 8(9)}$-*o*-menthadiene was obtained by the action of dehydrating agents in the usual manner

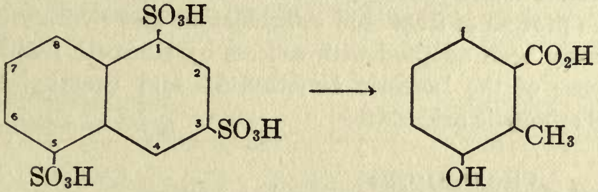


The synthesis of Δ^5- and Δ^6-*o*-menthenol(8) and $\Delta^{5.8(9)}$ and $\Delta^{6.8(9)}$-*o*-menthadiene



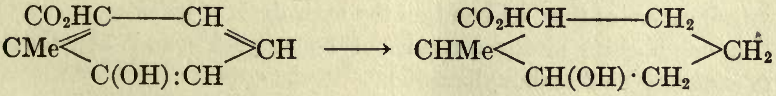
Δ^5- Δ^6-

proved to be a matter of very considerable experimental difficulty and, as the process introduces some new features, it has been selected for discussion. The starting point is 6-hydroxy-*o*-toluic acid, which cannot be prepared from *o*-toluic acid by any convenient process, but which fortunately can be obtained in quantity by a remarkable decomposition, namely, from naphthalene-1:3:5-trisulphonic acid by fusion with caustic potash, a process which has been patented by Messrs. Kalle & Co. of Biebrich.



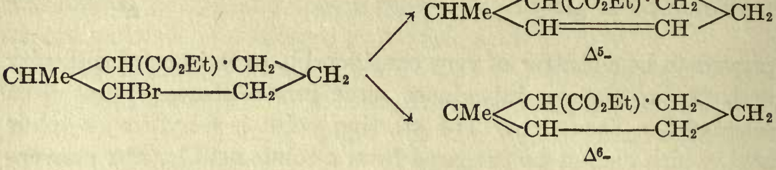
In this process carbon atom 1 is oxidized to the carboxyl group, the carbon atoms 2 and 3 are removed as carbon dioxide, and carbon atom 4 is reduced to the methyl group. In the other ring the sulphonic group is replaced by the hydroxyl group in the ordinary way.

When 6-hydroxy-*o*-toluic acid is reduced by sodium and alcohol, it yields the *cis*- and *trans*-modifications of 1-methyl*cyclo*hexan-6-ol-2-carboxylic acid



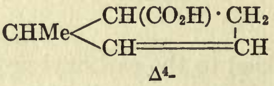
6-Hydroxy-*o*-toluic acid

1-Methyl*cyclo*hexane-6-ol-2-carboxylic acid which have been separated and characterized but need not be further described. The mixture of these acids was converted into the mixed bromo acids by the action of hydrobromic acid, and the esters of these were digested with diethylaniline, when hydrogen bromide was readily eliminated and an unsaturated ester resulted which proved to be a mixture of the esters of 1-methyl-Δ^5- and 1-methyl-Δ^6-*cyclo*hexenecarboxylic acids



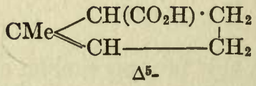
$$\mathrm{CHMe}\left<\begin{array}{l}\mathrm{CH(CO_2Et)\cdot CH_2}\\ \mathrm{CHBr}\text{———}\mathrm{CH_2}\end{array}\right>\mathrm{CH_2} \begin{array}{l}\nearrow \mathrm{CHMe}\left<\begin{array}{l}\mathrm{CH(CO_2Et)\cdot CH_2}\\ \mathrm{CH{=\!=\!=}CH}\end{array}\right>\mathrm{CH_2}\quad \Delta^5\text{-}\\ \searrow \mathrm{CMe}\left<\!\!\left<\begin{array}{l}\mathrm{CH(CO_2Et)\cdot CH_2}\\ \mathrm{CH}\text{———}\mathrm{CH_2}\end{array}\right>\right.\mathrm{CH_2}\quad \Delta^6\text{-}\end{array}$$

The mixed Δ^5- and Δ^6-acids, obtained by the hydrolysis of these esters, are liquid, and do not appear to yield characteristic salts; their separation by the fractional crystallization of their salts was therefore found to be impossible. The only course left seemed to be the process of fractional esterification and hydrolysis which had already been adopted with success by Haworth and Perkin[1] in the case of the isomeric 1-methyl-Δ^4- and 1-methyl-Δ^5-*cyclo*pentenecarboxylic acids



$$\mathrm{CHMe}\left<\begin{array}{l}\mathrm{CH(CO_2H)\cdot CH_2}\\ \mathrm{CH{=\!=\!=}CH}\end{array}\right. \quad \Delta^4\text{-}$$

and



$$\mathrm{CMe}\left<\!\!\left<\begin{array}{l}\mathrm{CH(CO_2H)\cdot CH_2}\\ \mathrm{CH}\text{———}\mathrm{CH_2}\end{array}\right.\right. \quad \Delta^5\text{-}$$

Of these isomeric acids, the Δ^4-modification esterifies more rapidly at the ordinary temperature than the Δ^5-, and again the ester of the Δ^4-modification is hydrolyzed by methyl-alcoholic potassium hydroxide in the cold with greater ease than the ester of the Δ^5-acid. These results seem to indicate that the grouping, >C:CMe–, contained in the Δ^5-acid, has a retarding effect on the esterification of that acid and on the hydrolysis of its ester.

A comparison of the formulæ of 1-methyl-Δ^5- and 1-methyl-Δ^6-*cyclo*hexene-2-carboxylic acids

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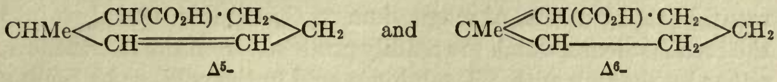
[1] Trans., *93,* 577 (1908).



$$\mathrm{CHMe}\left\langle\begin{matrix}\mathrm{CH(CO_2H)\cdot CH_2}\\ \mathrm{CH{=\!=\!=}CH}\end{matrix}\right\rangle\mathrm{CH_2}\qquad\text{and}\qquad\mathrm{CMe}\left\langle\!\!\left\langle\begin{matrix}\mathrm{CH(CO_2H)\cdot CH_2}\\ \mathrm{CH{-\!-\!-}CH_2}\end{matrix}\right\rangle\right.\!\mathrm{CH_2}$$

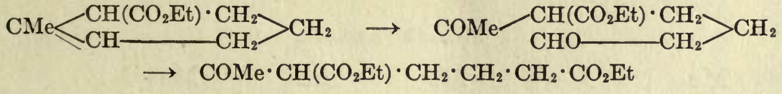
$$\Delta^5\text{-}\qquad\qquad\qquad\qquad\Delta^6\text{-}$$

with those of the pentene acids pictured above, shows that there is great similarity in constitution, and that the essential groupings are the same and in the same positions in both series. In conformity with this view, experiment proved that 1-methyl-Δ^6-*cyclo*hexene-2-carboxylic acid, which contains the grouping >C:CMe–, does actually esterify less readily than 1-methyl-Δ^5-*cyclo*hexene-2-carboxylic acid, and that its ester is less readily hydrolyzed than the ester of the Δ^5-acid. By repeating the process of fractional esterification and hydrolysis a great number of times, what is believed to be an almost complete separation of these acids was ultimately accomplished.

The constitution of 1-methyl-Δ^5-*cyclo*hexene-2-carboxylic acid was controlled by oxidation, first with ozone, and then with permanganate, when an acid was obtained which melted at 177°–178°, and was found to be identical with the pentane-$\beta\gamma\epsilon$-tricarboxylic acid which Haworth and Perkin[1] had previously prepared synthetically

$$\mathrm{CHMe}\left\langle\begin{matrix}\mathrm{CH(CO_2H)\cdot CH_2}\\ \mathrm{CH{=\!=\!=}CH}\end{matrix}\right\rangle\mathrm{CH_2}\longrightarrow\mathrm{CHMe}\left\langle\begin{matrix}\mathrm{CH(CO_2H)\cdot CH_2}\\ \mathrm{CO_2H\qquad CO_2H}\end{matrix}\right\rangle\mathrm{CH_2}$$

On the other hand, ethyl 1-methyl-Δ^6-*cyclo*hexene-2-carboxylate is converted, by oxidation with ozone, into an aldehydo-ester, which, on further oxidation with chromic acid and subsequent esterification, yields a ketonic ester the alcoholic solution of which gives a violet coloration on the addition of ferric chloride. There can be no doubt that these changes are to be represented thus:



$$\mathrm{CMe}\left\langle\!\!\left\langle\begin{matrix}\mathrm{CH(CO_2Et)\cdot CH_2}\\ \mathrm{CH{-\!-\!-}CH_2}\end{matrix}\right\rangle\right.\!\mathrm{CH_2}\longrightarrow\mathrm{COMe}\!\diagup\!\begin{matrix}\mathrm{CH(CO_2Et)\cdot CH_2}\\ \mathrm{CHO{-\!-\!-}CH_2}\end{matrix}\!\right\rangle\mathrm{CH_2}$$

$$\longrightarrow\mathrm{COMe\cdot CH(CO_2Et)\cdot CH_2\cdot CH_2\cdot CH_2\cdot CO_2Et}$$

The next step was to convert the esters of 1-methyl-Δ^5- and 1-methyl-Δ^6-*cyclo*hexene-2-carboxylic acids into the corresponding

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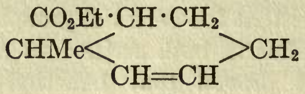
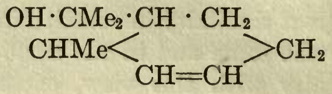
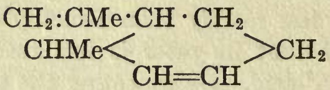
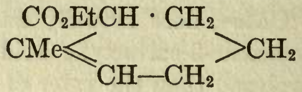
[1] Trans., *93*, 581 (1908).

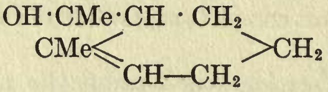
menthenols by means of magnesium methyl iodide, and then into the menthadienes, which are readily produced from the menthenols, either by shaking with 5% sulphuric acid in the cold, or by boiling with 6% oxalic acid.

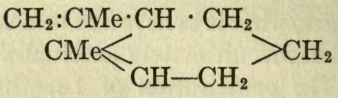

Δ5-


Δ5-


Δ5-


Δ6-

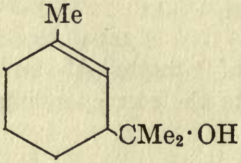

Δ6-

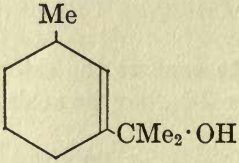

Δ6-

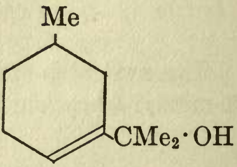
and the properties of these have already been given in the general table of the *o*-menthenols and *o*-menthadienes.

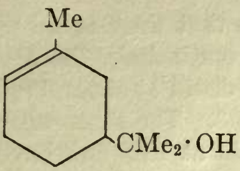
Following this brief description of the synthesis of some of the menthenols and menthadienes belonging to the *o*-series there remains still the discussion of that section of the terpene group which comprises the derivatives of *m*-cymene, and it has always seemed to the author that, partly perhaps on account of its complexity and difficulty, the chemical development of this section has been even more fascinating than that of either of the other sections. The chemistry of the *m*-series is complete, all the possible inactive *m*-menthenols and *m*-menthadienes of the type of terpineol and dipentene have been prepared synthetically. The following table contains a list of the *m*-menthenols with their boiling points under 30 mm. pressure.

m-MENTHENOLS

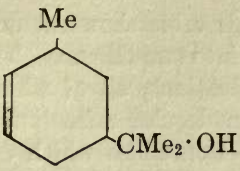

Δ1- 108°/30


Δ2- 110°

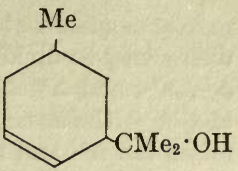

Δ3- 110°



Δ^6- 115°



Δ^5- 114°

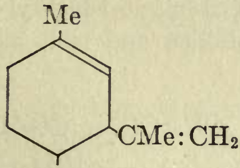


Δ^4- 114°

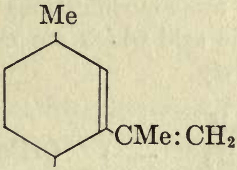
and it will be observed that they all boil approximately at the same temperature. They are for the most part colorless, viscid oils which possess, in a very pronounced degree, the odor of terpineol and menthol. When a drop of sulphuric acid is added to the solution of any of these *m*-menthenols (or the corresponding menthadienes) in acetic anhydride, an intense violet coloration is produced, and this reaction is characteristic of the *m*-series and is not shown by the menthenols or menthadienes of either the *p*- or *o*-series.

In the next table the *m*-menthadienes have been arranged with their boiling points and molecular refractions.

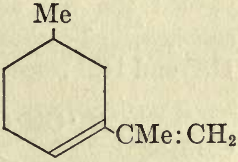
m-MENTHADIENES



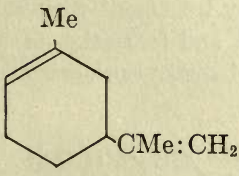
Δ^1- 177°
M = 45.3



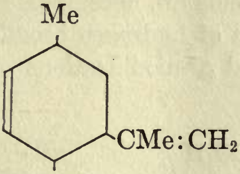
Δ^2- 182°
M = 46.6



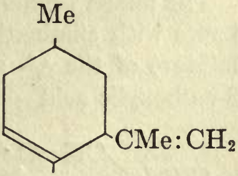
Δ^3- 182°
M = 46.4



Δ^6- 176°
M = 45.4



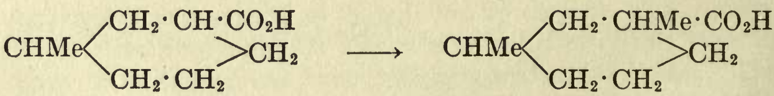
Δ^5- 176°
M = 45.3
Calc. $C_{10}H_{16}|\!\!=^2 = 45.24$



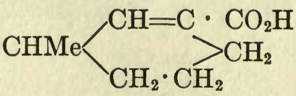
Δ^4- 176°
M = 45.3

A brief glance at this table shows at once that these menthadienes may be divided into two classes. The one includes the Δ¹-, Δ⁴-, Δ⁵-, and Δ⁶-modifications, all of which distill at about 176° and have the normal molecular refraction 45.3. The other comprises the Δ²- and Δ³- isomerides which distill at 182° and have approximately the molecular refraction 46.5. If the formulæ of these modifications are examined, it will be seen that, as in the *p*- and *o*-series, this rise in boiling point and in molecular refraction is obviously connected with the fact that both menthadienes contain conjugated double linkings. In confirmation of this view, the observation was also made that the Δ¹-, Δ⁴-, Δ⁵-, and Δ⁶-isomerides all combine with two molecules of bromine or halogen acids, whereas the Δ²- and Δ³- isomerides are only capable of absorbing one molecule of halogen or halogen acid.

In dealing with the development of this group the best plan will perhaps be to describe, in the first place, the methods which were employed in the synthesis of the Δ²- and Δ³- menthenols and menthadienes. The first synthesis of these substances was carried out in conjunction with Mr. G. Tattersall, and had for its starting point *m*-toluic acid, which was converted into 1-methyl*cyclo*hexane-3-carboxylic acid by reduction with sodium and isoamyl alcohol in the usual manner. When this acid was brominated, it yielded the *cis*- and *trans*-modifications of 3-bromo-1-methyl-*cyclo*hexane-3-carboxylic acid which are crystalline and melt at 118° and 142° respectively

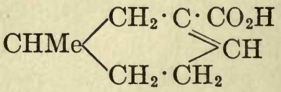


The mixed bromo acids are decomposed by treatment with alkalies with elimination of hydrogen bromide and formation of a mixture of the Δ²- and Δ³-modifications of 1-methyl*cyclo*hexene-3-carboxylic acid



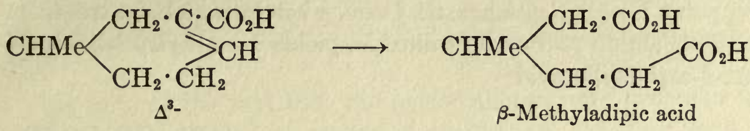
Δ²- Liquid

and

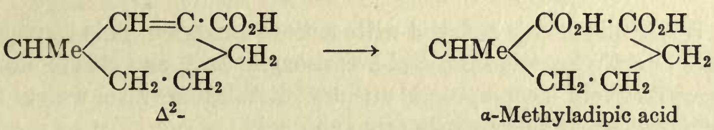


Δ³- m.p. 60°

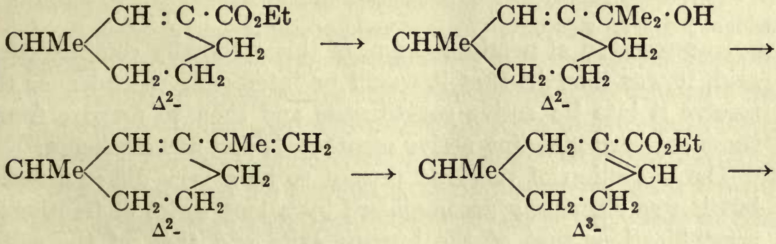
Great difficulty was experienced in separating these two acids, but complete separation was ultimately accomplished by taking advantage of the fact that the calcium salt of the Δ^2-acid is less soluble in water than that of the Δ^3-acid. 1-Methyl-Δ^3-*cyclo*hexene-3-carboxylic acid is crystalline and melts at 60°, whereas the isomeric Δ^3-acid is liquid and distills at 150°/11 mm. Having separated these isomeric acids, it was next necessary to determine their constitutions, and this was done in each case by oxidizing first with permanganate and then with chromic acid. It was found that under these conditions the acid melting at 60° yields β-methyladipic acid and consequently must be the Δ^3-isomeride

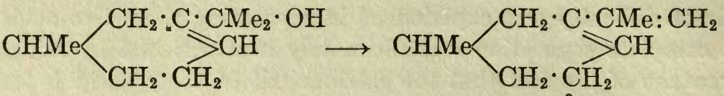


On the other hand, the liquid tetrahydro-acid is oxidized to α-methyladipic acid, a fact which proves that it must be 1-methyl-Δ^2-*cyclo*hexene-3-carboxylic acid



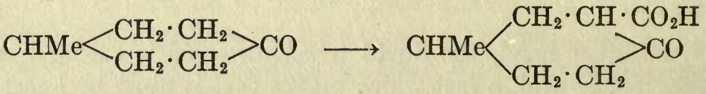
The isomeric acids were then converted into the esters, and these, on treatment with magnesium methyl iodide and subsequent dehydration, yielded the corresponding *m*-menthenols and *m*-menthadienes in the usual manner





Δ³- Δ³-

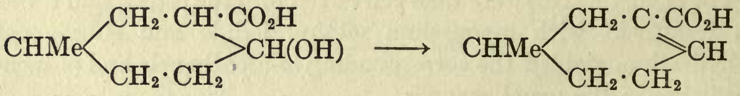
The method of preparation and separation of the 1-methyl-Δ²- and Δ³-*cyclo*hexene-3-carboxylic acids which has just been described is exceedingly laborious, and it is therefore fortunate that a second method for the preparation of the Δ³-acid was shortly afterwards discovered, which, although still laborious, is a great improvement on the first method. This synthesis, which was worked out in conjunction with Mr. B. D. W. Luff, has for its starting point 1-methyl*cyclo*hexane-4-one, a ketone which, on treatment with sodamide and carbon dioxide, yields 1-methyl*cyclo*hexane-4-one-3-carboxylic acid



1-Methyl*cyclo*hexane-4-one

1-Methyl*cyclo*hexane-4-one-3-carboxylic acid

When this acid is reduced with sodium amalgam, it is converted into 1-methyl*cyclo*hexane-4-ol-3-carboxylic acid, and this is almost quantitatively decomposed on dry distillation into water and 1-methyl-Δ³-*cyclo*hexane-3-carboxylic acid



1-Methyl*cyclo*hexane-4-Ol-3-carboxylic acid

1-Methyl-Δ³-*cyclo*hexene-3-carboxylic acid

In possession of nearly 200 gm. of this externally compensated acid, it was thought that it would be interesting to endeavor to resolve it into its active constituents and then to prepare from these the corresponding active menthenols and menthadienes.

The resolution of this acid proved to be a very difficult task, but it was ultimately accomplished by a long series of fractional crystallizations first of the brucine salts and then of the salts with *l*-menthylamine, an operation which required several months, and even then separation was not quite complete.

The *d*- and *l*-acids were then converted into the menthenols and menthadienes in the ordinary way, and the final results can be clearly seen from the following table:

	d-Series $[\alpha]_D$	*l*-Series $[\alpha]_D$
1-Methyl-Δ^3-*cyclo*hexene-3-carboxylic acid	40.1°	−35.8°
Ethyl methyl*cyclo*hexenecarboxylate	32.5	28.9
Δ^3-*m*-Menthenol(8)	20.9	18.5
$\Delta^{3.8(9)}$-*m*-Menthadiene	17.5	12.9

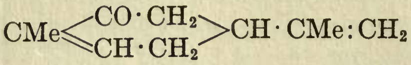
In spite of the fact that the menthadienes were prepared from the menthenols by so gentle a process as digesting with 5% aqueous oxalic acid, it is obvious that racemization has taken place probably to a considerable extent.

When these synthetical experiments in the terpene series were commenced, only two menthadienes of the *m*-series had been described, or, strictly speaking, only one, and these were sylvestrene, which was isolated from Swedish turpentine by Atterberg as far back as 1877 and is the only *m*-menthadiene which has so far been met with in natural oils, and carvestrene, the inactive modification of sylvestrene, which was prepared in 1894 from carvone by Baeyer.

Baeyer supplied the proof that sylvestrene is a derivative of *m*-cymene by employing a method which he had discovered and which is applicable to the diagnosis of any terpene. Sylvestrene was combined with hydrobromic acid, and the dry dihydrobromide, $C_{10}H_{16},2HBr$, was brominated in the presence of iodine. The resulting product was then reduced by zinc dust and alcoholic hydrochloric acid, and finally by sodium and alcohol, when a hydrocarbon was obtained which was found to be *m*-cymene.

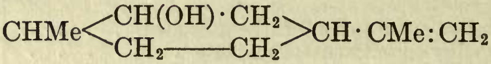
Before detailing the work which subsequently led to the synthesis both of carvestrene and sylvestrene, it will be advisable to give a brief sketch of the method employed by Baeyer in his brilliant researches on the preparation and properties of carvestrene.

When carvone, $C_{10}H_{14}O$, a substance which occurs in oil of caraway, is reduced by sodium and alcohol, it is converted into *dihydrocarveol*, and this, on oxidation with chromic acid, yields *dihydrocarvone*



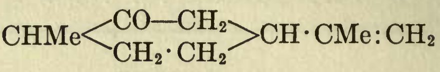
$$CMe\left<\begin{matrix}CO\cdot CH_2\\CH\cdot CH_2\end{matrix}\right>CH\cdot CMe:CH_2$$

Carvone



$$CHMe\left<\begin{matrix}CH(OH)\cdot CH_2\\CH_2\text{——}CH_2\end{matrix}\right>CH\cdot CMe:CH_2$$

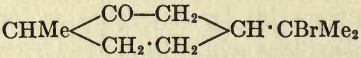
Dihydrocarveol



$$CHMe\left<\begin{matrix}CO\text{—}CH_2\\CH_2\cdot CH_2\end{matrix}\right>CH\cdot CMe:CH_2$$

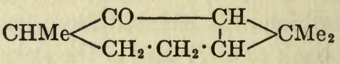
Dihydrocarvone

Hydrobromic acid converts dihydrocarvone into a hydrobromide, $C_{10}H_{17}OBr$, which, when treated with alcoholic potash at 0°, readily loses hydrogen bromide. Instead, however, of the unsaturated substance, dihydrocarvone, being regenerated as the result of this decomposition, a remarkable formation of a trimethylene ring takes place and *carone* is produced.



$$CHMe\left<\begin{matrix}CO\text{—}CH_2\\CH_2\cdot CH_2\end{matrix}\right>CH\cdot CBrMe_2$$

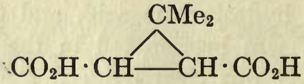
Hydrobromide of dihydrocarvone



$$CHMe\left<\begin{matrix}CO\text{————}CH\\CH_2\cdot CH_2\cdot CH\end{matrix}\right>CMe_2$$

Carone

In order to demonstrate the presence of the dimethyltrimethylene ring in carone, Baeyer and Ipatieff studied the behavior of this ketone on oxidation with permanganate and succeeded in isolating the *cis*- and *trans*-caronic acids



$$\begin{array}{c}CMe_2\\ CO_2H\cdot CH\text{——}CH\cdot CO_2H\end{array}$$

The subsequent synthesis of these acids by Perkin and Thorpe[1] by a method which left no doubt as to their constitutions, afforded

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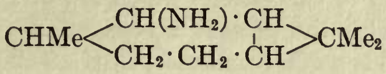
[1] Trans., *75*, 48 (1899).

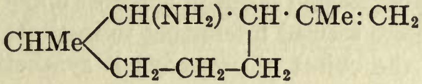
additional evidence of the presence of the dimethyltrimethylene ring in carone.

When caroneoxime is reduced by sodium and alcohol it yields *carylamine,* $C_{10}H_{17}NH_2$, and since this base is stable to permanganate, Baeyer[1] concluded that it could not be unsaturated and must therefore still contain the dimethyltrimethylene ring. The constitution of carylamine is for this reason derived from that of caroneoxime in a simple manner without molecular change and is represented by the formula



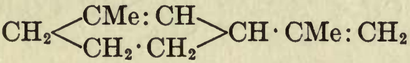
$$\mathrm{CHMe}\left\langle\begin{array}{l}\mathrm{CH(NH_2)\cdot CH}\\ \qquad\qquad\quad\;|\\ \mathrm{CH_2\cdot CH_2\cdot CH}\end{array}\right\rangle\mathrm{CMe_2}$$

The most characteristic property of carylamine is the decomposition which it undergoes when its solution in dilute acids is evaporated, during which process the dimethyltrimethylene ring suffers disruption and the unsaturated isomeric base, *vestrylamine*



$$\mathrm{CHMe}\left\langle\begin{array}{l}\mathrm{CH(NH_2)\cdot CH\cdot CMe:CH_2}\\ \qquad\qquad\quad\;|\\ \mathrm{CH_2{-}CH_2{-}CH_2}\end{array}\right.$$

is formed. Lastly, the hydrochloride of vestrylamine is readily decomposed on distillation, with elimination of ammonium chloride and formation of *carvestrene,* an inactive terpene to which Baeyer[2] assigned the constitution

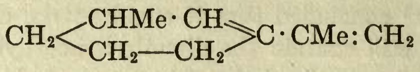


$$\mathrm{CH_2}\left\langle\begin{array}{l}\mathrm{CMe:CH}\\ \mathrm{CH_2\cdot CH_2}\end{array}\right\rangle\mathrm{CH\cdot CMe:CH_2}$$

This formula represents carvestrene as a derivative of *m*-cymene, and direct evidence in favor of this view was subsequently obtained by Baeyer,[3] who showed that, when carvestrene dihydrobromide is treated with excess of bromine and the product reduced by zinc dust and alcoholic hydrochloric acid, it actually yields *m*-cymene. The position of the double linking in the above formula for car-

[1] Ber., *27*, 3486 (1894).
[2] Loc. cit., 3485.
[3] Ber., *31*, 1402 (1898).

vestrene is rendered probable by the fact that it is formed from vestrylamine by the simple elimination of ammonia, but this decomposition might equally well lead to the expression



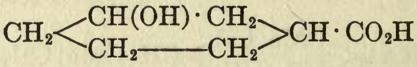
$$CH_2<\begin{array}{l}CHMe\cdot CH\\CH_2{-\!-}CH_2\end{array}>C\cdot CMe:CH_2$$

That this formula is incorrect is shown by the fact that carvestrene does not contain conjugated double linkings.

The properties of carvestrene which are of special importance in connection with the present investigation are these: It distills at 178°, yields a *dihydrochloride,* $C_{10}H_{16},2\,HCl$, which melts at 52.5°, and a *dihydrobromide,* $C_{10}H_{16},2\,HBr$, of melting point 48°–50°, and gives a deep blue coloration when a drop of sulphuric acid is added to its solution in acetic anhydride.

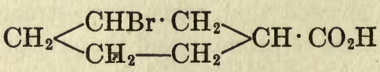
Carvestrene occupies the same position in the *m*-cymene group of terpenes as dipentene does in the *p*-cymene series, and for this reason it is to be considered as one of the most important of the terpenes. It therefore seemed interesting to institute a series of experiments with the object of preparing it synthetically by some process which would leave no doubt as to the constitution of the terpene, and in this we were ultimately successful.

The starting point in this synthesis was *m*-hydroxybenzoic acid, which is reduced by sodium and alcohol to cyclo*hexanol*-3-*carboxylic acid*



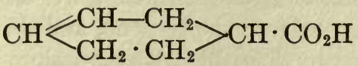
$$CH_2<\begin{array}{l}CH(OH)\cdot CH_2\\CH_2{-\!-\!-}CH_2\end{array}>CH\cdot CO_2H$$

which reacts readily with hydrobomic acid with formation of the *cis*-modification (m. p. 63°) of 3-*bromo*cyclo*hexanecarboxylic acid*



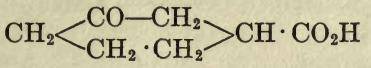
$$CH_2<\begin{array}{l}CHBr\cdot CH_2\\CH_2{-\!-}CH_2\end{array}>CH\cdot CO_2H$$

whereas the *trans*-hydroxy-acid is converted, by treatment with hydrobromic acid, into the corresponding *trans*-bromo-acid of melting point 167°. When the latter is digested with diethylaniline, it is decomposed apparently quantitatively, with elimination of hydrogen bromide and formation of Δ^3-cyclo*hexenecarboxylic acid* (Δ^3-tetrahydrobenzoic acid)



$$CH{<}\begin{matrix}CH{-}CH_2\\ CH_2\cdot CH_2\end{matrix}{>}CH\cdot CO_2H$$

The second step in the synthesis of carvestrene was the conversion of *cyclo*hexanol-3-carboxylic acid into cyclo*hexanone*-3-*carboxylic acid*



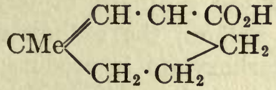
$$CH_2{<}\begin{matrix}CO{-}CH_2\\ CH_2\cdot CH_2\end{matrix}{>}CH\cdot CO_2H$$

by oxidation with chromic acid mixture, and in this way we have prepared large quantities of this important acid in a crystalline condition.

Ethyl *cyclo*hexanone-3-carboxylate reacts readily with magnesium methyl iodide, and the product, on hydrolysis, yields 1-methyl*cyclo*hexane-1-ol-3-carboxylic acid, which is converted by hydrobromic acid into 1-bromo-1-methyl*cyclo*hexane-3-carboxylic acid

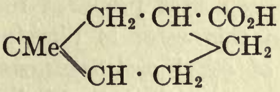
$$OH\cdot CMe{<}\begin{matrix}CH_2\cdot CH\cdot CO_2H\\ CH_2\cdot CH_2\end{matrix}{>}CH_2 \longrightarrow Br\cdot CMe{<}\begin{matrix}CH_2\cdot CH\cdot CO_2H\\ CH_2\cdot CH_2\end{matrix}{>}CH_2$$

and this, when digested with pyridine, is decomposed with elimination of hydrogen bromide and formation of an acid which, since it yielded adipic acid on oxidation, was at first thought to consist entirely of 1-methyl-Δ^1-*cyclo*hexene-3-carboxylic acid, but there is now reason to suppose that it contains small quantities at least of the corresponding Δ^6-acid



$$CMe{<}\begin{matrix}CH\cdot CH\cdot CO_2H\\ CH_2\cdot CH_2\end{matrix}{>}CH_2$$

Δ^1-



$$CMe{<}\begin{matrix}CH_2\cdot CH\cdot CO_2H\\ CH\cdot CH_2\end{matrix}{>}CH_2$$

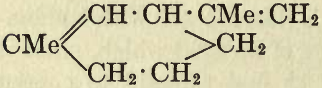
Δ^6-

This matter will be discussed again, and for the purpose of describing the synthesis of carvestrene the Δ^1-acid need only be considered at this stage. This acid was converted into the ester, and this, on treatment with magnesium methyl iodide, yielded dihydrocarvestrenol or Δ^1-*m*-menthenol(8). The next step was to convert the menthenol into the terpene, and this was accomplished in the usual manner by digesting with potassium hydrogen sulphate, when the hydrocarbon obtained exhibited all the properties ascribed to carvestrene by Baeyer

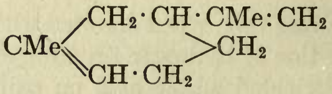
Dihydrocarvestrenol *Carvestrene*

Both preparations gave the same blue coloration when sulphuric acid was added to their solution in acetic anhydride; both yielded a dihydrochloride melting at 52.5° and a dihydrobromide melting at 48°–50°; moreover, the mixture of the two specimens of the dihydrobromide melted sharply at the same temperature, 48°–50°.

This, then, was the first synthesis of carvestrene. The next synthesis of carvestrene, in the carrying out of which the author had the valuable assistance of Mr. K. Fisher, was an indirect one and indeed is actually a synthesis of Δ^6-*m*-menthadiene, which, on account of its close relationship to carvestrene, has been named *iso*carvestrene

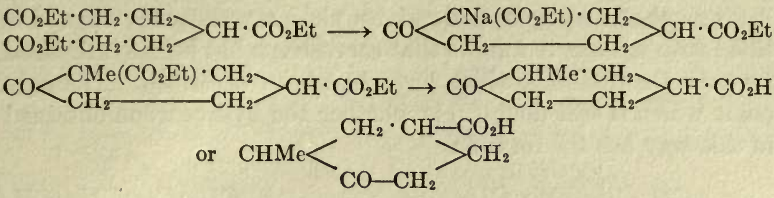


Carvestrene
$\Delta^{1\cdot8(9)}$-*m*-Menthadiene

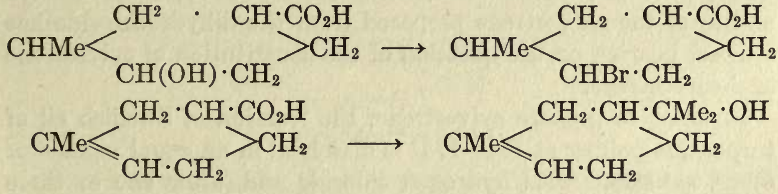


*Iso*carvestrene
$\Delta^{6\cdot8(9)}$-*m*-Menthadiene

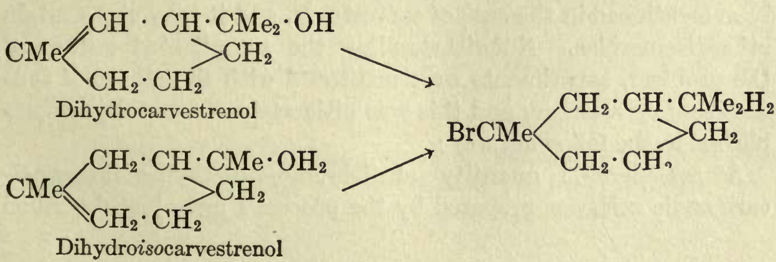
The starting point was ethyl pentane-*αγε*-tricarboxylate, which had been first prepared for use in the synthesis of terpineol. When this ester is digested with sodium, the sodium derivative of ethyl *cyclo*hexanone-2:4-dicarboxylate is produced, and this reacts with methyl iodide to yield ethyl 1-methyl*cyclo*hexane-6-one-1:3-dicarboxylate, an ester which, on hydrolysis, is converted into 1-methyl*cyclo*hexane-6-one-3-carboxylic acid



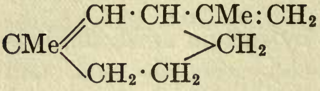
When this new keto acid is reduced by sodium amalgam, it is converted into 1-methyl*cyclo*hexane-6-ol-3-carboxylic acid, and the ester of the bromo acid, obtained by treating the hydroxy acid with hydrobromic acid and subsequent esterification, is decomposed by boiling diethylaniline with the formation of ethyl 1-methyl-Δ^6-*cyclo*hexene-3-carboxylate. When the ester of this acid is added to an ethereal solution of magnesium methyl iodide, it is quantitatively converted into dihydro*iso*carvestrenol or Δ^6-*m*-menthenol(8)



This interesting substance reacts with hydrogen chloride and bromide, yielding a dihydrochloride and a dihydrobromide which melt at 52.5° and 48°–49°, respectively, and careful comparison showed that these halogen derivatives are identical with the dihydrochloride and dihydrobromide of carvestrene. In other words, if we assume that dihydrocarvestrenol has the constitution which was assigned to it on p. 260, then both this substance and dihydro*iso*carvestrenol yield the same substances on treatment with halogena cids, as was indeed to be expected



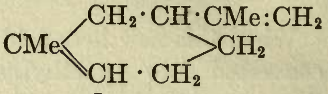
Since these halogen derivatives yield carvestrene when distilled with aniline, it follows that carvestrene has been synthesized by both the methods which have just been described. The only point which is still doubtful is whether the hydrocarbon obtained in this way has the formula



$$\mathrm{CMe}\begin{array}{l}\diagup\mathrm{CH\cdot CH\cdot CMe{:}CH_2}\\ \qquad\qquad\quad >\mathrm{CH_2}\\ \diagdown\mathrm{CH_2\cdot CH_2}\end{array}$$

Carvestrene

or



$$\mathrm{CMe}\begin{array}{l}\diagup\mathrm{CH_2\cdot CH\cdot CMe{:}CH_2}\\ \qquad\qquad\quad >\mathrm{CH_2}\\ \diagdown\mathrm{CH\cdot CH_2}\end{array}$$

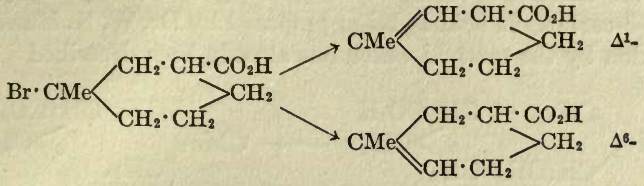
*Iso*carvestrene

in other words, whether it is carvestrene or *iso*carvestrene, and no evidence is as yet available to decide this point.

This is perhaps not a matter of much moment in the case of carvestrene, because there can be little doubt that the carvestrene prepared by Baeyer from vestrylamine is the pure Δ^1-isomeride. But, on the other hand, this view of the probable mixed nature of the carvestrene prepared from the dihydrochloride has a direct bearing on the question of the constitution of sylvestrene or *d*-carvestrene.

In order to prepare sylvestrene, the fraction of Swedish oil of turpentine boiling at 174°–178° is dissolved in an equal volume of ether, saturated with hydrogen chloride and, after two or three days, the ether is distilled off and the residue left to crystallize for months in an extremely cold place, an operation which is frequently carried out in the north of Siberia. In this way sylvestrene dihydrochloride is obtained, and after recrystallization melts at 72° and has $\alpha_D + 22°$; this pure dihydrochloride is then distilled with aniline and yields sylvestrene, which boils between 176°–180° and has a rotation varying from +60° to above +80° according to the fraction examined. No doubt this hydrocarbon consists of a mixture of the two modifications which have just been mentioned in the case of carvestrene, and it may also contain other isomerides. Notwithstanding the complicated nature of the problem, experiments were instituted with the object of synthesizing sylvestrene, and this was ultimately successfully accomplished in the following way:

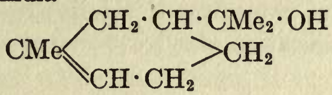
A considerable quantity of 1-bromo-1-methyl*cyclo*hexane-3-carboxylic acid was prepared by the process I have just described and converted by elimination of hydrogen bromide into the mixed Δ^1- and Δ^6-acids



in which apparently the Δ^1-isomeride largely predominates.

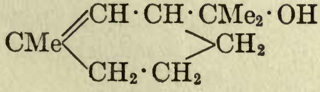
This mixture of acids was then combined with brucine, and after a large number of recrystallizations an acid was isolated in small quantities which had $\alpha_D + 90°$ and which appears to be the *d*-Δ^6-acid; in other words, the brucine had selected and resolved the small quantity of the Δ^6-acid which was present in the mixture.

The ester of this acid yielded, on treatment with magnesium methyl iodide, a *d*-dihydro*iso*sylvestrenol or *d*-Δ^6-*m*-menthenol(8) of the probable formula



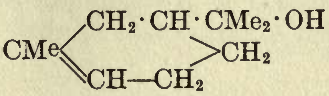
Δ^6-*m*-Menthenol(8)

and it is remarkable that the first specimen of this substance which was prepared was, as far as could be seen with the polarimeter at the author's disposal, optically inactive. This seemed to point to racemization having taken place, and yet, to the author's surprise, when treated with hydrochloric acid, it yielded at once sylvestrene dihydrochloride melting at 72° and with exactly the same rotation (+22°) as the dihydrochloride obtained from Swedish turpentine, and, on distillation with aniline, it yielded sylvestrene with the rotation +66°, and thus the synthesis of sylvestrene was accomplished. A second preparation of the *d*-dihydrocarvestrenol was then made and sent to Professor Pope at Cambridge for examination in his more accurate polarimeter, and he reported that it had the slight rotation of $\alpha_D + 2°$. Whether this *d*-dihydrocarvestrenol has the constitution



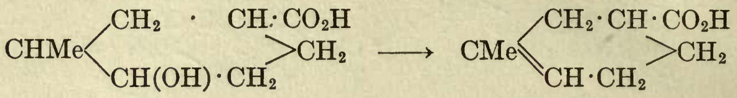
Δ^1-

or



Δ^6-

it is impossible to say, but the following experiment will probably decide the matter. A considerable quantity of 1-methyl-Δ^6-cyclohexene-3-carboxylic acid is being prepared by Dr. W. N. Haworth in London by the method which has already been described



and in this case only the Δ^6-isomeride can be produced.

The intention is to resolve this acid by means of brucine or some other suitable active base, and then to convert the *d*-isomeride into the corresponding menthenol in the usual way. If this substance exhibits the striking properties already mentioned in the case of the *d*-dihydrocarvestrenol of rotation +2°, then it is clear that that substance is the Δ^6-isomeride; if not, it must be the Δ^1-isomeride.

The elimination of water from this *d*-dihydrocarvestrenol should then yield one modification of sylvestrene, at all events, in a pure condition.

THE POSSIBILITY OF REDUCING THE COST OF MALIC ACID

By W. H. Warren and M. R. Grose

Clark University, Worcester, Mass., U. S. A.

Malic acid has attracted little commercial attention because of its high cost, but if a way to produce it cheaply could be found, there is reason to think that it might find a wider use. This acid closely resembles tartaric acid in chemical structure as well as in properties. Both are widely distributed in the plant kingdom in many acid fruits. If the two acids were alike in price, there would be little choice between them for many purposes. Being somewhat diliquescent and not crystallizing well, malic acid does not present the attractive appearance of tartaric acid, but in certain respects it is preferable to the latter. For example, according to some pharmacologists, malic acid in food products possesses properties that make it more desirable than tartaric acid.

Turning to its chemical properties, we find in malic acid a compound of great theoretical importance. From it can easily be obtained fumaric and maleic acids. Many chemical researches have centered about these two unsaturated acids, and widely divergent opinions as to their structure have been expressed. Yet the number of chemists who have studied fumaric and maleic acids is comparatively small on account probably of the prohibitive cost of these compounds. The relative amount of attention bestowed upon these acids by chemists will appear if we note the number of pages required to record experimental results in Beilstein's Handbuch.

BEILSTEIN

	Third edition Vol. I, pages	Total number of pages
Acetic acid	398–418	20
Tartaric acid	788–802	15
Oxalic acid	638–648	10
Maleic acid	701–706	6
Malic acid	740–746	5.5
Fumaric acid	697–701	4

It hardly seems as if these differences could be due to the less interesting chemical character of malic, fumaric, and maleic acids.

The following prices from the European lists of three well-known manufacturers show the differences in the cost of these acids and some of their derivatives. In each case the cost is per kilogram (= 2.2 pounds), and the German mark has been taken as twenty-four cents. The quality is that of a very pure product such as is ordinarily used in organic research work.

	Kahlbaum	Schuchardt	Merck
Acetic acid glacial 98–100%	$0.34	$0.28	$0.28
Oxalic acid	0.48	0.48	0.44
Tartaric acid	0.82	0.84	0.67
Malic acid	. . .	16.80	18.00
Fumaric acid	42.48	42.48	38.40
Maleic acid	60.00	60.00	60.00
Maleic anhydride	120.00	120.00	. . .
Fumaryl chloride	93.60	. . .	. . .
Calcium malate	. . .	9.60	. . .
Calcium bimalate	. . .	8.40	9.60

These figures explain why chemists have not more freely used malic acid and derivative compounds.

Though unable to state the exact source of the malic acid on the market, we presume it comes from some acid fruit, for example, the unripe berries of the mountain ash. We should naturally expect a compound thus obtained to be expensive. Recently one of us[1] published the analysis of the so-called "sugar sand," which is a by-product in the maple-sugar industry. The material examined contained about 50% of malic acid present as a calcium salt. In this paper we wish to call attention to the possible commercial value of this waste product.

COLLECTION OF SUGAR SAND

In the evaporation of maple sap the precipitation of calcium salts begins just before the concentration is sufficient to produce syrup of required density. The finished syrup is clarified by being strained through a cloth which is cleaned as often as the collected sediment retards filtration. Relative to the quantity of syrup the precipitate is small and, as it has never been shown to have any value, is thrown away. To obtain this material in good condition it should be transferred from the strainer to a pail and, when a considerable quantity has been collected, hot sap should be added, the solid thoroughly stirred and allowed to settle. Adherent syrup is thus washed out, and the sap can be drawn off without disturbing the sediment. Two such washings with sap and one with water will yield a product that can be drained and air-dried on a cloth stretched over a wooden frame. In appearance it will vary from a gray, friable, sandy substance, that can be powdered in a mortar, to a sticky, lumpy mass containing considerable saccharine matter.

In the beginning it was not supposed that the total quantity of this material obtained by the average maple-sugar maker would amount to much, but this did not turn out to be the case. A sugar orchard numbering about one thousand trees yielded nearly thirty

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[1] W. H. Warren, "Sugar Sand" from Maple Sap; a Source of Malic Acid, Journ. Am. Chem. Soc., *33*, 1205–11(1911).

pounds. For some wholly unknown reason the quantity of this product varies from year to year, and the same thousand trees have yielded as low as sixteen pounds. A merely nominal price of ten cents per pound was paid at first, but, as this hardly made it worth while to save the calcium salts, it was raised to twenty cents. Thus malic acid in the form of a crude calcium salt can be obtained for not more than fifty cents per pound and, since the methods of purification are simple and the yield good, the pure acid and derivative products can be had at prices far below those charged by the manufacturers.

A few words as to the best way to get into touch with maple-sugar makers will perhaps be of use to those who may wish to procure this material. This industry is in the hands of farmers scattered throughout regions where the maple tree is most abundant. Ohio, New York, and Vermont in the United States, and the Dominion of Canada are the districts producing the bulk of the maple sugar. The season varies somewhat according to the locality, but lasts as a rule from three to four weeks during March and April. In Vermont and possibly in other states there is a Maple Sugar Makers' Association, the secretary of which for 1912 is H. B. Chapin, Middlesex, Vermont. This association publishes annually a pamphlet containing its proceedings and a list of about one hundred and sixty members with their addresses.

PURIFICATION OF CRUDE MATERIAL

Calcium bimalate, $Ca(C_4H_5O_5)_2 \cdot 6\,H_2O$, is the best salt to use in preparing malic acid. If the quantity of the crude material permits, it may be converted direct into this acid salt, but as a rule a preliminary purification is advisable. This is the case especially when the sugar sand contains much of a certain impurity, colloidal in character and of unknown composition, which impedes and often entirely prevents filtration. Place 500 gm. of sugar sand in a glass cylinder and add 460 gm. of 35% hydrochloric acid, which may be diluted or not, depending on the ease with which the insoluble matter settles. Calcium salts are completely dissolved, and a gelatinous brown substance about the color of chocolate gradually settles, leaving the upper solution dark but clear. When there is no further subsidence of this insoluble matter, carefully siphon off the supernatant solution. Construction of the siphon so that the shorter arm is bent at the end into a U-tube will prevent the outgoing current of liquid from disturbing the light sediment. Filter the solution remaining in the sediment on a large Büchner funnel so that there is a broad surface and but little depth of liquid. The residue on the filter when dry is a grayish powder.

Neutralize the clear acid solution with an excess of strong ammonia. There is no sign of precipitation at first, but after a time, especially if the side of the container is scratched with a glass rod, crystals appear and gradually form a considerable deposit. Filter, wash, and dry this precipitate. Concentration of the mother liquor will give an additional quantity of crystals mixed with ammonium chloride, but, as the compound is only slightly soluble in water, most of it is in the first precipitate. This salt is a neutral calcium malate and is practically free from impurity.

NEUTRAL CALCIUM MALATE

This salt, which is only slightly soluble in water, will vary in composition according to the method of preparation. An anhydrous, amorphous calcium malate may be obtained by neutralizing malic acid with calcium carbonate. Addition of calcium chloride to a solution of neutral ammonium malate will precipitate a crystalline calcium malate whose water of crystallization seems to vary between $2\,H_2O$ and $3\,H_2O$. As the latter conditions practically exist when the hydrochloric acid solution of calcium salts is neutralized with ammonia, we expected one of these salts. The following analyses of an air-dried product show that the calcium malate obtained probably crystallizes with $2\,H_2O$.

0.5615 gm. of substance gave upon ignition 0.1530 gm. of calcium oxide; and 0.7474 gm. gave 0.2037 gm. of calcium oxide.

	Calculated for $CaC_4H_4O_5 \cdot 3\,H_2O$	Calculated for $CaC_4H_4O_5 \cdot 2\,H_2O$	Found	
			1	2
Calcium	17.7	19.23	19.28	19.49

The only important point about this salt is its percentage of calcium, which has a practical value in calculating the quantity of oxalic acid needed for the exact precipitation of calcium. Prepared as described, this salt will contain on the average 19.5% of calcium.

CALCIUM BIMALATE

To convert the neutral into the acid calcium salt, we have used the following method. Dissolve 302 gm. of crystallized oxalic acid in 1000 c.c. of water, reserve 100 c.c. of this solution, and add 500 gm. of neutral calcium malate to the remainder. Stir well, and heat for some time on the water bath. Let the precipitate settle, and test a small portion of the clear solution for both oxalic acid and calcium. The latter should be in excess. Then add some of the reserved solution of oxalic acid, heat for some time, and test again. With care it is possible to obtain a solution that will contain neither oxalic acid nor calcium. Filter, and wash the precipitate free from malic acid. Add to this filtrate a second portion of 500 gm. of neutral calcium malate, and heat on the water bath at a temperature not exceeding 60°. When solution is complete, filter and cool the filtrate, stirring constantly to obtain granular crystals. If these crystals are centrifugalized, the product will be pure enough to use in the preparation of malic acid and derivatives.

Calcium bimalate is the most important salt of malic acid, since it can be obtained very pure and serves as a starting point in preparing other compounds.

Malic Acid. — Dissolve 152 gm. of crystallized oxalic acid in 500 c.c. of water, add 500 gm. of air-dried calcium bimalate, and heat for some time on the water bath. Filter, wash the precipitate free from acid, evaporate, and crystallize *in vacuo* over sulphuric acid.

Fumaric Acid. — Without isolating malic acid itself raise the temperature, when most of the water has been expelled, and heat at 140°– 150° for some time.

Maleic Anhydride and Maleic Acid. — Treat the syrupy malic acid, which has been freed from water as completely as possible, with acetyl chloride according to the method of Anschütz,[1] and thus convert it into maleic anhydride from which maleic acid can be prepared.

Cream of Tartar Substitute. — If calcium bimalate can be produced cheap enough, it will have a commercial value as the acid constituent of baking powder, for it has all the requisite properties of such a substance. It is only slightly soluble in cold water and therefore acts gradually upon sodium bicarbonate as does cream of tartar. Malic acid is an organic acid that is wholly utilized by the animal organism during digestion. Calcium is a necessary inorganic constituent of the body. The reaction between calcium bimalate and sodium bicarbonate may be expressed as follows:

$$Ca(C_4H_5O_5)_2 \cdot 6\,H_2O + 2\,NaHCO_3 = Na_2C_4H_4O_5 + CaC_4H_4O_5 + 8\,H_2O + 2\,CO_2$$

On the basis of this reaction we have prepared a baking powder of the customary strength, that is to say, one yielding 12% by weight of available carbon dioxide. The materials were used in the following proportions:

Calcium bimalate	57	parts
Sodium bicarbonate	25	"
Starch	18	"
	100	"

As compared with the highest grade baking powders on the market, we were unable to detect any difference in the effectiveness or keeping qualities of such a powder.

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[1] Ber. d. Deutsch. Chem. Ges., *14*, 2789.

ABSTRACT

THE REACTIONS OF CERTAIN FUMAROID AND MALEINOID COMPOUNDS WITH AROMATIC AMINES

By W. H. Warren and M. R. Grose
Clark University, Worcester, Mass.

Fumaroid as well as maleinoid compounds, through anil-formation and addition under the influence of aniline, give the same derivative of asparagin-imide. Substituted aromatic amines containing methyl and ethoxyl groups give similarly constituted compounds, but the presence of substituents like bromine and carbmethoxyl prevents the reaction. Since all compounds of the above type contain one secondary amine group, they can be identified by their nitrosamines. Fumaroid compounds react with secondary aromatic amines to form anilide-like bodies which will not add aniline. The conclusion is that addition depends upon anil-formation.

Monomethyl-fumarate from dimethyl-fumarate and CH_3OH-KOH; flat prisms m. 143° (uncor.). This ester with aniline gives phenyl-amino-succin-phenyl-imide, which is colorless from alcohol but distinctly yellow from glacial acetic acid. The cause of this difference in color has not been studied. β-naphthyl-amino-succin-β-naphthyl-imide from fumaric acid and β-naphthylamine; needles, m. 250°–252° (uncor.). This compound is also colorless from alcohol, but yellow from glacial acetic acid. β-naphthyl-nitrosamino-succin-β-naphthyl-imide from β-naphthyl-amino-succin-β-naphthyl-imide and HNO_2; rhombic crystals, m. 260° (decomp.). *o*-Tolyl-amino-succin-*o*-tolyl-imide from fumaric acid and *o*-toluidine; needles, m. 112°–113° (uncor.). *o*-Tolyl-nitrosamino-succin-*o*-tolyl-imide from *o*-tolyl-amino-succin-*o*-tolyl-imide and HNO_2; does not crystallize well, m. 85° (uncor.). *m*-Tolyl-amino-succin-*m*-tolyl-imide from fumaric acid and *m*-toluidine;

needles, m. 130° (uncor.). *m*-Tolyl-nitrosamino-succin-*m*-tolyl-imide from *m*-tolyl-amino-succin-*m*-tolyl-imide and HNO_2; white plates, m. 120° (uncor.). *p*-Tolyl-amino-succin-*p*-tolyl-imide from fumaric acid and *p*-toluidine; needles, m. 209°–211° (uncor.). White from alcohol; yellow from glacial acetic acid. *p*-Tolyl-nitrosamino-succin-*p*-tolyl-imide from *p*-tolyl-amino-succin-*p*-tolyl-imide and HNO_2; needles, m. 169°–170° (uncor.). 2, 4-Dimethyl-phenyl-amino-succin-2, 4-dimethyl-phenyl-imide from fumaric acid and xylidine; needles, m. 132°–133° (uncor.). 2, 4-Dimethyl-phenyl-nitrosamino-succin-2, 4-dimethyl-phenyl-imide from 2, 4-dimethyl-phenyl-amino-succin-2, 4-dimethyl-phenyl-imide and HNO_2; yellow and amorphous, m. between 80° and 90°. Semi-benzid-amino-succin-semi-benzid-imide from fumaric acid and benzidine; yellow and amorphous; does not melt. Benzyl-amino-succin-benzyl-imide from fumaric acid or diethyl fumarate and benzylamine; needles, m. 205° (uncor.); it has a distinctly bitter taste. Benzyl-nitrosamino-succin-benzyl-imide from benzyl-amino-succin-benzyl-imide and HNO_2; needles, m. 156° (uncor.). *p*-Ethoxy-phenyl-amino-succin-*p*-ethoxy-phenyl-imide from fumaric acid and *p*-phenetidine; needles, m. 204°–205° (uncor.). *p*-Ethoxy-phenyl-nitrosamino-succin-*p*-ethoxy-phenyl-imide from *p*-ethoxy-phenyl-amino-succin-*p*-ethoxy-phenyl-imide and HNO_2; yellow needles, m. 133°–134° (uncor.). Fumar-methyl-anilide from fumaric acid, fumaryl chloride or maleic anhydride and methyl aniline; needles, m. 187°–188° (uncor.). Identical with Piutti's methyl-phenyl-amine-fumaride. Methyl-phenyl-amino-succin-phenyl-imide from maleinanil and methyl aniline; needles, m. 173° (uncor.). Dibrom-succin-methyl-anilide from fumar-methyl-anilide and bromine; prisms, m. 214° (uncor.). Identical with Piutti's dibrom-methyl-phenyl-amine-fumaride. Fumar-tetra-phenyl-amide from fumaryl chloride and diphenylamine; needles, m. 272°–273°. Identical with Piutti's diphenylamine-fumaride. Dibrom-succin-tetra-phenyl-amide from fumar-tetra-phenyl-amide and bromine; needles, m. 231° (uncor.).

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SECTION IV*a*—COAL TAR COLORS AND DYESTUFFS

CONTENTS

ACTION DE LA FORMALDÉHYDE SUR LES SOIES ARTIFICIELLES ET LES CELLULOSES ET LES AMIDONS

Applications et Usages

Par Francis J. G. Beltzer

Ingénieur-Chimiste. Expert-Conseil. Levallois-Perret (Seine) France

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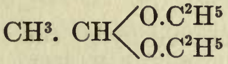
INTRODUCTION

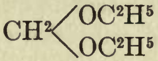
On sait que la formaldéhyde et les aldéhydes agissent sur les alcools pour donner des formals et des acétals.

L'aldéhyde acétique: $CH^3.CHO$ agit sur l'alcool ordinaire: $C^2H^5.OH$ en présence d'agents déshydratants pour donner l'acétal ordinaire:



$CH^3.CH\left\langle\begin{matrix}O.C^2H^5\\O.C^2H^5\end{matrix}\right.$ par élimination d'eau.

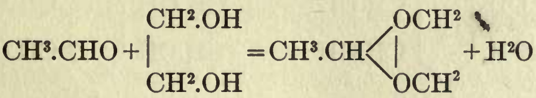
L'aldéhyde formique: $H.CHO$ agit de même pour donner un formal:



$CH^2\left\langle\begin{matrix}OC^2H^5\\OC^2H^5\end{matrix}\right.$ en présence d'agents de condensation.

D'une façon générale, on sait que les alcools agissent sur les aldéhydes et la formaldéhyde en particulier, en présence d'agents de condensation, pour donner des acétals ou des formals.

Wurtz a obtenu les acétals des glycols:



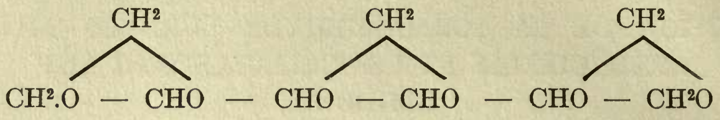
$$CH^3.CHO+\begin{matrix}CH^2.OH\\|\\CH^2.OH\end{matrix}=CH^3.CH\left\langle\begin{matrix}OCH^2\\|\\OCH^2\end{matrix}\right.+H^2O$$

la condensation s'opère par chauffage pendant huit jours au bain-marie.

Les formals des alcools polyatomiques s'obtiennent également par la condensation de l'aldéhyde formique avec l'alcool dont on veut avoir le formal.

On chauffe généralement les deux corps au bain-marie pendant un certain temps, en présence d'un agent de condensation.

On a obtenu le diformal de la pentaérythrite, le triformal de la mannite:



Dans ces conditions et par analogie, les corps à fonctions alcooliques devaient également donner par leur condensation avec les aldéhydes ou la formaldéhyde, des acétals ou des formals.

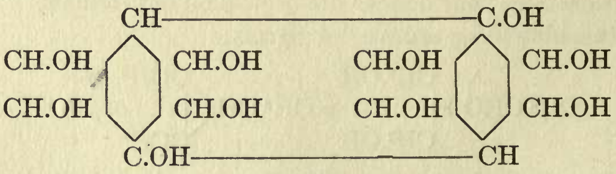
Nous avons dans ce but, étudié spécialement l'action de la formaldéhyde sur les celluloses, les hydrates de celluloses, les amidons, les fécules et les corps analogues.

Nous savons que la réaction xanthocellulosique découverte par Cross et Bevan, et plusieurs autres réactions, confèrent aux celluloses des fonctions alcooliques; la réaction formaldéhydique d'Eschalier confirme encore une fois la nature alcoolique de la cellulose.

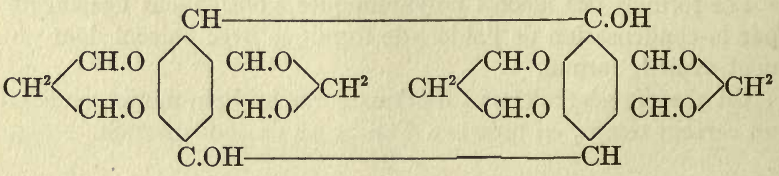
Cette dernière réaction provoque une heureuse application dans l'industrie des soies artificielles.

En faisant réagir les aldéhydes ou la formaldéhyde, sur les celluloses ou les hydrates de cellulose, en présence d'agents de condensation, on devait obtenir de véritables acétals ou formals cellulosiques ayant des propriétés autres que celles des celluloses primitives.

Si nous empruntons le schéma de constitution cellulosique établi par Cross et Bevan:



nous voyons qu'il est possible d'obtenir *le tétraformal* de cette cellulose en C^{12}:



Pour des celluloses plus condensées, en C^{18}; C^{24}; C^{30}; etc., on obtiendrait des hexa, octo et décaformals, . . . etc.[1]

Le trioxyméthylène, l'hexaméthylène-tétramine, les diverses aldéhydes, le glyoxal et les corps pouvant engendrer des aldéhydes d'acides gras ou des aldéhydes glycoliques. . .etc., peuvent agir sur les celluloses comme le formol lui-même en donnant des formals ou des acétals.

D'après Eschalier, on fait agir ces composés aldéhydiques sur les hydrates de celluloses ou les soies artificielles, en présence d'acides et d'agents déshydratants.

Généralement, on utilise la formaldéhyde; (la condensation s'effectuent avec plus d'énergie en présence de cette aldéhyde.)

Nous étudierons surtout les applications principales tirées de cette réaction et dénommées *Stenosage* ou *renforcement des textiles cellulosiques artificiels.*

Lorsqu'on soumet le coton, les pâtes de bois, les amidons ou les fécules à la réaction d'Eschalier, ces celluloses ou ces hydrates de carbone acquièrent également des propriétés spéciales; les celluloses deviennent insensibles à l'action du mercerisage et à la réaction xanthique; les amidons et les fécules "*sténosées*" ne forment plus d'empois par l'eau bouillante ou les lessives caustiques. On peut tirer de ce fait, des applications nombreuses pour la préparation des cartons cuirs, insensibles à l'eau, la fabrication des apprêts . . . etc.

La pâte de bois au bisulfite, traitée par une solution acétonique de Formol, additionnée d'une petite quantité d'acide sulfurique à 66° Bé, à la température de 60° à 70° C. pendant 8 ou 10 heures et séchée, devient absolument imperméable et résistante aux solutions mercerisantes de soude caustique. Il est impossible par conséquent d'obtenir une solution xanthique dans la suite. L'amidon et la fécule traités dans les mêmes conditions, deviennent très durs; il est impossible d'obtenir dans la suite des empois par l'eau bouillante ou par les lessives caustiques.

Cette dernière réaction pourrait trouver une application intéressante pour la préparation des apprêts insolubles à l'eau.

Il suffirait d'imprégner les tissus avec une solution ou un apprèt à la fécule, sécher et traiter par l'aldehyde formique en solution

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[1] Moniteur Scientifique. 1908 P. 16—Schémas de constitutions cellulosiques.

dans l'acétone, légérement acidée par l'acide sulfurique, à une température de 60° à 80° C, en vases clos, pendant 8 ou 10 heures; ou par des vapeurs de formol, en présence de l'acide sulfurique comme déshydratant. On obtiendrait ainsi un apprèt solide à l'eau. Le formol agit sur ces corps comme sur la gélatine et les insolubilise.

APPLICATIONS

Sthénosage des Soies Artificielles et Teinture des Soies Sthénosées

La principale application de la réaction formaldéhydique sur les celluloses, est celle obtenue avec les soies artificielles.

On sait que les soies de Chardonnet, les soies au cuivre et les soies Viscose sont très fragiles, surtout à l'état mouillé; elles se désagrègent facilement dans l'eau et dans les lessives caustiques.

Après "*sthénosage*", c'est-à-dire après la réaction d'Eschalier *avec le formol*, ces mêmes soies acquièrent une résistance supérieure à l'état sec et à l'état mouillé et elles ne se désagrégent plus dans les lessives caustiques.

Ces propriétés apportent un appoint considérable à l'industrie des soies artificielles car ces textiles étaient inemployables dans beaucoup de cas, à cause de leur peu de résistance à l'état mouillé.

On peut, après sthénosage, faire bouillir les fils et les tissus dans les lessives de soude, sans les désagréger; on a obtenu ainsi la soie artificielle lavable, recherchée par la consommation.

On peut procéder au sthénosage des fils et tissus de diverses façons.

1°. Action de la formaldéhyde en présence d'agents déshydratants à diverses températures et à la pression atmosphérique.

2°. Action de la formaldéhyde dans les mêmes conditions mais en opérant dans le vide.

Technique des Opérations du Sthénosage

On peut considérer deux cas, suivant qu'on *traite les fils ou les tissus de soie artificielle.*

Actuellement *c'est surtout la soie Viscose* qui tend à prendre la prépondérance dans l'Industrie de la soie artificielle, nous nous attacherons surtout à décrire les procédés relatifs au renforcement de cette soie.

On peut également sthénoser les soies de Chardonnet et de Givet, mais pour chaque qualité de soie, les détails d'exécution du sthénosage diffèrent, quoique les grandes lignes de l'action du formol restent les mêmes.

Pour plus de précision, nous donnerons dans la suite, les détails relatifs au sthénosage des fils et des tissus en soie Viscose.

Deux méthodes sont employées:

1. Sthénosage à l'étuve, sous la pression atmosphérique ou dans le vide.
2. Sténosage en bain plein.

Sténosage à l'étuve

Dans cette méthode, on imprègne la soie Viscose préalablement blanchie à l'hypochlorite de soude, passée en bisulfite de soude, lavée et séchée, dans un bain de formol composé comme il suit:

Formol à 40% CH^2O	20 à 25 Kgs.
Acide lactique à 80%	5 Kgs.
Alun de potasse	4 Kgs.
Eau distillée	75 à 70 Kgs.

L'imprégnation peut s'effectuer dans une essoreuse spéciale garnie d'ébonite.

On dispose les écheveaux convenablement dans le panier en ébonite et on fait arriver le bain de formol cidessus en quantité suffisante pour que les fils soient complètement immergés. On laisse l'imprégnation s'effectuer pendant ½ heure environ et on débouche l'orifice de sortie de l'essoreuse pour laisser écouler l'excès de bain qui se rend dans une cuve située en contre bas et qui servira dans les opérations suivantes, jusqu'à épuisement.

On actionne l'essoreuse pour chasser le bain d'imprègnation, jusqu'à ce que les fils en contiennent encore leur propre poids. 100 Kgs de fils secs doivent donc peser après essorage, 200 Kgs; ils retiennent donc 100 Kgs exactement de la solution ci-dessus.

Les écheveaux imprégnés sont abandonnés pendant 12 heures dans les toiles qui les enveloppent. On les étend ensuite sur des guindres dans une étuve pouvant être close hermétiquement.

Les guindres sont installés de telle sorte à l'intérieur de l'étuve, pour qu'on puisse les animer d'un mouvement de rotation permettant le déplacement continuel des écheveaux et évitant leur emmèlement.

L'étuve doit contenir une bache remplie d'acide sulfurique à 65° ou 66° Baumé pour hâter la dessiccation.

On ferme la porte autoclave et on chauffe l'intérieur de l'étuve à 60° C. environ, à l'aide d'un tuyau à ailettes étanche, dans lequel circule de la vapeur. On actionne les guindres pendant la dessiccation qui dure environ 6 ou 8 heures.

L'opération terminée, les écheveaux devant être secs; on ouvre la porte autoclave et on dégarnit les guindres.

On lave les fils, on les passe dans un bain de savon à 5 Grs par litre d'eau douce, on rince et on passe dans une solution d'acide lactique à 10 Grs par litre. On essore finalement et on sèche à douce température ou à l'air.

Lorsqu'on opére la dessiccation sous le vide, on fait usage d'une étuve semblable pouvant résister au vide; on dispose les écheveaux de façon semblable, mais on chauffe seulement à 30° ou 40° C.

La dessiccation sous le vide offre l'avantage d'opérer à plus basse température et par suite de conserver plus d'élasticté aux fils. D'autre part, les inconvénients résultant de l'opération, c'est-à-dire le dégagement du formol dans l'étuve, qui peut incommoder les ouvriers lorsque ceux-ci viennent à dégarnir, sont supprimés. L'atmosphère de l'étuve est purifiée par suite du vide et les ouvriers ne sont plus incommodés par les vapeurs de formol au moment du dégarnissage.

Sthénosage en bain plein

On plonge les écheveaux de soie Viscose dans 5 fois leur poids d'un bain acétonique, composé avec:

Acétone (56°—58° C.)	100 Kgs.
Formol à 40% CH^2O	5 Kgs.
Acide sulfurique à 66° Bé	0 Kg. 050

L'opération s'effectue dans une cuve autoclave en aluminum ou en cuivre. On chauffe cette cuve par circulation d'eau chaude, vers 60° C. et on maintient la température pendant 6 ou 8 heures. On laisse refroidir, on fait écouler l'excès de bain, on ferme hermétiquement et on fait le vide pour évaporer complètement l'acétone qui imprègne les écheveaux et les sécher. L'acétone est recueillie et redistillée pour la récupérer et l'employer à nouveau dans les opérations suivantes. Les écheveaux sont lavés, savonnés, rincès et passés en acide lactique comme ci-dessus.

On essore et on sèche à l'air.

Les fils de soie Viscose ainsi traités, gagnent en ténacité à l'état mouillé, plus du double de leur ténacité primitive.

Ci-dessous les résultats moyens:

Soie Viscose (130 deniers.)

	Avant sthénosage	Après sthénosage
Ténacité à l'état sec	146 grs.	230 grs.
Ténacité à l'état mouillé	40 grs.	105 grs.
Elasticité à l'état sec	10,2%	7%
Elasticité à l'état mouillé	10%	7,5%

D'après les chiffres ci-dessus, obtenus sur des fils sthénosés sous la pression atmosphèrique, nous voyons que la ténacité a augmenté de plus du double à l'état mouillé; par contre, l'élasticité a diminué sensiblement.

Lorsqu'on opère la dessiccation sous le vide et à basse température, l'élasticité est conservée.

Les tissus peuvent être sthénosés à la continue à l'aide d'une méthode analogue à celle pratiquée depuis longtemps pour la teinture en noir d'aniline d'oxydation.

On opère le foulardage au large, dans un jigger approprié et on opère la dessiccation dans une chambre hermétiquement close, sous le vide ou à la pression ordinaire. Les tissus sont étendus dans la chambre, sur une bache contenant de l'acide sulfurique comme agent de dessiccation. L'opération terminée, on lave, savonne, rince et passe en acide lactique au large. On essore et on sèche à l'air.

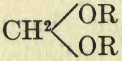
Propriétés des Soies Artificielles Sthénosées Teinture

Nous avons vu que la propriété capitale des soies de Viscose traitées par la formaldéhyde, suivant les procédés Eschalier, consistait surtout dans l'augmentation de leur résistance à la rupture à l'état sec et surtout à l'état mouillé. Cette propriété permet d'étendre la consommation de la soie artificielle à certains articles pour lesquels on ne pouvait jusqu' à présent l'employer; elle devra, dans un avenir prochain, favoriser le développement de l'industrie de la soie de Viscose et permettre la confection de tissus en pure soie artificielle résistant à l'eau et pouvant être lessivés.

Une autre propriété acquise, non moins importante au point de vue pratique, est celle qui confère aux soies sthénosées, la résistance aux lessives alcalines de soude caustique, même bouillantes. Tandis que les fils de soie Viscose ordinaire sont désagrégés et dissous dans les lessives caustiques froides, les mêmes fils sthénosés résistent à ces traitements.

Il semble que les filaments cellulosiques traités par la formaldéhyde, deviennent pour ainsi dire moins perméables à l'eau et se rapprochent des éthers de la cellulose. Cependant, leur résistance aux alcalis irait à l'encontre de cette hypothèse puisque les fils sthénosés résistent aux lessives caustiques, alors que les éthers nitriques, benzoïques, formiques et acétiques de la cellulose, sont décomposés.

La soie de Chardonnet nitrée est dissociée par les lessives caustiques, mais sa résistance à l'état mouillé est comparable à celle de la soie de Viscose; il en est de même de la soie à l'acétate de cellulose.

Si l'on envisage au contraire les propriétés générales des *formals* on voit que *la soie sthénosée* se comporte absolument comme un *formal cellulosique.* On sait que les formals peuvent être considérés comme des *éthers-oxydes:*  $CH^2\langle{}^{OR}_{OR}$; la plupart sont insolubles dans l'eau et inattaquables par les alcalis caustiques ou carbonatés. Les acides les décomposent en régénérant le trioxyméthylène ou la formaldéhyde. (Nous verrons plus loin comment on utilise cette derniére réaction pour déceler et doser le formol dans les soies sthénosées).

La soie de Viscose sthénosée, se comporte donc à la fois comme un éther et comme un formal; elle possède ces deux qualités si recherchées de résistance à l'état humide et au lessivage.

Ces qualités, dans un autre ordre d'idées, devaient modifier profondément la nature des soies artificielles et la facon de se comporter pour d'autres opérations.

Teinture

La teinture des soies sthénosées est en effet différente de celle des mêmes soies non sthénosées.

Tandis que la soie de Viscose ordinaire par exemple, absorbe avec avidité la plupart des colorants directs, à la façon du coton mercerisé ou des hydracelluloses, la soie de Viscose sthénosée se teint difficilement avec ces mêmes colorants; les nuances obtenues sont beaucoup plus claires et souvent irrégulières.

Il semble que le colorant glisse à la surface des fibres et que leur faculté d'absorption soit annulée en grande partie. (Ce fait est général pour tous les éthers cellulosiques; les soies de Chardonnet nitrées et les soies à l'acétate de cellulose se teignent difficilement ou pas, avec les colorants substantifs; c'est une résultante de leur imperméabilité à l'eau et par suite aux bains de teinture directs.)

Pour donner aux soies sthénosées plus d'affinite, Eschalier propose de les traiter préalablement aux lessives caustiques et à l'hypochlorite de soude.

Après lessivage et chlorage, la soie sthénosée ne perd pas de résistance; mais, elle se teint en nuances plus foncées et plus unies avec les couleurs Benzidine ou les colorants Diamines. On arrive même à obtenir des noirs diazotés assez profonds.

Les couleurs au soufre et en particulier les noirs immédiats ou katiguène, donnent également des hauteurs de tons assez foncées.

Les colorants de la série de l'Indanthrène sont aussi applicables.

Cependant, malgrè ces traitements préalables, il arrive parfois que des fils sthénosés irrégulièrement ressortent barrés après la teinture; nous avons en conséquence recherché les méthodes de teinture qui donnent les meilleurs résultats au point de vue de l'unisson et du foncé de la nuance.

Les colorants sur mordants, le noir d'aniline d'oxydation, les couleurs formées directement sur les fibres et les noirs de Campêche, donnent dans ce sens les meilleurs résultats.

Nous avons effectué une série d'essais avec *les colorants d' Alizarine* et obtenu des résultats parfaits sous tous les rapports: On passe en solution tannique à 10 grammes par litre d'eau et on essore; on mordance ensuite en bain d'alun de potasse à 10 grammes par litre et on essore.

La fibre mordancée et lavée à grande eau, est teinte immédiatement jusqu'à l'ébullition avec la marque d'Alizarine désirée et d'après les proportions requises pour le foncé de la nuance.

En mordançant avec tannin et alun de chrome ou autres mordants habituellement en usage et teignant avec les marques employées d'Alizarine, on obtient toute une gramme de couleurs solides, brillantes, foncées et unies.

(Rouges d'Alizarine, Bleus d'Alizarine, Orangés d'Alizarine, Grenats, Paliacats, Violets, Lilas, etc. Verts de Céruléine, Violets de Galléine. . . .etc.)[1]

Les couleurs d'aniline, sur tannin et émétique donnent également des couleurs brillantes et unies, même dans les tons clairs:

(On mordance dans des solutions faibles de tannin à 5 ou 10 grammes par litre; on essore à fond et on passe en émtique ou *antimoinine* (lactate d'antimoine) à 5 ou 10 grammes par litre et on rince à fond. On teint de suite jusqu' à 80° C. environ ou jusqu' au bouillon, dans le colorant d'aniline requis, à la façon habituelle, employée pour le coton.)

(Rhodamines, Phtaléines, Auramines, Verts, Bleus et Violets d'aniline, Fuchsines, . . . etc.)

La teinture en noir d'aniline d'oxydation, telle que nous l'avons décrite dans une de nos études parues dans le Moniteur Scientifique de Février 1907, p. 88–101, s'applique parfaitement aux soies de Viscose sthénosées et donne des noirs trés unis, profonds et brillants.

Les couleurs formée directement sur la fibre imprégnée de B Naphtolate de soude ou *couleurs de la série Paranitraniline,* s'obtiennent comme sur le coton; les nuances sont très unies, mais le brillant est légèrement atténué par suite du précipité insoluble qui se forme sur la fibre.

Les noirs au Campêche et la série des couleurs analogues fournit peut-être une des meilleures applications sur soies sthénosées. On procède généralement de la façon suivante:

L'extrait de Campêche, l'hématine, la brésiléine ou autres principes colorants végétaux analogues, sont dissous et réduits en proportions convenables, dans une solution d'acide sulfureux, de bisul-

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[1] Voir notre ouvrage: "*La Grande Industrie Tinctoriale.*"

fite ou d'hydrosulfite de soude. La liqueur claire est filtrée rapidement et sert de bain de teinture.

On plonge les écheveaux dans ce bain et on les imprégne fortement; on lève, on essore et on étend à l'air pendant quelque temps jusqu'à ce que l'oxydation ait commencé à développer la nuance.

On passe ensuite les fils dans un bain d'oxyde de cuivre ammoniacal, (bleu céleste), ou dans un bain de bichro mate alcalinisé légèrement avec l'ammoniaque. La nuance se développe immédiatement; on lève, on exprime et on laisse à l'air pour que l'oxydation se poursuive.

La nuance se développe de plus en plus; après 12 ou 24 heures, on lave, on savonne, on rince et on séche.

Pour corser les noirs, il est souvent utile d'effectuer deux teintures successives; on passe d'abord dans la solution sulfitée d'hématine, on oxyde à l'air, on développe dans la liqueur cupro-ammoniacale (sulfate de cuivre ammoniacal de concentration requise), on oxyde à l'air, on lave et on essore.—On passe une seconde fois en solution d'hématine et on repète les opérations précédentes comme ci-dessus. Finalement, on lave, on savonne, on rince, essore et sèche.

Les noirs ainsi obtenus possèdent un éclat supérieur; le brillant de la soie est rehaussé, comme s'il avait été soumis au glaçage. Les nuances sont corsées et unies; elles correspondent au beau noir-soie exigé dans le commerce et elles sont très solides aux savonnages et aux lessives alcalines habituellement employées par les ménagères.

La façon dont les soies artificielles sthénosées se comportent à la teinture, montre bien qu'on a affaire à un véritable éther cellulosique et surtout à un éther oxyde ou formal, non décomposable par les alcalis.

Ce fait va se confirmer dans les essais suivants, relatifs aux examens microscopiques et aux dosages des soies et celluloses sthénosées.

Nous avons publié nos études sur la teinture des soies artificielles ordinaires et spécialement des soies artificielles sthénosées, dans "*L'Industria Chimica*" de Turin 10 Aprile 1911 p. 101 à 107, sous le titre:

"Candeggio e tintura delle fibre cellulosiche e spécialmente di quelle artificiali."[1]

Examens Microscopiques et Réactions Microchimiques des Soies de Viscose Sthénosées

Nous résumerons ci-dessous, nos travaux microscopiques en les classant comme il suit:

Caractères des soies de Viscose sthénosées comparativement á ceux des soies de Viscose ordinaires.

1° Par l'action des lessives caustiques mercerisantes.
2° Par la réaction avec l'iode dissous dans l'iodure de potassium.
3° Par la coloration avec le Rouge de Ruthénium.[2]
4° Par la coloration avec le Bleu de Méthylène.

Les soies de Viscose ordinaires présentent à l'examen microscopique deux caractéres différents, suivant qu'elles ont été préparées à l'aide du procédé Stearn, (coagulation avec les sels ammoniacaux), ou à l'aide du procédé Muller, (coagulation par les solutions de bisulfate de soude).

Les premières se présentent sous la forme de filaments droits et unis, avec quelques légères excoriations à la surface et un canal central très peu marqué et quelquefois invisible.

Les secondes prèsentent des filaments droits, avec stries longitudinales très apparentes et canal central plus marqué.

Les mêmes soies sthénosées, montrent des caractères semblables pour chaque catégorie de soie Viscose, mais on remarque une différence appréciable dans le diamètre des filaments; ceux sthénosés apparaissent de plus petit diamètre sous le champ du microscope; l'examen étant fait comparativement, sur des fibres immergées dans de l'eau glycérinée.

(Il est probable que les filaments ordinaires de soie Viscose se gonflent plus dans l'eau, que ceux de Viscose sthénosés. Le sthénosage a aussi pour effet de resserrer le diamètre des fibres.)

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[1] Voir également: notre ouvrage sur "*la grande Industrie Tinctoriale*" pp. 987–1011.—Teinture des soies artificielles. Nos études sur "*la teinture des soies et textiles artificiels.*"—*Moniteur Scientifique* 1907, pp. 88-101 et 237-244.

[2] Voir également: *Moniteur Scientifique,* Octobre 1911 p. 633–641.—Différenciation des soies artificielles à l'aide du Rouge de Ruthénium.

En faisant agir comparativement les lessives caustiques mercerisantes, sur des filaments de Viscose sthénosées et non sthénosés, on remarque immédiatement la différence de gonflement des fibres. Les fibres sthénosées sont trés peu attaquées et leur diamètre reste sensiblement le même tandis que les filaments non sthénosés se gonflent considérablement et se dissolvent presque après 12 heures de contact.

Les fibres colorées, avec *une solution d'iode dans l'iodure de potassium*, montrent une différence caractéristique:

Tandis que les fibres de soie Viscose ordinaire se colorent de suite en bleu violacé fonçé, comme le coton mercerisé ou tous les hydrates de cellulose, les mêmes soies sthénosées se colorent à peine en brun-jaune clair.

Les fibres sthénosées passées à l'eau acidulée d'acide sulfurique, ne se colorent même pas par ce réactif tandis que le coton passé dans le même acide et rinçé, est coloré en bleu comme le coton mercerisé. (La Viscose sthénosée ne serait donc pas attaquée à la température ordinaire par l'acide sulfurique de concentration moyenne, son hydrolyse serait moins facile.)

La soie sthénosée, immergée dans une lessive caustique mercerisante, lavée et passée à l'eau acidulée d'acide sulfurique, donne seulement une très légère coloration brune tandis que la soie non sthénosée est colorée en noir-bleu avec intensité, par le même réactif iodé.

Les colorations comparatives avec *le Rouge de Ruthénium* ou *le bleu de Méthylène*, sont encore très caractéristiques:

La soie de Viscose ordinaire se colore de suite en nuance moyenne tandis que la même soie sthénosée reste incolore. Ce fait est une conséquence de la moindre affinité de ces dernières fibres pour les colorants. (Voir: *Teinture.*)

Pour déceler la présence du formol sur la fibre sthénosée, on peut utiliser *la réaction de la phloroglucine:*

On traite préalablement les filaments à essayer avec la potasse caustique, on lave et on passe à l'eau acidulée d'acide sulfurique; on rince à fond et on trempe les fibres dans une solution aqueuse de phloroglucine légèrement alcalinisée à la soude caustique.

La présence du formol libre est décelée de suite par une légère coloration rose saumon qui se développe sur les fils.

Le chlorhydrate de Phénylhydrazine permet également de déceler la présence du formol dans les fibres.

Les filaments traités préalablement comme ci-dessus, sont immergés dans une solution de $C^6H^5—AzH—AzH^2.HCl$ à 10 grammes par litre.

On exprime et on ajoute un peu de solution de nitro-prussiate de soude et de potasse caustique sur les filaments imprégnés de chlorhydrate de phénylhydrazine. La coloration bleue qui se produit caractérise aussi la présence de *formol libre* sur les fibres.

Dans notre ouvrage: *Les Matieres Cellulosiques,* nous avons publié nos diverses études à ce sujet:

Voir: Acétals cellulosiques. p. 192–207.

Essais Analytiques et Dosage de la Formaldéhyde sur les Soies Artificielles Sthénosées

Les essais précédents montrent bien la présence du formol libre sur les fibres, mais pour caractériser surement le formol combiné, nous devons procéder à d'autres essais analytiques que nous résumerons ci-dessous:

Recherche et dosage de la Formaldéhyde combinée, dans les soies sthénosées.[1]

On commence par séparer la formaldéhyde ou le trioxyméthylène qui peut s'être fixé à l'état libre sur les fibres, en faisant bouillir celles-ci dans l'eau distillée et sous pression. On obtient ainsi une dissolution compléte du trioxyméthylène non combiné. On lave à grande eau et on peut essayer sur le liquide distillé les réactions du formol ci-dessus.—Les fibres lavées sont alors traitées par une solution contenant 50 grammes par litre, d'acide sulfurique à 66° Bé, en présence d'un peu de sulfate de soude, pour favoriser l'ébullition.

On distillé jusqu'à recueillir environ les 8/10e du liquide. A ce moment, la soie est complètement dissoute et hydrolysée.

Le distillat essayé à la phloroglucine ou à la phénylhydrazine doit donner les colorations rose-saumon ou bleue caractéristiques.

Pour doser le formol dans le distillat, on utilise son action réductrice sur le nitrate d'argent ammoniacal.

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[1] Voir notre ouvrage: *F. Beltzer et J. Persoz.—Les Matières Cellulosiques.* p. 203.

La liqueur d'argent est préparée en dissolvant 10 grs. de AzO^3Ag dans 100 centimètres cubes d'eau distillée, puis 10 grammes de NaOH dans 100 centimètres cubes également. On mélange les deux solutions et on ajoute une certaine quantité d'ammoniaque pour redissoudre le précipité. On dose le formol sur *100 centimètres cubes* du distillat, neutralisé avec AzH^3, en ajoutant 25 centimètres cubes de liqueur d'argent. Il se précipite une poudre noire d'argent métallique, qu'on filtre, lave, sèche et calcine. 216 grammes d'argent correspondent à 30 grammes de formol.

Les celluloses et les hydrates de carbone traités par les réactions d'Eschalier, à l'étuve ou en bain plein, absorbent des quantités différentes de formaldéhyde, suivant la concentration des bains et suivant la température.

A haute température, les soies artificielles deviennent cassantes et perdent leur élasticité; nous avons remédié à cet inconvénient, en opérant la dessiccation à basse température et sous le vide.

Dans ces conditions, l'élasticité est conservée et le formol réagit quand même: l'eau seule est évaporée.

La quantité de formol absorbée paraît d'autant plus forte que les celluloses sont plus hydratées.

Les hydrocelluloses et les oxycelluloses en absorbent une plus grande proportion et deviennent très dures. La soie de Chardonnet dénitrée en particulier, durcit considérablement par un sthénosage poussé.

[Comparativement avec la soie de Viscose qui reste souple, les soies cuproammoniques et nitracellulosiques deviennent très rigides.]

La propriété d'absorption du formol par les hydrates de cellulose, peut servir jusqu'à un certain point de mesure à leut degré d'hydratation.

Les dosages comparatifs effectués permettant d'obtenir un "*indice formaldéhydique*" en relations directes avec le degré d'hydratisation ou d'hydrolyse.

L'action de la formaldéhyde sur les soies artificielles et les celluloses, confirme en résumé la réaction xanthique de Cross et Bevan, en assimilant ces hydrates de carbone aux alcools; elle apporte une importante contribution à la chimie des celluloses et permettra dans un avenir prochain de poursuivre les études sur la constitution cellulosique.

THE DEVELOPMENT OF HYDROSULPHITES IN THEIR RELATION TO MODERN DYESTUFFS

By Philip S. Clarkson
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In 1869 when Schuetzenberger first made sodium hydrosulphite and in 1872 when he, together with Lalande, applied it to the preparation of indigo-white and introduced a vat for indigo dyeing based on its use, a basic foundation was laid for the practical application to the fibre of the latest and the most desirable group of synthetic dyestuffs. These are now known technically as "vat colors," but some better term should be applied to them, than one derived from the large vats or dye vessels, necessary on account of the quantity of sediment in the old style method of indigo dyeing. As is well known these products are insoluble in water and require reduction, generally in an alkaline solution, to render them soluble and suitable for use in the dye kettle. The old methods of fermentation, etc., used with indigo are not applicable here and the hydrosulphites are found to be the most satisfactory agents, being most energetic in reducing action, and in the form of their sodium salts, giving no insoluble combinations with the dyestuffs.

Before the discovery and invention of the now large group of vat dyestuffs, the use of hydrosulphite in dyeing was small and the improvement in manufacture of hydrosulphites not marked, but coincident with the discovery of new coloring matters suitable for use in vat dyeing came new interest in the use of hydrosulphites as discharging agents in calico printing. This led to the discovery of the formation of stable compounds with formaldehyde for which the first American patent appeared in 1904—followed by that for the production of pure sodium hydrosulphite powder in 1905 and that for sodium formaldehyde sulphoxylate in the same year and the two zinc salts, the last in the year 1911.

These may be said to represent the products now in commercial use, the pure sodium hydrosulphite powder ($Na_2S_2O_4$) representing the product used for dyeing, the formaldehyde compounds those used for printing and for discharging. These are:

Sodium-formaldehyde-sulphoxylate $NaSO_2CH_2$ plus $2H_2O$, which is commercially known as hydrosulphite N F conc., rongalite C and hyradite C extra, according to the maker. This is the compound of especial interest to the calico printers.

Di-zinc-formaldehyde sulphoxylate ($ZnSO_2CH_2O$) is known to the trade as hydrosulphite A Z, decroline or hyraldite Z. This is used only for stripping or removing dyestuff from dyed materials.

Mono-zinc-formaldehyde sulphoxylate $Zn(HSO_2CH_2O)_2$ which is hydrosulphite A Z soluble conc. This is used for the same purpose as the di-zinc salt but is more effective and is soluble in water.

The other commercial marks represent mixture with various substances for special purposes.

Practical Applications: These comprise dyeing, printing, discharge-printing on dyed materials, and stripping or the removal of dyestuffs and coloring matters from previously dyed material. The dyestuffs which require the use of hydrosulphites are as commonly classed: indigo and substituted indigoes, usually halogen substitution for hydrogen, indigoids, those having the molecular construction of indigo but having other replacements and anthracene compounds.

Dyeing: The method of application for all these classes of dyestuffs is practically the same, the dyestuff is reduced with 1½ times to twice the amount of sodium hydrosulphite in the presence of alkali to dissolve the leuco compound formed. This reduced dyestuff is then applied to the fibre in the well known manner and the color finally developed by oxidation. Various assistants are added to secure technically perfect results. The shades obtained are generally speaking much in advance of any previously known in regard to fastness to all injurious influences combined with brilliancy of shade.

Printing: It is in this branch of the art of coloring that the most marked change has taken place. Previous to the development of the application of vat colors in this industry, the dyer was far ahead of the printer in the production of shades of extreme fastness, especially to manufacturing and finishing processes depending on the production of insoluble color lakes in the process of coloring. The hydrosulphite-vat color process of printing provides this nearly in perfection. The required installation of machinery is not extensive, the success or failure of the operation depending mainly on the proper construction and condition of the steamer, preferably a Mather-Platt. This must be arranged so that all access of air is excluded and suitable steam plates provided for heating so that the interior is at all times at a temperature of 102° to 104° C. With proper conditions here and the usual care in making up the print colors failure is not to be anticipated. The present application of the vat colors in the printing process depends on the use of sodium-formaldehyde-sulphoxylate. This is stable at ordinary temperatures and enables the pastes to be made up without difficulty and the prints from the machine are uniform throughout the length. On steaming, the sulphoxylate is liberated and at once reduces the dyestuff to its soluble condition in which it combines with the fibre. After steaming, the material is treated with either soap or oxidizing agents which fully develop the color in an insoluble condition.

By the proper selection of dyestuffs the printer can furnish shades which can be guaranteed as fast to light, washing, wearing and other injurious influences, in fact almost that the color will last longer than the fibre. This condition has undoubtedly been brought about by the discovery and perfection of the hydrosulphite-formaldehyde compounds. This is the present state of direct printing industry and now the printer is ahead of the dyer for he can work more economically and the results are in every way satisfactory to the consumer. One of the very apparent results is "laundry-proof shirts for one dollar."

The method of discharging azo colors by the use of these salts has been used for sometime and cannot be said to have been very recently developed—only improved by the use of sodium-formaldehyde-sulphoxylate in place of the zinc dust-bisulphite mixtures of the original formulas.

But the use of formaldehyde-sulphoxylate for discharging white patterns on material dyed with indigo is the most recent and the most notable advance in the printing industry brought about by the use of hydrosulphites. It has long been known, and use has been made of the fact that oxidizing agents would destroy indigo blue and render it colorless and all the discharge printing on indigo has been based on this. The great disadvantage has been, however, that these agents also acted on the cotton fibre and the formation of oxycellulose with material loss of strength has occurred. By the use of reducing agents this could be avoided but the difficulty was to remove the indigo-white produced in the pattern before it became reoxidized.

In 1907 one of the foreign manufacturers of indigo suggested the use of anthraquinones in the printing paste with sodium formaldehyde sulphoxylate. This rendered the discharge more energetic and also hindered the reoxidation, but it was necessary to handle the material very quickly to avoid tarnishing the whites. The usual conditions of the printing rooms rendered the production of uniform results almost impossible and little practical use was made of the process in this country.

However, in the last two years a notable advance has been made owing to the discovery that certain bases of the substituted ammonium type would combine with indigo-white to form stable compounds, which did not oxidize in the air. Further experience proved that this property was characteristic of compounds of certain tertiary bases with benzyl chloride, its homologues and analagous bodies and their substitution products. In the presence of zinc oxide desirable reddish to yellow shades can be obtained by this method.

But in order to obtain white discharges the compounds obtained in the discharge process had to be made readily soluble. This it was found could be done by the substitution of a sulphonic group in the benzyl nucleus. The yellow compound obtained by using a substance of this nature in the formaldehyde sulphoxylate discharge paste is readily soluble in alkalies and being easily removed from the material leaves the patterns clear.

Thus the problem of satisfactory indigo discharges was solved. For certain considerations the discharges material is not sold as such but in combination with sodium formaldehyde sulphoxylate as hydrosulphite C L or rongalite C L, according to the maker.

The practical method of handling is simple. The discharge pastes are made up with 20% of the sulphoxylate discharge compound, 8% zinc oxide, 4% anthraquinone, 30% paste with suitable thickening. The material is printed, dried, steamed in the before described steamer for 3 to 5 minutes at 100 to 193 deg. C., washed in hot water, then passed through an alkaline bath, washed and dried. In this process, the pastes are perfectly stable and after printing and steaming the material can be left indefinitely before clearing. The writer kept a piece for two months before clearing and the resulting whites are perfect.

The process has been adopted by the largest indigo printers in this country in spite of the fact of the higher cost and the commercial product now represents the standard of indigo prints. The gain to the consumers is in the same proportion; as the strength of the material is not affected and after the garments are washed three times the whites are no longer holes but remain the original material.

The zinc-formaldehyde-hydrosulphites are used solely for removing the dyestuff and colors from previously dyed material and have little interest for the phase of the subject under consideration. Their great advantage lies in the fact that the strength of the fibre is not affected.

The increase in the use of hydrosulphites and the formaldehyde compounds has been most marked and probable consumption in the textile industry in the United States for the year 1911 was not far from one million pounds.

ACTION DES ALCALINO-TERREUX SUR LA LAINE

PAR TH. VALETTE
Paris, France

Diverses substances augmentent notablement l'affinité de la laine pour les colorants. Parmi elles se trouvent le chlore les alcalis, le bisulfite de soude, la chaux.[1]

Le chlore est employé industriellement, le bisulfite également. Les alcalis caustiques attaquent aisément la fibre. Le procédé à la chaux, bien que donnant d'excellents résultats ne s'est pas répandu.

Nous avons voulu voir si les autres oxydes alcalino-Terreux donnaient des résultats analogues et dans quelles conditions la fixation avait lieu. La laine placée dans l'eau de chaux saturée (Igr 34 par litre de CaOà 18°) absorbe 2, 40% de son poids en chaux. Ce chiffre est un maximum atteint au bout de 6 heures de contact.

La quantité de chaux n'augmente pas sensiblement après plusieurs jours. Une partie très faible de la laine se dissout en combinaison avec la chaux.

La laine placée de même dans l'eau de baryte, de strontiane ou de lithine soit 3 gr. 69% de BaO. 2 gr. 4% de SrO. 0,7% de Li^2O employées en quantités proportionnelles à leurs poids moléculaires, absorbe également ces oxydes.

Un avivage à l'acide chlorhydrique à 1% en une demi-heure en fait disparaître toute trace. Les cendres normales même diminuent de poids.

Les laines teintes immédiatement après passage en alcalis ont pour les divers colorants une affinité bien supérieure à la laine ordinaire, supérieure même à celle de la laine chlorée pour laquelle on ne peut pousser l'action du chlore bien loin sans attaquer la fibre.

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[1] Congrès de Chimie appliquée de Londres Juin 1909. Action des produits employés dans le dégraissage et le blanchiment sur la laine—Th. Valette.

Les nuances obtenues sont plus corsées et résistent mieux au frottement.

L'action est maximum pour la chaux et la baryte, un peu moindre pour la strontiane, et minimum pour la lithine. La fibre est mouillée plus rapidement par l'eau.

L'avivage acide ne modifie pas ces propriétés, l'affinité est donc due à une modification de la fibre et non à la présence de l'oxyde. L'attraction pour les colorants se manifeste même en solution alcoolique.

Elle persiste également après un blanchiment à l'eau oxygénée.

Les matières en suspension dans l'eau et dans l'alcool sont attirées plus vivement que par la laine ordinaire.

ORIGINAL COMMUNICATIONS

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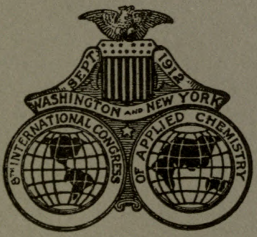

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VOLUME VIII.

SECTION Va: INDUSTRY AND CHEMISTRY OF SUGAR.

CONTENTS.

THE STATUS OF CANE SUGAR MANUFACTURE IN THE HAWAIIAN ISLANDS

By Noel Deerr

Honolulu, Hawaii

The rapid growth and remarkable results obtained in the cane sugar industry in the Hawaiian Islands forms a matter of sufficient interest to warrant a short account of the present status of the manufacturing side of the industry.

General. At the present time there are in operation forty-six factories which produced for the year ending Sept. 30, 1911, 566031 short tons. The output of the individual factories varied from 595 tons to 55,050 tons; the following schedule classifies the factories according to the magnitude of their annual output:

	No. of Factories
Over 50,000 tons per crop	1
Over 30,000 tons per crop	4
Over 20,000 tons per crop	3
Over 10,000 tons per crop	9
Over 5,000 tons per crop	15
Over 1,000 tons per crop	13
Under 1,000 tons per crop	1

The factories naturally fall into two groups: those which were erected after reciprocity with the United States, and those which have been in existence for a longer period; the first group includes the larger factories all of which have been erected to one design; the smaller and older factories have been enlarged and added to from time to time so that little of the original design remains; they are hence less efficient than the factories of more recent date. In comparing the size of the Hawaiian factories with those in other districts it must be remembered that the crop season lasts there about 30 weeks, so that a mill with an output of 30,000 tons need only have a capacity of 1000 tons per week.

The Raw Material. The canes forming the raw material for the manufacture of sugar in the Hawaiian Islands are distinguished by the exetremely high sugar content. At the present time and for a number of years past two principal varieties have been grown. The Lahaina (Syn. Bourbon, Otaheite) is the standard variety on the irrigated plantations forming the great bulk of the cultivation on the Islands of Oahu, Maui, and Kauai. The unirrigated plantations on the Island of Hawaii and some irrigated ones on Kauai culitvate the Yellow Caledonia (syn. White Tanna) cane; it is the Lahaina cane grown under peculiar climate conditions that affords a raw material of such high sugar content; for short periods as a week during which as much as 10,000 tons of cane or more may be worked up in the larger mills, the raw material may contain exceptionally as much as 18% of cane sugar; 16% is quite a common average for periods of a month's run or longer; on an average, however, over the year's crop the Lahaina cane grown on irrigated plantations averages 15% of cane sugar with a purity in the first expressed juice of slightly over 90. The Yellow Caledonia cane grown on the unirrigated plantations seldom contains as much as 15% of cane sugar the average over the whole year's crop being about 13.5%. Including both Lahaina and Yellow Caledonia in one average the whole cane crop of the Hawaiian Islands contains about 14.5% of cane sugar with no great variation from this figure.

Extraction of Juice. No diffusion plants now remain and the whole crop of cane is crushed in multiple trains of mills. Up to 1904 a nine roller train was the maximum, but since then practice has tended towards the more efficient twelve roller trains, since it has been found that not only is the quantity of juice obtained and the capacity of the plant increased but that the water required in maceration is decreased. At the present moment there are eight twelve roller trains which treat about 37% of the crop; in one instance an eighteen roller train is used; this mill accounts for 5% of the crop of the islands; 55% of the crop is treated in nine roller trains and the balance of 3% is ground in trains of less than nine rollers; in nearly all cases the train of rollers is preceded by a preparatory crusher.

All the mills employ greater or less quantities of maceration water which is generally applied before the last mill, the dilute juice thus obtained being systematically returned to the preceding mills; the system of maceration employed is one of simple imbibition; that is to say the diluting agent is sprayed or sprinkled on to the blanket of bagasse; intermediate maceration baths or diffusion tanks are not employed.

The amount of water used varies from a minimum of 10% to a maximum of 50% and generally amounts to about 30%, expressed as a percentage on weight of raw material; with the average quantity of water the diluted juice equals the weight of the raw material; in many cases the amount of water added is controlled by the capacity of the evaporating apparatus and not by the economic limit to which the bagasse might be exhausted.

The amount of sugar extracted per 100 sugar in cane, falls below 90% only in very exceptional cases; with the eighteen roller train over a whole crop 96.75% of the sugar in the cane has been extracted with added water equal to 40% of the raw material; on individual weeks runs this figure has several times exceeded 97%.

A tabular comparative statement of the average performances of different trains of mills follows.

Size of rollers	No. of rollers	Short tons cane per hour	Water added % cane	Sugar extracted per 100 sugar in cane	Fiber % cane
34″ x 78″	9	35–40	30–40	93.0–94.0	12
34″ x 78″	12	45–60	30–40	94.5–95.5	12
34″ x 78″	15	60	30–40	96.0–96.5	12
34″ x 78″	18	60	30–40	96.5–97.5	12

The smaller factories with mills 30″ x 60″ seldom work up more than 25 short tons of cane per hour and are generally nine roller trains; in these factories the extraction varies between 90% and 93%. A general average over the whole crop of the islands indicates that 93% to 93.5% of the sugar actually present in the canes is extracted by the crushing machinery.

Purification of Juice. All the factories employ a defecation process none having adopted carbonation. Lime is almost the only agent used, sulphur and phosphoric acid being employed as clarifiant only very rarely; the process of clarification raises the purity of the raw juice rather under two units as an average. The preliminary separation of the clear juice from the scum is usually effected intermittently in subsiders, but several factories have installed continuous settlers and there is a tendency toward development in this direction.

Filtration. The scums are filtered in frame presses of conventional design; in distinction to other cane sugar producing districts, the extraction of the scums is carried to an extreme limit, and in some factories the scums are discharged containing less than 1% of sucrose. In addition to the clarification produced by settling in many cases and always in the factories of more recent date; the juices are passed through mechanical filters; these filters were originally installed as sand filters but lately the sand as a filtering material has been replaced in many cases by wood shavings.

Evaporators. The most commonly adopted method of evaporation is the vertical submerged tube type in quadruple effect, and this is the type that has been adopted most recently; horizontal tube film evaporators are operated in five large factories, but not only has no extension of this type taken place recently but four apparatus of this type have been replaced by the vertical submerged tube. Horizontal submerged tube apparatus are in use in three factories, triple effects are confined entirely to the smaller and older factories.

One of the great difficulties connected with evaporation in these islands is the frequent formation of a hard and refractory calcium sulphate scale, and it is in connection with accessibility for cleaning that preference is often given to the submerged tube type.

Neither the Rillieux-Lexa system of multiple reheating or the Pauly-Greiner scheme of pre-evaporation is in use.

Vacuum Pans. The greater number of apparatus still consists of the " Standard " type of Vacuum Pan with long helical coils for heating surface. There are a certain number of short coil pans and a few Greiner Pans. Lately the most recently built houses have adopted a pan with tubular calandrias, with the tubes set at an angle of about 45° from the vertical, and a number of older pans have been remodelled to this deisgn, which have proved very satisfactory and efficient.

Condensers. Both wet and dry systems are in use; central condensation is in use in few houses; the vacuum obtained in the last cell of the effects or in the pans is seldom below 25 inches; generally there is an abundance of water available, but a few smaller and older factories are obliged to use cooling towers.

Process of Boiling. In four at least of the largest factories a complete suppression of low products is obtained by means of carefully controlled schemes of return of molasses combined with crystallization in motion. In all factories the systematic return of molasses to syrup massecuites is followed but the majority of the factories still eliminate low sugars by the process of remelting and thus carry forward from season to season large quantities of low grade massecuites.

Sugars. It is only exceptionally that any sugars are shipped of a lower polarization than 96° and the average polarization for the last few years is a shade over 97°; the sugars contain nearly always less than 1% of water, and great attention is paid to this point, so as to prevent bacterial deterioration in view of the long periods sugars remain in transit to New York.

Molasses. The true purity of the waste molasses lies between the limits of 40 and 50 and generally approximates to the value of 45, which also with a small variation represents the yearly average of all the molasses produced in the islands. The economic disposal of this waste product is one of the least satisfactory points of the industry; until a few years ago all of the material was actually wasted; latterly several firms have shipped the molasses in bulk to Pacific Coast concerns for use as cattle food and in the preparation of alcohol; at the present time up to one-third of the production is thus disposed of; the remainder is partially used locally as stock feed; in other cases some is returned to the soil in irrigation water; yet very large quantities are actually and literally wasted.

Fuel. Although the dilution practiced is very high, in nearly all cases the bagasse forms sufficient fuel; in some cases, however, the dilution and consequently the extraction of juice is regulated by the amount of bagasse available as fuel and not by the amount of sugar remaining in the bagasse.

The furnaces employed are of the Dutch oven type in combination with multitubular fire tube boilers, 20 ft. x 7 ft. being the usual size; this type of boiler is generally installed in preference to water tube multitubular boilers of which however several installations are in operation.

Summary. The general status of manufacture may be seen from the annexed summary, which is based on statistics covering over 90% of the output of the last five years. The mean figures are true averages and take into account the different amounts produced in the different factories. The figures except when otherwise indicated refer to percentages of the sucrose in the raw material.

	High	Low	Mean
Sucrose % cane	16.6	11.2	14.4
Fiber % cane	15.0	11.0	12.3
Sucrose obtained by mills	96.8	89.0	93.5
Sucrose lost in bagasse	11.0	3.2	6.5
Sucrose lost in scums	1.0	.03	.2
Sucrose lost in molasses	11.0	5.0	6.5
Unknown losses	4.0	.1	1.3
Sucrose in sugars	90.0	70.0	85.5
Sucrose in sugars per 100 sucrose in juice	94.0	82.0	91.5
Purity clarified juice	92.0	82.0	88.0
Purity Sugars	99.0	97.2	98.0
Purity waste molasses	57.0	39.0	45.0
Commercial sugars % on cane	14.7	9.1	12.7

THE PRODUCTION OF ALCOHOL AND SUGAR FROM THE SAP OF THE NIPA PALM

By H. D. Gibbs

Bureau of Science, Manila, P. I.

It long has been known that the saps of certain palms contain sucrose, and in portions of India, Australia, and Malaya crude sugar is produced from these sources in quantities rarely sufficient to meet the local demands. As a commercial proposition the industry never has been successful on a large scale for a number of valid reasons. Among the palms which have been utilized for this purpose are: Arenga Saccharifera Labill., the sugar palm; Borassus flabellifer Linn., the Palmyra palm; Caryota urens Linn., fish-tail palm; Cocos nucifera L., the cocoanut palm; Corifa elata Roxb., the buri palm; Nipa fruticans Wurmb., the nipa palm; Phoenix dactylifera Linn., the date palm; and Phoenix sylvestris Roxb., the wild date palm. Four of these, the nipa, cocoanut, buri, and sugar palms found widely distributed in the Philippine Islands, have been investigated. The best quality saps obtained from them have been found to be remarkably similar in composition, which is as follows:—

Density 15°	1.0700
Solids 15°	17.5 per cent.
Acidity	Trace
Ash	0.46
Sucrose	16.5
Reducing sugars	Trace
Nitrogenous compounds and undetermined	0.54

The saps as they exude from the trees are practically neutral and contain no sugar other than sucrose. The processes of inversion of the sucrose and fermentation commence almost immediately.

Since the nipa is the only palm which promises to be of any great commercial importance as a producer of sugar sap, no others will be considered here[1].

It is an erect, stemless palm, the leaves and inflorescences arising from a branched rootstock, the leaves pinnate, 3 to 10 meters long. Inflorescence from near the base of the leaves, erect, brown, 1 to 1.5 or 2 meters high, bearing numerous sheathing spathes and both male and female flowers. This palm grows only along the mouth of tidal rivers in low tide lands subject to overflow of brackish water as the tides rise each day, and it will not thrive in localities where either fresh or sea water alone is available. It reproduces itself, and in many localities extends its growing area, encroaching upon the sea. Nipa swamps of considerable size and importance occur in a number of the provinces of the Philippines. Swamp lands, subject to daily overflow by the tides, to the uninitiated, would appear to be of no value, but this palm growing in great abundance in these localities, gives a profitable crop when properly exploited.

Since the nipa palm sends its inflorescence up from the base, and hence is near the ground, the flower stalk is conveniently situated for the gathering of sap. Four years after planting the seed, it bears fruit, but it is not tapped for its sap until the fifth year. Some time after the fruit has formed, the stalk is cut across near its top, usually just below the fruit, and each day a thin slice is removed to keep the wound fresh and to facilitate exudation. The sap as it flows from the stalk is clear and transparent, almost colorless, and very sweet to the taste. It is collected in small receptacles usually once a day and transported in boats to the distilleries. In some districts palms, which are to-day in a perfectly healthy and thriving condition, have been known to have yielded sap on a commercial basis for the past fifty years. The industry is in many respects capable of improvements which would lead to greater profits. No doubt the transportation of

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[1] The Alcohol Industry of the Philippine Islands, Part I. The Study of Some Palms of Importance with Special Reference to The Saps and Their Uses, by H. D. Gibbs, W. B. Gonder, R. R. Williams, and F. Agcaoili, *Philip. J. Science*, Sec. A, 1911, VI, 99-206.

sap by pipe line can be successfully accomplished and greatly reduce the cost of production.

ALCOHOL AND ALCOHOLIC BEVERAGES

The nipa palm sap is probably the cheapest raw material now being utilized for the production of alcohol and alcoholic beverages. The industry is confined to the Philippine Islands where it reaches considerable magnitude, over 90,000,000 litres of sap being produced yearly and distilled in pot stills, continuous process stills, and modern rectifyers. The pot stills produce a beverage varying in composition from 20 to 55 per cent. alcohol, the continuous process stills, alcohol of about 50 per cent. purity and the modern rectifyers, 93 to 96 per cent. spirits. One of the distilleries now in operation is producing 93 per cent. alcohol at a cost of less than 0.04 dollars (United States Currency) per litre. The pot still beverages are consumed near the place of production while the other grades of alcohol are manufactured into a variety of beverages in imitation of well known brands and shipped to various parts of the Islands, or used as denatured alcohol. Approximately, 10,000,000 proof liters are produced annually by nearly thirty distilleries, and the industry is increasing. Over 98 per cent. of the alcohol is consumed locally in a variety of beverages and a small increasing quantity is used industrially. The pot still beverages[1] possess considerable merit and steps have been taken to improve them in quality and extend their market. The Food and Drugs Board of the Philippine Islands has established standards and promulgated directions for manufacture, ageing and labeling. These standards require an alcoholic content between 40 and 50 per cent. and place limits upon the higher alcohols, esters, acids, and aldehydes. Beverages manufactured according to the prescribed methods are called " Philippine Nipa Palm Brandy " and after ageing in wood for a definite period are entitled to the prefix, " old " or " aged." They are of the character of brandy, have a very agreeable flavor and odor, and, among a discriminating class of consumers, should command a broader market, both foreign and domestic.

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[1] Gibbs and Holmes. Ibid Sec. A. (1912) 7, No. 1.

SUGAR

Sugar is not produced in commercial quantities from the sap of the nipa palm but all indications point to the possibility of creating a profitable industry of considerable magnitude. A conservative estimate of production is as follows: 2,000 plants per hectare yield 86,000 litres of sap containing 12 per cent. recoverable sugar equivalent to 10,750 kilograms of 96 per cent. centrifugal sugar. An equipment corresponding to a 500 ton sugar mill can be kept running for 180 days of the year on the sap from 750 to 1,000 hectares of nipa lands and should produce annually about 9,000 tons of 96 per cent. sugar.

The cost of refining will probably be approximately the same as for cane sugar, for, owing to the absence of bagasse, fuel will have to be purchased, opposed to which is a saving due to the absence of crushers. The sap arrives at the mill in the same condition as the juice of the sugar cane after the addition of the lime.

In order to inhibit inversion of the sucrose of the juice, the collecting vessels must be coated with a thick mixture of lime[1] and water before being placed in position to collect the sap dropping from the cut stem. Sap has been found to undergo no change in ten days when treated in this way. Laboratory experiments on the process of refining gave the following results:

Four litres of sap, analyses given in Table I, column I, were heated to boiling in a large porcelain evaporating dish and carbon dioxide run in until the alkalinity was reduced to 0.10 gram calcium oxide for 100 cubic centimeters of solution. The solution was then filtered and analyzed. See column II. The process of evaporization was then continued and the alkalinity further reduced with sulphur dioxide to 0.011 gram calcium oxide for 100 cubic centimeters of liquid. The solution was again filtered and analyzed. See column III. This solution contained, according to the analysis, 236 grams of sucrose.

On boiling down to a massecuite and cooling, crystals of good grain were obtained. These, on drying in a hand centrifuge and finally in an air bath at about 90°, weighed 157 grams, were pure white, and polarized at 96.8 per cent.

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[1] Large deposits of limestone and marble are available.

The molasses and washings were boiled down to a second massecuite and treated in the same way. A yield of 79 grams of very light yellow sugar polarizing at 93.8 was obtained. The second molasses was light yellow, measured 20 cubic centimeters and polarized at 58.6. A third sugar could easily have been crystallized from it if the volume had been sufficient. The losses were entirely due to the numerous samples taken for analysis during the course of the work and to the handling of small quantities of material in the centrifugal machine which was much too large for the samples.

Ten days later, a second portion of the same raw material was treated in practically the same manner. The original analysis is given in column IV, the analysis after the carbon dioxide treatment in column V, and after the sulphur dioxide treatment in column VI. Two liters of this solution, containing theoretically 276 grams of sucrose, yielded 210 grams of first sugar which was almost pure white and polarized at 96.8. The quantity of molasses was too small to handle successfully in the apparatus, so no further attempt was made to refine it, although with larger quantities it could easily be handled. The analyses are given in the following table:

TABLE I. Analyses of solution of nipa sap during the process of purification for sugar making.

	First Run			Second Run		
	I.	II.	III.	IV.	V.	VI.
Density $\frac{15^\circ}{15^\circ}$	1.0615	1.0570	1.0620	1.0619	1.0615	1.0636
Solids by table	15.0	14.0	15.2	15.2	15.1	15.5
Polarization	10.2	12.2	13.4	10.2	12.2	13.8
Alkalinity:						
CC—per 100 cc.	450	36	4.0	461	111	3.0
g. CaO per 100cc.	1.26	0.10	0.011	1.29	0.311	0.008
Purity	67.3	87.1	88.2	67.1	80.8	90.0
Color	Brown	Yellow	Pale straw	Brown	Yellow	Very pale straw

The refining of this sap will require with the exception of the crusher, the ordinary equipment of a sugar mill and, at present, I am strongly of the opinion that more profit is to be made from the nipa lands through the establishment of sugar refineries than distilleries. I fully appreciate that claims which never have been realized have been made for the profits to be derived from the use of other palms, Arnega saccherifera and Caryota urens, in Java and India, for sugar production on a commercial scale attractive to the investment of European and American capital. However, in the case of the nipa, many of the difficulties encountered with the other palms do not exist. Some of the points of special advantage to the nipa are as follows: — The swamps now exist in a state ready to bring them into active production merely by thinning, or, in the case of the swamps employed in the alcohol industry, this work is already well under way; many large areas are not now put to any use and are to be had for a small investment; the plants reproduce themselves and it is probable that each plant is capable of producing continuously for more than fifty years; the flower stems are close to the ground and the work of gathering the sap is quickly and easily performed; the producing plants grow very close together and the production per hectare is large; transportation of the sap is cheaply accomplished through the numerous waterways and may be still further reduced by the construction of pipe lines.

In conclusion, I must point out that while these estimates are the results of accurate laboratory and field investigations, they must be substantiated on a small factory scale. If no unforeseen difficulty is encountered, I believe splendid returns will accrue.

SUR LA PRÉCIPITATION INCOMPLÈTE PAR LE CARBONATE DE SOUDE DE LA CHAUX COMBINÉE DANS LES JUS SUCRÉS.[1]

PAR I. DE GROBERT

Ingénieur-Conseil, Paris

Quand on ajoute à un jus sucré du carbonate de soude pour éliminer la chaux combinée et transformer les sels de chaux en sels de soude qui sont moins nuisibles à la cristallisation, on constate que le carbonate de soude ne précipite pas une quantité équivalente de chaux.

Ainsi, à du sirop filtré contenant $0^{gr}086$ de chaux % gr., nous avons ajouté la quantité équivalente de carbonate de soude pur et sec, soit $0^{gr}163$, en ayant soin de diluer fortement la liqueur. Le liquide filtré après 5 minutes d'ébulition contenait encore $0,^{gr}041$ CaO par 100 gr. de sirop. La quantité de chaux précipitée a donc été de:

$$0,086 - 0,041 = 0,045$$

soit 52%.

En présence de ce résultat on est porté à conclure que les $^{48}/_{100}$ du carbonate de soude ajouté sont restés libres, mais alors l'alcalinité du sirop a dû augmenter d'autant, c'est-à-dire de $0,^{gr}041$ (en CaO). Or le titrage alcalimétrique (àchaud) n'indique que $0,^{gr}015$ d'augmentation: il y a donc une certaine quantité de carbonate de soude, correspondant à la différence $0,051 - 0,015 = 0,026$ qui n'a pas été employée à précipiter la chaux et qui ne se retrouve pas à l'état libre dans la liqueur; elle représente $^{30}/_{100}$ du carbonate de soude introduit. On ne peut attribuer ce résultat, même partiellement, à la solubilité du carbonate de chaux en vertu de laquelle une petite quantité de chaux échappant au dosage entrerait dans les $0,^{gr}026$ de chaux

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[1] Les expériences ont porté sur des jus de betteraves.

ci-dessus trouvés, car le carbonate de chaux qui a pu rester en dissolution dans le filtrae n'a pas échappé au titrage alca imétrique et est compris dans les 0,^{gr}015 représentant l'augmentation de l'alcalinité.

Nous pensons que cette fraction du carbonate de soude, qui n'a pas été utiliseé à précipiter la chaux et qu'on ne retrouve pas à l'état libre, a été employée à décomposer une partie du non-sucre organique susceptible de donner des produits acides en milieu alcalin. L'asparagine et la glutamine sont dans ce cas det on sait que leur transformation en acides amidés se poursuit pendant tout le cours de la fabrication. Cette considération nous autorise à admettre qu'une partie du carbonate de soude ajouté au sirop a été transformée en sels organiques, notamment en aspartate et en glutamate de soude.

Nous avons ensuite recherché comment agit le carbonate de soude ajouté en excès sur la dose théorique nécessaire à la précipitation de la chaux.

A une autre portion du même sirop, nous avons ajouté le double de la quantité de carbonate desoude employée dans le premier essai, c'est-à-dire, 0,^{gr}163 × 2 = 0,^{gr}326 pour 100 gr. de sirop contenant 0,^{gr}086 CaO.

Dans la liqueur étendue, bouillie et filtrée, il est presté 0,^{gr}016 de chaux. La quantité précipitée a donc été de:

$$0{,}086 - 0{,}016 = 0{,}070$$

soit 81%.

L'alcalinité du sirop est passée de 0,^{gr}042 à 0,^{gr}106, elle a donc augmenté de 0,^{gr}064; elle aurait dû augmenter de:

$$0{,}806 \times 2 - 0{,}070 = 0{,}102$$

si tout le carbonate de soude qui n'a pas agi était resté libre. En nous basant sur les considérations indiquées plus haut, nous sommes fondé à admettre qu'une partie du carbonate de soude a été neutralisée par des acides organiques. Cette partie est représentée, en chaux, par la différence:

$$0{,}012 - 0{,}064 = 0{,}038$$

Dans le tableau qui suit nous avons réuni les résultats des deux essais en les rapportant à 100 parties de carbonate de soude introduit.

	En employant la dose théorique de carbonate de soude	En employant le double de la dose théorique
100 parties de carbonate de soude introduites se divisent en:		
1°—Quantité employée a précipiter la chaux	52	40
2°—Quantité neutralisée par le non sucre organique:	30	22
3°—Quantité restée libre:	18	38
	100	100
Sur 100 parties de chaux existant dans le sirop, on a précipité:	52	81

De ces essais, on peut conclure que l'action totale du carbonate de soude sur les jus sucrés en présence des sels de chaux qui y sont contenus se divise en trois actions partielles: une partie du réactif est employée à précipiter la chaux, une partie se combine à certaines matiéres organiques (notamment aux amides); le surplus reste à l'état libre dans le jus dont il augmente l'alcalinité. Il convient de remarquer ici que l'augmentation de l'alcalinité constatée après l'action du carbonate de soude peut ne pas correspondre exactement à l'excés de ce réactif, la présence du carbonate de chaux en solution influant sur le titrage alcalimétrique. Tandis que l'eau pure ne dissout que 0,^{gr}035 de carbonate de chaux par litre, on rencontre dans les jus sucrés des crops qui augmentent cette solubilité: tels sont les sels neutres de potasse, de soude, de chaux, de magnésie (Frésénius) et les citrate alcalina (Spiller, Rube). Toutefois, la présence du carbonate de chaux ne pourrait influencer le résultat qui nous occupe que si la quantité existant dans la solution n'était pas la même *avant* et *après* l'addition du carbonate de soude. Le cas peut se présenter quand on opère sur des jus fortement carbonatés et qui n'ont pas été soumis après la carbonatation à une ébulition suffisante.

Au point de vue de la pratique, il résulte de nos expériences que le carbonate de soude doit être employé avec circonspection; on ne peut pas espérer par son usage éliminer plus de 50 à 60% de la chaux organique contenus dans le jus, ce qui correspond à l'emploi d'une quantité de carbonate de soude égale ou un peu supérieure à la dose théorique, car il faut remarquer que d'après les résultats qui précèdent, l'emploi de la dose théorique laisse dans le jus, pour 1 gr. de chaux éliminée, 1,7 gr. de carbonate de soude, et, en employant le double de cette dose, il en reste dans le jus 2,7 gr. Or cette augmentation du non sucre minéral dans les jus n'étant pas sans inconvénients pour la cristallisation et pour la qualité du sucre fabriqué, on ne doit pas s'exposer à perdre de ce côté les avantages obtenus par la transformation des sels organiques de chaux en sels de soude.

D'après nos observations, dans le travail industriel la dose théorique de carbonate de soude est celle qui donne les meilleurs résultats.

BESTIMMUNG DES REINHEITS-QUOTIENTEN DES RÜBENSAFTES IN DER DIGESTIONSLÖSUNG

VON FRANZ HERLES

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Der Reinheits-Quotient der Rübensäfte diente seit Langem neben der Saftpolarisation und dem Zuckergehalte der Rüben zur Beurteilung der Rübenqualität. Durch zahlreiche Versuche wurde jedoch bewiesen, dass diese Grundlage fehlerhaft ist, denn der Reinheits-Quotient des auch aus einer und derselben Rübe gewonnenen Saftes hängt von der Feinheit des erzeugten Breies, von beim Pressen verwendeten Drucke, von der Höhe der gepressten Schicht, von der Zeit, welche von der Breierzeugung bis zu dessen Auspressung verflossen ist, von der Temperatur bei der Pressung, etc., ab. Diese Umstände verursachen recht beträchtliche Differenzen, sodass auf solcher Grundlage ermittelter Reinheits-Quotient des Rübensaftes keinen grösseren Wert haben kann.

Falls diese Bestimmung dennoch manchenorts durchgeführt wird, lässt sich dies nur noch mehr auf die alte Gewohnheit zurückführen, denn heute, wo mittels der Digestionsmetoden der Zuckergehalt der Rüben leicht sich bestimmen lässt und heidurch über die Rübenqualität verlässlicher Masstab gewonnen wird, hat die Bestimmung des Reinheits-Quotienten des Rübenpressaftes keine Bedeutung mehr.

Man kann nämlich auf Grund der Erfahrung voraussetzen, dass mit dem Zuckergehalte der Rüben auch die Reinheits-Quotiente ihrer Säfte steigen. Anders wäre es jedoch, falls es bei dieser Bestimmung möglich wäre die auf die Resultate ungünstig einwirkende Umstände bei der Saftgewinnung zu eliminiren und ein Verfahren auszuarbeiten, welches ein Arbeiten unter möglichst gleichen Umständen gestatten würde.

Der erste Schritt hiezu wurde von *K. Krause* gethan, welcher von dem Bestreben geleitet die langwierige Zubereitung des Rübensaftes durch das bisher übliche Auspressen des Rübenbreies umzugehen, die Bestimmung des Reinheits-Quotienten des Rübensaftes mit dem Digestionsprozesse verknüpfte, indem er die ungeklärte, in der Wärme hergestellte Digestionslösung verwendete. Hiedurch gelang es ihm den grössten Teil der Umstände, welche bei der Rübensaftbereitung auf die Resultate der Reinheitsquotienten-Bestimmung Einfluss ausübten, namentlich den Einfluss des Pressens, zu beseitigen. Der Einfluss der verschiedenen Feinheit des Breies und der bei der Digestion angewendeten Temperatur blieb jedoch weiter zu bestehen.

Nebstdem auch die vorgeschlagene Bestimmung der saccharometrischen Trockensubstanz mittels besonderer hiezu konstruirten Saccharometer liess sich nicht immer genügend genau ausführen, wodurch ziemlich grosse Unterschiede vorkamen. Diesen Mangel beseitigte zwar *VI. Staněk* (Zeitschrift für Zuckerindustrie in Böhmen 1911–12, S. 375), indem er die Trockensubstanz der Digestionslösung refraktometrisch zu bestimmen vorschlug, aber gegen die Bereitung seiner Digestionslösung bestehen auch weiter die oben erwähnten Einwendungen, denn auch Staněk verwendet eine Digestionslösung, welche aus verschieden feinen Brei nach einer halbstündigen Einwirkung bei einer Temperatur von 80–85°C, welche auf die Löslichkeit vershciedener Rübennichtzucker und somit auch auf den Reinheitsquotient vom Einflusse sein kann, erhalten wurde.

Inwieweit hiedurch eine dem Diffusionssafte analogische Lösung erhalten wird, lässt sich mit Bestimmtheit nicht beurteilen, denn man kann dafür halten, dass die Zusammensetzung des durch heisse Digestion des Breies gewonnenen Saftes eine andere werden kann als diejenige des durch die Diffusion ganzer Schnitte gewonnenen Saftes.

Ich bin deshalb schon von mehreren Jahren auf den Gedanken, (welchen ich auch im J. 1906 der vom Herrn Dir. Krause geleiteten Zuckerfabrik schriftlich mitteilte) gekommen, zu der Bestimmung des Reinheitsquotienten des Rübensaftes die ungeklärte, durch die kalte Wasserdigestion des mittels meines Breigewinnungsapparates (Herlesschen Breipresse) erzielten Breies gewonnene Digestionslösung zu verwenden.

Der mittels der Herlesschen Breipresse gewonnene Brei wird nämlich stets unter gleichen Umständen und stets in ganz gleicher Feinheit erhalten. Seine vollständige Digestion vollzieht sich in Folge seiner ungewöhnlichen Feinheit bereits in der Kälte fast augenblicklich.

Die Zusammensetzung des auf diese Weise aus dem Breieeiner und derselben Rübe gewonnenen Digerates bleibt ziemlich gleich und somit auch dessen Reinheitsquotient, sodass hiedurch für den Vergleich und Beurteilung des Reinheitsquotienten verschiedener Rüben- und Schnittenproben massgebende Zahlen erhalten werden.

Dass sich diese, in der Kälte aus dem durch die Herles sche Breipresse hergestellten Breie gewonnene Digestionslösung auch vorteilhaft zur Bestimmung des Reinheitsquotienten auf Grund des Staněkschen refraktometrischen Verfahrens eignet, ist selbstverständlich. Da aber nicht immer das Refraktometer bei der Hand ist, empfehle ich zur Bestimmung des Reinheitsquotienten der Digestionslösung auch folgendes Verfahren:

Man wiegt z. B. 2 x n Menge des mittels der Herlesschen Breipresse gewonnenen Breies in ein mit Kautschukplatte zu verschliessenden Becher (resp. in ein von le Docte, Herzfeld, Staněk u. Urban, etc. empfohlenes Gefäss) ab, setzt 354 cc destillirtes Wasser zu, schüttelt tüchtig durch und filtrirt durch ein Papierfilter. In 50 oder 100 cc des Filtrates wird (bei 20° C) das specifische Gewicht (resp. die Saccharometergrade) entweder mit dem *Herlesschen* Pipettenpiknometer—(Zeitschrift für Zuckerindustrie in Böhmen 1897–98, XXII, S. 401) oder mit dem Piknometer nach *Kovář* bestimmt, wodurch bis auf Hundertstel Saccharometergrade genaue Resultate erhalten werden. Zur Polarisation wird das Piknometer vollständig in den Becher entleert, 1/10 seines Volums von 25%-iger Bleiessigwassermischung zugesetzt, durchgerührt, filtrirt und polarisirt. Zu der gefundenen Polarisation wird aus den Schmitzschen Tabellen der entsprechende Zuckergehalt ausgesucht. Der Zuckergehalt der Rübe gleicht der ursprünglichen Polarisation vermehrt um ⅒ derselben.

Beispiel. Specifisches Gewicht des Digerates = 1.0207, entsprechend 5.25° Sacch.; Polarisation = 16.5°, entsprechend laut der Schmitzschen Tabelle für geklärte Lösungen 4.61% Zucker. Reinheits–Quotient der Digestionslösung demnach $\frac{4.61 \times 100}{5.25}$ = 87.6. Der Zuckergehalt der Rübe: 16.5 + 1.65 = 18.15%.

HOW THE NETHERLAND SUGARFABRICANTS ARE BEING KEPT INFORMED, DURING CAMPAIGN, ABOUT QUALITY OF THE RAW SUGARS PRODUCED

By M. G. Henninelinck
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In Holland it is taken for granted that the inner grain of sugars obtained from well cured juices must be white. The refiners require that the raw sugars should be able to stand a certain quality criterion. For that purpose the sugar is not judged as brown raw sugar, but as white sugar, that is to say without the adhering brown syrup. One uniform white spinning method, as described, is always followed.

For the control the G.T.S. takes a standard colour (quality criterion fixed by Sugarfabricants and Refiners) and its colour is indicated by the number 1.

A very white sugar, showing f. i. only half as much colour as the standard is indicated by 0.5.

The method followed to determine the colour is fully described and illustrated by a photo (Fig. 1).

In order to learn the quality of each factory's sugar separately the following control is made:

An average 1 K.G. sample of the sugar manufactured in a certain period is forwarded to the Secretary of the G.T.S. The sample is spun white and tested, the colour number communicated without delay to the factory. By marking the numbers on a printed table and combining these points, a curve is obtained, indicating a reliable picture of the produced sugar quality of that factory.

In this manner the fabricants are warned if mistakes in the manufacturing take place; in the same way the result of an amelioration on the quality may be learnt.

To ascertain the average quality of the sugar produced in the Netherlands every factory forwards weekly an average 100-gram sample of his produced sugars to the Secretary of the G.T.S. All these samples are thoroughly mixed, spun white and the colour recorded on a printed table. The combination line of these points forms the colour line during the campaign (see Fig. 2).

To illustrate what may be reached by this control the colour line of a factory which changed its method of sulfitation is here published (see Fig. 3).

CONCLUSION

A control, giving within a few days a reliable picture of the produced sugar quality, is of much use to the Sugarfabricants.

CONTRIBUTION A L'ETUDE DES TOURTEAUX D'ECUMES DE SUCRERIE

Par MM. L. Lindet et Charpentier

Paris, France

Les tourteaux d'écumes de Sucrerie renferment toujours une quantité variable de sucrate tribasique insoluble, qui semble s'autant plus élevée que la chaux a été moins complètement éteinte, et plus rapidement carbonatée. Cette quantité peut être établie en se basant sur la différence entre le taux de sucre extrait en présence de l'acide acétique et le taux de sucre extrait en présence de l'eau seule.

L'acide acétique est encore le meilleur réactif pour décomposer ce sucrate tribasique; l'acide phénigque, dont l'un de nous, M. Lindet, a préconisé l'emploi pour le dosage de la chaux dans les laits de chaux de sucrerie, ne dissout guère, au bout d'une heure, plus de sucre que l'eau pure (0.77% de la quantité extraite par l'acide acétique au lieu de 0.66% moyenne de 20 expériences).

On ne peut attribuer cette différence de polarisation entre les liqueurs acétiques et les liqueurs phéniquées à une autre substance active que l'acide acétique serait seul à dissoudre; le dosage au saccharimètre coincide avec le dosage à la liqueur de cuivre, après inversion. Nous avons vérifié également que l'acétate de chaux, dans les conditions de l'expérience, n'a pas d'influence sur la rotation des liqueurs.

Les expériences précédentes montrent que le sucre du sucrate tribasique représente de 5 à 66% du sucre total (moyenne de 8 écumes analysées, provenant de 5 sucreries différentes. Le reste, 95 à 34%, se trouve à l'état soluble, et provient d'un lavage imparfait.

Mais ce sucre soluble est-il à l'état libre ou à l'état de sucrate soluble, mono ou bibasique?

La liqueur, provenant de la maceration au contact de l'eau pure ou même de l'eau sucrée ne renferme pas de chaux, susceptible d'être précipitée par l'acide carbonique. Elle est alcaline (de 0.03 à 0.22% du tourteau, compté en CaO), jais par l'ammoniaque des eaux dites ammoniacales (provenant de la condensation des vapeurs de jus) et qui servent à laver le filtre-presse. Avant le lavage, les écumes, chargées de jus, renferment un peu de sucrate de chaux soluble; elles cessent d'en contenir après le lavage, du fait du passage des eaux ammoniacales, chargées de carbonate d'ammoniaque.

Quand on substitue, pour la recherche de la chaux, l'eau phéniquée à l'eau pure, on obtient des chiffres qui oscillent entre 0.58% du tourteau et 1.41% (8 analyses); mais cette quantité de chaux est en moyenne cinq fois supérieure à celle qui serait contenue dans le sucrate tribasique dosé par le procédé indiqué ci-dessus. L'eau phéniquée a donc enlevé une partie de la chaux combinée à l'albumine, à l'acide pectique, etc. Une expérience directe nous a permis de constater que si l'eau phéniquée ne dissout pas le carbonate de chaux, elle décompose les combinaisons de l'albumine et de l'acide pectique avec la chaux.

En résumé, les tourteaux d'écumes ne renferment pas de chaux libre, quand ils sont bien préparés, et lavés, comme on le fait ordinairement avec des eaux ammoniacales; le sucre que le lavage n'a pas enlevé, s'y trouve, non pas à l'état de sucrate soluble, mais à l'état libre; les tourteaux se montrent en outre plus ou moins chargés de sucrate tribasique insoluble que la carbonatation n'a pas eu le temps de décomposer.

ACTION OF DISINFECTANTS ON SUGAR SOLUTIONS

By George P. Meade

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This work was started with the idea of determining the efficiency of Chloride of Lime as a preservative for sugar solutions. Later the experiments were extended to include the action of Formaline, Ammonium, Fluoride, and a Commercial Preservative of the Cresol variety. The work was done at odd intervals during the last six months under conditions which made an extended investigation impossible. Therefore, the results are somewhat fragmentary.

All polarizations were with alcohol — 50% of 95% alcohol — and a minimum of lead subacetate solution.

The addition of the disinfectant was effected by adding 1 c.c. of a solution of proper concentration to 100 c.c. of sugar solution. For instance "Chloride of Lime 1:10,000" means that 1 c.c. of a 1% solution of Chloride of Lime was added to 100 c.c. of the sugar solution. In the " Control without Disinfectant " 1 c.c. of sterile water was always added to compensate for the dilution due to the addition of the disinfectant in the treated samples.

Acidities are quoted in number of c.c. of n/10 K O H necessary to neutralize 10 c.c. of solution, phenol phthalein as indicator.

Sterilized flasks stoppered with cotton were used in all the work.

Experiment I and II. Cane syrup from the Triple Effect 28°Be[1] was infected with a portion of a sucrose peptone culture of Bacillus Vulgatus. The artificial infection was probably superfluous. The syrup was divided into 100 c.c. portions and treated as shown. The formaline, 1:1000, was employed as a comparison since this is the commonest preservative and the ordinary dilution used in sugar work.

ACTION OF CHLORIDE OF LIME ON ARTIFICIALLY INFECTED CANE SYRUPS AFTER SIX DAYS' INCUBATION AT 35°-37° C.

	I			II		
	Pol.	Reducing Sugars	Acidity	Pol.	Reducing Sugars	Acidity
Control	—	—	—	38.7	5.03	—
Control No Disinfectant	39.2	6.15	3.0	38.3	3.13	10.5
Chloride of Lime 1:100	—	—	—	37.0	7.32	Sl.Alk.
1:1000	21.8	17.52	2.1	37.4	6.03	14.4
1:10,000	37.9	4.44	3.2	36.8	5.73	13.5
1:100,000	30.1	10.16	3.1	33.7	4.92	13.0
Formaline 1:1000	40.1	5.64	0.7	37.6	5.31	2.0

The Chloride of Lime used in this and subsequent experiments contained 19.75% Available Chlorine.

The noteworthy point in both these tabulations is that the treated samples in the majority of cases show greater deterioration than the untreated control. Platings and a microscopic examination of the samples in Experiment II showed no growth with Formaline 1:1000 so the deterioration in that sample must have been due to the acidity. Chloride of Lime 1:100 and 1:1000 showed numerous organisms. No difference could be detected between the control and Chloride of Lime 1:100,000 so far as the bacterial examination went. It may be that the artificial infection was a disturbing factor in these two experiments.

EXPERIMENTS III AND IV. In experiment III juice from sound cane was treated and in IV juice from frozen cane. The incubation period was 65 hours in both cases. There was no artificial infection in these or any of the subsequent experiments on solutions taken from the factory.

ACTION OF CHLORIDE OF LIME ON CANE JUICE 65 HOURS IN INCUBATOR AT 35° - 37° C.

	III			IV		
	Pol.	Reducing Sugars	Acidity	Pol.	Reducing Sugars	Acidity
Original	10.7	—	—	8.75	—	3.0
Control No disinfectant	8.8	1.14	11.4	4.4	2.88	12.0
Chloride of Lime 1:200	—	—	—	8.3	2.83	0.2
1:1000	8.4	2.35	2.5	6.8	3.79	2.9
1:10,000	4.5	1.94	13.5	2.4	3.26	9.5
1:20,000	—	—	—	2.3	3.36	10.0
1:100,000	9.5	0.93	9.5	4.75	2.35	10.8
Formaline 1:1000	9.15	3.26	1.9	6.75	4.06	3.2

EXPERIMENT V. Two sets of samples of the same juice were treated identically. One set was polarized at the end of two days, care being taken to prevent contamination, and again at the end of three days. The second set was polarized at the end of five days. In this experiment the incubation was at room temperature.

ACTION OF CHLORIDE OF LIME ON CANE JUICE AT ROOM TEMPERATURE (23° - 30°C.)

Polarizations only. Original juice = 9.75 Polarization.
3.2 Acidity.

	After 2 Days	After 3 Days	After 5 Days	Acidity After 5 Days
Control No Disinfectant	8.2	7.4	5.85	12.0 c.c.
Chloride of Lime 1:200	9.45	9.30	8.85	0.8
1:1000	8.90	8.55	1.25	6.0
1:10,000	6.30	1.5	1.75	7.5
1:100,000	6.90	3.8	4.2	5.5
Formaline 1:1000	8.25	8.1	7.05	3.5

The three sets of results obtained on cane juice (III, IV and V) are consistent in that they all show a markedly greater deterioration in the presence of Chloride of Lime, 1:10,000 than in the samples where no disinfectant is used. The acidities and invert sugar determinations give no basis from which definite conclusions can be drawn as to the manner in which the organisms have acted on the sugar. Microscopic examinations and platings on sucrose agar of the juice in Experiment V after two days' incubation show both yeast and bacteria in profusion in the control, and in Chloride of Lime 1:10,000 and 1:100,000. There were only a few bacteria, all of the gum forming type, in Formaline 1:1000, Chloride of Lime 1:200 and 1:1000.

The next five experiments dealt with the action of various disinfectants. Chloride of Lime, Formaline, (Containing 40% Formaldehyde), Ammonium Fluoride and a Cresol compound designated as "Commercial Disinfectant" were the materials employed.

Cane juice was no longer available as a medium, so the Raw Sugar Washings of the Refinery were diluted for the purpose. These washings are the heavy syrups purged from the Raw Sugar in the first steps of the process. Necessarily they are heavily infected with all the organisms which are on the outside of the raw sugar crystals.

EXPERIMENT VI. Action of various Disinfectants on Raw Sugar Washings diluted to 15° Be[1]. 90 hours' incubation at 33° C.

Original	Pol.	21.8	Acidity	1.8 c.c.
Control No Disinfectant		3.5		19.5 c.c.

	Chloride of Lime		Formaline		Commercial Disinfectant	
	Pol.	Acidity	Pol.	Acidity	Pol.	Acidity
1:200	8.5	9.0	—	—	—	—
1:1000	7.5	17.0	19.2	6.0	21.9	2.0
1:10000	1.8	21.5	0.0	17.0	0.2	17.0
1:100000	1.6	21.0	2.2	20.0	2.4	20.5

Experiment VII. Action of various disinfectants on Raw Sugar Washings diluted to 15° Be[1] 66 hours' incubation at 30°-33° Polarization only.

Original Solution	22.2
Control no Disinfectant	5.4

	Ammonium Fluoride	Chloride of Lime	Formaline	Commercial Disinfectant
1:200	22.2	—	—	—
1:1000	0.4	2.4	21.2	22.0
1:10000	1.8	5.4	3.0	4.5
1:100000	2.7	—	3.4	2.9

The Chloride of Lime used in Experiments VI and VII was found to contain only 7.35% Available Chlorine.

Experiment VIII. Action of various Disinfectants on Raw Sugar Washings, at 20° Be[1] after 2 and 3 days' incubation respectively. Polarizations only.

Original Solution	27.0	
Control — 2 days	10.7	3 days — 5.3

	Ammonium Fluoride		Chloride of Lime		Formaline		Commercial Disinfectant	
	2 days	3 days	2 days	3 days	2 days	3 days	2 days	3 days
1:1000	9.5	2.8	12.2	6.1	25.6	25.1	25.4	24.8
1:10000	9.2	4.1	10.2	4.6	12.2	6.7	14.5	10.3
1:100,000	10.5	5.1	12.1	6.1	8.4	3.2	9.3	4.3

Experiment IX. Action of Formaline on Raw Sugar Washings 20° Be[1]. Four days' incubation at 33° - 35° C.

Sample		Polarization
Original		30.9
Control no Disinfectant		15.8
Formaline	1:1000	24.1
	1:5000	16.7
	1:10000	15.8
	1:20000	14.6
	1:50000	11.2
	1:100000	16.2

EXPERIMENT X. Action of various Disinfectants on Raw Sugar Washings 15° Be[1]. 60 hours' incubation at 30° - 33° C.

Original	24.1
Control	13.0

	Chloride of Lime	Ammonium Fluoride	Formaline
1:1000	11.8	14.7	19.6
1:5000	11.7	14.8	18.2
1:10000	11.7	14.4	16.7
1:20000	12.3	—	10.6
1:50000	—	—	12.1
1:100000	—	—	12.2

Microscopic Examination of some of the samples in Experiment X showed yeasts and bacteria to be about equally numerous in the Control, in Formaline 1:5000 and 1:50000 and in Chloride of Lime 1:10000. Ammonium Fluoride 1:1000 showed yeasts in abundance but few bacteria. All of the samples including Formaline contained much gas.

The foregoing experiments all show that the disinfectants dealt with actually aid deterioration when present in sugar solutions in small amounts.

Ammonium Fluoride is employed in distilleries in the proportion of 4—8 grams per hectolitre (about 1:10,000) for the purpose of inhibiting the growth of butyric acid bacteria without preventing the development of yeast. The Flouride stimulates the decomposing power of the yeasts when present in certain proportions. ("Sugar and the Sugar Cane," Noel Deerr, page 367.)

Since the results with other disinfectants were of the same general character as those obtained with Ammonium Fluoride, it seemed possible that the action was similar, although microscopic examinations had failed to indicate that such was the case.

EXPERIMENTS WITH DISINFECTANTS IN ARTIFICIALLY INFECTED SUCROSE PEPTONE SOLUTIONS

The medium employed for these experiments was the same as that described by Owen, " Bacterial Deterioration of Sugars " (Louisiana Bulletin No. 125).

Peptone	0.10%
Sodium Phosphate	0.20
Potassium Chloride	0.50

The percentage of sucrose was varied in the different experiments.

EXPERIMENT XI. One portion of a sucrose peptone solution containing 10% sucrose was inoculated with a pure culture of yeast; a second portion with Bacillus Vulgatus. These solutions were incubated for 24 hours. They were then transferred in 100 c.c. portions to sterilized flasks, care being exercised to avoid contamination. Chloride of Lime was then added in various proportions. The " Original Polarization " is on the infected solutions after the twenty-four hours' incubation.

ACTION OF CHLORIDE OF LIME ON INFECTED SUCROSE, PEPTONE SOLUTION (10% SUCROSE) 3 DAYS' INCUBATION

	Yeast	Bacillus Vulgatus
Original	5.5	7.6
Control, no disinfectant	0.5	2.9
Chloride of Lime 1:200	5.2	7.4
1:1000	Unable to Clarify	Unable to Clarify
1:10000	0.9	Unable to Clarify
1:100000	–1.0	–1.1

EXPERIMENT XII. Action of Chloride of Lime on infected Sucrose Peptone Solution (10% sucrose) 3 days' incubation. Room temperature.

	Yeast		Bac. Vulgatus		Mixture of Yeast and Bac. Vulgatus	
	Pol.	Acidity	Pol.	Acidity	Pol.	Acidity
Original	16.1	1.6	17.0	0.45	16.4	1.7
Control No Disinfectant	12.1	1.3	3.1	0.6	12.2	1.3
Chloride of Lime 1:200	15.7	Neut.	16.5	Neut.	16.5	Sl. Alk.
1:1000	15.0	0.4	16.2	0.2	15.4	Sl. Alk.
1:10000	11.9	1.40	2.6	0.5	12.3	1.3
1:100000	12.1	1.0	3.0	0.6	11.6	1.45

EXPERIMENT XIII. Another Experiment using Chloride of Lime with Yeasts and Bacteria was carried out in 30% Sucrose Peptone. For the bacteria in this experiment a pure culture of a gum-forming organism isolated from a Cuban Raw Sugar was used. The organism corresponded in all particulars to the "Bacillus D" described in Lawton Brain and Deers' Bulletin on the "Bacterial Flora of Hawaiian Sugars."

ACTION OF CHLORIDE OF LIME ON INFECTED SUCROSE PEPTONE SOLUTION (30% SUCROSE). THREE DAYS' INCUBATION. ROOM TEMPERATURE

	Yeast	Bacillus "D"
Original	30.0	30.0
Control no Disinfectant T	27.7	21.0
Chloride of Lime 1:1000	26.7	23.7
1:5000	29.8	16.6
1:10000	30.0	21.4
1:20000	29.6	24.9

The experiments with Yeasts and Bacteria in pure culture with Chloride of Lime gave results fairly consistent with those obtained on Solutions from the factory. There is nothing in these experiments to indicate that the action of the Chloride of Lime is the same as that of the Ammonium Fluoride. In fact the solutions containing bacteria gave more positive results, so far as stimulating action is concerned, than those with yeasts. The results are not very conclusive however as the stimulating action of the Chloride of Lime is not so marked (except in Experiment XIII) as it was where factory solutions were employed.

Experiment XIV. Experiments with yeast and bacteria were run using Formaline as the disinfectant.

Action of Formaline on Infected Sucrose Peptone Solution (20% Sucrose) After Two Days' and Three Days' Incubation Respectively

	Yeast		Bac. Vulgatus	
Original	16.7		16.7	
	2 days	3 days	2 days	3 days
Control No Disinfectant	12.5	9.8	4.5	3.4
1:5000	16.7	15.5	16.7	16.6
1:10000	14.4	11.8	16.6	16.4
1:20000	13.8	11.1	16.7	15.3
1:50000	13.4	10.6	5.1	3.4

EXPERIMENT XV. Action of Formaline on Sucrose Peptone Inoculated with a mixture of Yeasts and Bacillus Vulgatus. At Room Temperature.

	Yeasts and Bacteria Mixed	
Original	15.95	
	2 days' incubation	3 days' incubation
Control no disinfectant	7.7	4.25
Formaline 1:1000	12.4	9.70
Formaline 1:5000	10.3	6.80
Formaline 1:10000	11.5	8.2
Formaline 1:50000	9.2	5.4
Formaline 1:100000	9.5	5.6

The two experiments with Formaline in artificially infected sucrose peptone solution failed to show any stimulating action whatever.

In order to see whether the unsatisfactory results so far obtained with infected sucrose peptone solutions were due to the inoculation or to the medium, four experiments were carried out as follows: —

Sucrose peptone solution in 100 c.c. portions was infected with one c.c. of a 10% solution of Raw Sugar Washings such as had been used as a medium in previous experiments.

EXPERIMENT XVI. Action of Formaline on Sucrose Peptone Solution (30% Sucrose) infected with 1% of a 10% Raw Sugar Washing Solution. 30°—33° C.

	2 days' incubation	4 days' incubation	Acidity at end of 4 days
Control, no disinfectant	19.1	10.2	17.0 c.c.
Formaline			
1:5000	23.5	19.4	5.8
1:10000	23.5	15.8	6.8
1:20000	19.7	12.3	4.0
1:50000	20.0	12.5	17.8
1:100000	19.2	10.8	19.6
1:200000	19.7	11.9	14.7

Experiment XVII. Action of various disinfectants on Sucrose peptone (30% Sucrose) infected with 1% of 10% Solution of Raw Sugar Washings. Four days' incubation. 30°—33° C.

Original = 28.2.

	Amm. Fluoride		Formaline		Chloride of Lime	
	Pol.	Acidity	Pol.	Acidity	Pol.	Acidity
Control, no disinfectant	25.3	3.1	25.3	3.1	25.3	3.1
1:1000	27.8	1.8	28.6	.8	28.2	.2
1:5000	—	—	25.9	1.9	26.8	4.4
1:10000	21.5	3.2	24.9	2.1	22.5	4.4
1:20000	—	—	24.7	2.5	26.5	5.0
1:50000	18.0	3.2	23.8	2.4	—	—
1:100000	—	—	21.5	2.9	—	—

Experiment XVIII. Action of Various Disinfectants on Sucrose Peptone (30% Sucrose) infected with 1% of 10% Solution of Raw Sugar Washings. Three days' incubation. 30°—35° C.

Original = 28.3.

	Amm. Fluoride	Formaline	Chloride of Lime
Control, no disinfectant	27.9	27.9	27.9
1:1000	28.3	—	28.0
1:5000	25.0	—	27.0
1:10000	24.8	26.5	27.4
1:20000	—	27.5	28.6

EXPERIMENT XIX. Action of Various Disinfectants on Sucrose Peptone (20% Sucrose) infected with 1% of 10% Solution of Raw Sugar Washings. Three days' incubation at 33°—35° C.

Original = 20.2.

	Amm. Fluoride	Formaline	Chloride of Lime
Control, no disinfectant	17.5	17.5	17.5
1:1000	20.2	20.2	20.0
1:5000	—	—	—
1:10000	18.1	20.0	19.4
1:20000	13.3	18.9	17.3
1:50000	—	18.1	—
1:100000	—	18.7	—

Of the four experiments with sucrose peptone inoculated with a small portion of raw sugar washings, two gave results of the same class as those obtained while working with solutions from the factory, while two failed to give such results.

If time had permitted, experiments of the same character as those just recorded, varying the reaction and composition of the medium, the time and temperature of incubation, and various other factors, would have been carried out. This class of work might have given an insight into the conditions under which the stimulation by the disinfectants takes place most readily.

In order to show that there is no action on the part of the disinfectants themselves, sterile sucrose peptone solutions, to which had been added Ammonium Flouride 1:1000 and Chloride of Lime 1:1000 respectively, were kept in the incubator at 38° C. for three days. No change in polarization was observed in either solution.

SUMMARY OF RESULTS

I. Chloride of Lime, ammonium flouride, formaline and the cresol disinfectant when present in sugar solutions in small amounts varying with the disinfectant and with undetermined conditions cause a markedly greater deterioration than occurs in untreated samples.

II. Experiments with chloride of lime in pure culture of yeast and gum-forming bacteria indicate that the stimulation occurs in the case of both organisms.

III. Ammonium fluoride one part to one thousand parts of *sterile* sucrose peptone and chloride of lime in like proportion caused no change in the polarization of the solution during three days' incubation at 38° C.

EXPANDED MEISSL-HILLER TABLE FOR INVERT SUGAR

By E. W. Rice

Yonkers, N. Y.

In cane sugar laboratories where analyses are made to control the working of a factory, it is necessary to determine the amount of invert sugar present in many samples and of widely varying composition.

To obtain approximately exact results, perfectly uniform conditions for all analyses are absolutely essential. Methods in which the weight of the precipitated copper oxide is required are probably most generally used, and with uniform conditions the accuracy depends on properly calculating the amount of invert sugar represented by the weight of copper precipitated.

As the total amount of all sugars present, as well as the ratio between cane sugar and invert sugar, affects the precipitation of copper, the calculation of results includes factors to cover the conditions in each individual analyses. These factors make the calculation a serious task if many determinations must be made, for beside time, there is always the likelihood of an error of calculation.

The conditions under which it seemed necessary to endeavor to simplify the method of calculation were as follows: Copper suboxide was precipitated from 50cc. mixed Fehling's solution by 50 cc. of sugar solution and its equivalent of invert sugar calculated according to the Meissl-Hiller method.

In an endeavor to simplify the calculation of results, it was found, that for variations such as occur under average conditions, it would be possible to construct a table with the following advantages: Percentages could be read directly without large interpolations, the table need not be so large as to be unhandy; by its use the operation of calculating the percentage from the weight of copper, the polarization, and the amount taken for analysis could be reduced from several minutes to the short period of a few seconds and the danger of error in a long calculation could be nearly eliminated by the simplicity of finding the percentage by the use of the table.

Desiring to have the decimal figures in this table represent possible attainment in practical work, some of the unavoidable sources of variation in results, due to manipulation, were investigated. It was found that different beakers from the same manufacturer, while apparently as nearly identical as it is possible to obtain them, may, due to differing thickness and bottom area, cause an average variation as high as .5% of the copper precipitated.

An average of twenty samples analyzed by one who had made a great many previous analyses, showed variations between duplicates due to other causes than the beakers of .36% in high and .24% in low purity goods, based on the copper precipitated.

In plotting the curves of the percentages shown in the table, some slight changes were made, to render the curve more uniform, in places where the results calculated from Meissl-Hiller factors, showed considerable variations in interpolations due to corresponding variations in the Meissl-Hiller factors. After consideration of the previously mentioned influences, it seemed that percentage figures could not be relied upon if extended beyond the limits as printed in this table.

EXPANDED MEISSL-HILLER TABLE FOR INVERT SUGAR

Wt. of Sample in 100cc.			1. Gram		2. Grams		5. Grams		10. Grams		20. Grams
Polarization			30°	35°	20°	30°	85°	95°	85°	95°	85° 95°
Wt. Obtained as											
Cu	Cu_2O	CuO									
.0999	.1125	.1250	10.28	10.26	5.13	5.12	1.661	1.600	.76	.76	
.1019	.1147	.1275	10.48	10.46	5.24	5.23	1.708	1.648	.78	.78	
.1039	.1170	.1300	10.69	10.67	5.34	5.33	1.755	1.696	.80	.80	
.1059	.1192	.1325	10.89	10.87	5.44	5.43	1.802	1.744	.82	.82	
.1070	.1215	.1350	11.10	11.08	5.54	5.53	1.849	1.792	.84	.84	
.1099	.1237	.1375	11.31	11.29	5.65	5.63	1.896	1.839	.86	.86	
.1119	.1260	.1400	11.52	11.50	5.76	5.74	1.942	1.886	.88	.88	
.1138	.1282	.1425	11.73	11.71	5.86	5.84	1.989	1.933	.90	.90	
.1158	.1305	.1450	11.94	11.92	5.96	5.95	2.036	1.980	.92	.92	
.1178	.1327	.1475	12.15	12.13	6.07	6.05	2.082	2.027	.94	.94	
.1198	.1350	.1500	12.36	12.34	6.18	6.16	2.128	2.074	.96	.96	
.1218	.1372	.1525	12.57	12.55	6.28	6.26	2.175	2.121	.98	.98	
.1238	.1395	.1550	12.78	12.76	6.38	6.36	2.221	2.168	1.00	1.00	
.1258	.1417	.1575	12.99	12.97	6.49	6.47	2.267	2.215	1.02	1.02	
.1278	.1440	.1600	13.21	13.19	6.60	6.58	2.313	2.262	1.05	1.04	
.1298	.1462	.1625	13.42	13.40	6.70	6.68	2.359	2.309	1.07	1.06	
.1318	.1485	.1650	13.64	13.62	6.81	6.79	2.405	2.356	1.09	1.08	
.1338	.1507	.1675	13.85	13.83	6.92	6.90	2.451	2.403	1.11	1.10	
.1358	.1530	.1700	14.07	14.05	7.03	7.01	2.497	2.449	1.13	1.12	
.1378	.1552	.1725	14.28	14.26	7.13	7.11	2.543	2.496	1.15	1.14	
.1398	.1575	.1750	14.50	14.48	7.24	7.22	2.589	2.543	1.17	1.16	
.1418	.1597	.1775	14.72	14.69	7.35	7.33	2.635	2.589	1.19	1.18	
.1438	.1620	.1800	14.93	14.91	7.46	7.44	2.680	2.635	1.22	1.21	
.1458	.1642	.1825	15.15	15.12	7.56	7.54	2.726	2.682	1.24	1.23	
.1478	.1665	.1850	15.37	15.34	7.67	7.65	2.772	2.728	1.27	1.25	
.1498	.1687	.1875	15.59	15.56	7.78	7.76	2.817	2.774	1.29	1.27	
.1518	.1710	.1900	15.81	15.78	7.89	7.87	2.862	2.820	1.31	1.30	
.1538	.1732	.1925	16.03	16.00	7.99	7.97	2.907	2.867	1.33	1.32	
.1558	.1755	.1950	16.25	16.22	8.10	8.08	2.952	2.913	1.35	1.34	
.1578	.1777	.1975	16.47	16.44	8.21	8.19	2.997	2.959	1.37	1.36	
.1598	.1800	.2000	16.69	16.66	8.32	8.30	3.042	3.005	1.40	1.38	
.1618	.1822	.2025	16.91	16.88	8.43	8.40	3.087	3.051	1.42	1.40	
.1638	.1845	.2050	17.13	17.10	8.54	8.51	3.132	3.097	1.44	1.42	
.1658	.1867	.2075	17.35	17.32	8.65	8.62	3.177	3.143	1.46	1.44	
.1678	.1890	.2100	17.57	17.54	8.76	8.73	3.221	3.188	1.49	1.47	
.1698	.1912	.2125	17.79	17.76	8.87	8.83	3.266	3.234	1.51	1.49	
.1718	.1935	.2150	18.01	17.98	8.98	8.94	3.310	3.280	1.53	1.51	.72
.1738	.1957	.2175	18.23	18.20	9.09	9.05	3.354	3.325	1.55	1.53	.73
.1758	.1980	.2200	18.45	18.42	9.20	9.16	3.398	3.370	1.58	1.56	.75
.1778	.2002	.2225	18.67	18.64	9.31	9.26	3.433	3.416	1.60	1.58	.76
.1798	.2025	.2250	18.89	18.86	9.42	9.37	3.488	3.461	1.62	1.60	.77
.1817	.2047	.2275	19.11	19.08	9.53	9.48	3.532	3.506	1.64	1.62	.78
.1837	.2070	.2300	19.34	19.30	9.64	9.59	3.576	3.551	1.67	1.65	.79
.1857	.2092	.2325	19.56	19.52	9.75	9.70	3.621	3.597	1.69	1.67	.80
.1877	.2115	.2350	19.78	19.74	9.86	9.81	3.666	3.642	1.71	1.69	.81

Wt. of Sample in 100cc.			1. Gram		2. Grams		5. Grams		10. Grams		20. Grams	
Polarization			30°	35°	20°	30°	85°	95°	85°	95°	85°	95°
Wt. Obtained as												
Cu	Cu_2O	CuO										
.1897	.2137	.2375	20.00	19.96	9.97	9.92	3.710	3.687	1.73	1.72	.82	.81
.1917	.2160	.2400	20.23	20.19	10.08	10.03	3.754	3.732	1.76	1.75	.83	.83
.1937	.2182	.2425	20.45	20.41	10.19	10.14	3.799	3.777	1.78	1.77	.84	.84
.1957	.2205	.2450	20.67	20.63	10.30	10.25	3.844	3.822	1.80	1.79	.85	.85
.1977	.2227	.2475	20.89	20.85	10.41	10.36	3.888	3.867	1.83	1.81	.86	.86
.1997	.2250	.2500	21.12	21.08	10.52	10.47	3.932	3.912	1.86	1.84	.88	.87
.2017	.2272	.2525	21.34	21.30	10.63	10.58	3.977	3.957	1.88	1.86	.89	.88
.2037	.2295	.2550	21.56	21.52	10.74	10.69	4.022	4.002	1.90	1.88	.90	.89
.2057	.2317	.2575	21.78	21.74	10.85	10.80	4.066	4.047	1.92	1.90	.91	.90
.2077	.2340	.2600	22.00	21.96	10.96	10.91	4.110	4.092	1.95	1.93	.92	.91
.2097	.2362	.2625	22.22	22.18	11.07	11.02	4.155	4.137	1.97	1.95	.93	.92
.2117	.2385	.2650	22.44	22.40	11.18	11.13	4.200	4.182	1.99	1.97	.94	.93
.2137	.2407	.2675	22.66	22.62	11.29	11.24	4.244	4.227	2.02	1.99	.95	.94
.2157	.2430	.2700	22.89	22.85	11.40	11.35	4.288	4.271	2.05	2.02	.97	.96
.2177	.2452	.2725	23.11	23.07	11.51	11.46	4.333	4.316	2.07	2.04	.98	.97
.2197	.2475	.2750	23.33	23.29	11.62	11.57	4.378	4.361	2.09	2.06	.99	.98
.2217	.2497	.2775	23.55	23.51	11.73	11.68	4.422	4.405	2.11	2.08	1.00	.99
.2237	.2520	.2800	23.78	23.74	11.84	11.79	4.466	4.449	2.14	2.12	1.01	1.00
.2257	.2542	.2825	24.00	23.96	11.95	11.90	4.511	4.494	2.16	2.14	1.02	1.01
.2277	.2565	.2850	24.22	24.18	12.06	12.01	4.556	4.538	2.18	2.16	1.03	1.02
.2297	.2587	.2875	24.44	24.40	12.17	12.12	4.600	4.582	2.20	2.18	1.04	1.03
.2317	.2610	.2900	24.67	24.63	12.28	12.23	4.644	4.626	2.23	2.21	1.06	1.05
.2337	.2633	.2925	24.89	24.85	12.39	12.34	4.689	4.671	2.25	2.23	1.07	1.06
.2357	.2655	.2950	25.11	25.07	12.50	12.45	4.734	4.716	2.27	2.25	1.08	1.07
.2377	.2677	.2975	25.33	25.29	12.61	12.56	4.779	4.761	2.29	2.27	1.09	1.08
.2397	.2700	.3000	25.56	25.52	12.73	12.67	4.823	4.805	2.32	2.30	1.10	1.09
.2417	.2722	.3025	25.78	25.74	12.84	12.78	4.868	4.850	2.34	2.32	1.11	1.10
.2437	.2745	.3050	26.00	25.96	12.95	12.89	4.913	4.895	2.36	2.34	1.12	1.11
.2457	.2767	.3075	26.22	26.18	13.06	13.00	4.958	4.940	2.39	2.37	1.13	1.12
.2477	.2790	.3100	26.45	26.41	13.18	13.11	5.003	4.985	2.42	2.40	1.15	1.14
.2497	.2812	.3125	26.67	26.63	13.29	13.22	5.049	5.031	2.44	2.42	1.16	1.15
.2517	.2835	.3150	26.90	26.85	13.40	13.33	5.095	5.076	2.46	2.44	1.17	1.16
.2537	.2857	.3175	27.12	27.07	13.51	13.44	5.141	5.121	2.48	2.46	1.18	1.17
.2556	.2880	.3200	27.35	27.30	13.63	13.56	5.186	5.166	2.51	2.49	1.19	1.18
.2576	.2902	.3225	27.57	27.52	13.74	13.67	5.232	5.212	2.53	2.51	1.20	1.19
.2596	.2925	.3250	27.80	27.75	13.85	13.78	5.278	5.258	2.55	2.33	1.21	1.20
.2616	.2947	.3275	28.02	27.97	13.96	13.89	5.324	5.303	2.57	2.55	1.22	1.21
.2636	.2970	.3300	28.25	28.20	14.08	14.01	5.371	5.348	2.60	2.58	1.24	1.23
.2656	.2992	.3325	28.47	28.42	14.19	14.12	5.418	5.394	2.62	2.60	1.25	1.24
.2676	.3015	.3350	28.70	28.65	14.30	14.23	5.465	5.440	2.64	2.62	1.26	1.25
.2696	.3037	.3375	28.93	28.87	14.42	14.35	5.512	5.486	2.66	2.64	1.27	1.26
.2716	.3060	.3400	29.16	29.10	14.54	14.47	5.558	5.532	2.69	2.67	1.28	1.27
.2736	.3082	.3425	29.39	29.32	14.65	14.59	5.605	5.578	2.71	2.69	1.29	1.28
.2756	.3105	.3450	29.62	29.55	14.76	14.70	5.652	5.624	2.73	2.71	1.30	1.29
.2776	.3127	.3475	29.85	29.77	14.88	14.81	5.699	5.671	2.75	2.73	1.31	1.30
.2796	.3150	.3500	30.08	30.00	15.00	14.93	5.746	5.718	2.78	2.76	1.33	1.32
.2816	.3172	.3525	30.31	30.23	15.11	15.04	5.793	5.765	2.80	2.78	1.34	1.33
.2836	.3195	.3550	30.54	30.46	15.22	15.15	5.840	5.812	2.82	2.80	1.35	1.34
.2856	.3217	.3575	30.77	30.69	15.34	15.27	5.888	5.859	2.84	2.82	1.36	1.35
.2876	.3240	.3600	31.00	30.93	15.46	15.39	5.936	5.906	2.87	2.85	1.37	1.36
.2896	.3262	.3625	31.23	31.16	15.57	15.50	5.983	5.953	2.89	2.87	1.38	1.37

Wt. of Sample in 100cc.			1. Gram		2. Grams		5. Grams		10. Grams		20. Grams	
Polarization			30°	35°	20°	30°	85°	95°	85°	95°	85°	95°
Wt. Obtained as												
Cu	Cu_2O	CuO										
.2916	.3285	.3650	31.46	31.40	15.69	15.61	6.031	6.000	2.91	2.88	1.39	1.83
.2936	.3307	.3675	31.69	31.63	15.81	15.73	6.079	6.048	2.93	2.91	1.40	1.39
.2956	.3330	.3700	31.93	31.87	15.93	15.85	6.127	6.096	2.96	2.94	1.42	1.41
.2976	.3352	.3725	32.16	32.10	16.04	15.96	6.174	6.144	2.98	2.96	1.43	1.42
.2996	.3375	.3750	32.40	32.34	16.16	16.08	6.222	6.192	3.00	2.98	1.44	1.43
.3016	.3397	.3775	32.63	32.67	16.28	16.20	6.270	6.240	3.03	3.00	1.45	1.44
.3036	.3420	.3800	32.87	32.81	16.40	16.32	6.318	6.288	3.06	3.03	1.46	1.45
.3056	.3442	.3825	33.10	33.04	16.52	16.44	6.366	6.337	3.08	3.05	1.47	1.47
.3076	.3465	.3850	33.34	33.28	16.64	16.56	6.414	6.386	3.10	3.07	1.48	1.48
.3096	.3487	.3875	33.58	33.52	16.76	16.68	6.462	6.434	3.12	3.09	1.49	1.49
3116	.3510	.3900	33.82	33.76	16.88	16.80	6.510	6.482	3.15	3.12	1.51	1.50
.3136	.3532	.3925	34.06	34.00	17.00	16.92	6.558	6.531	3.17	3.14	1.52	1.51
.3156	.3555	.3950	34.30	34.24	17.12	17.04	6.608	6.580	3.19	3.16	1.53	1.52
.3176	.3577	.3975	34.54	34.48	17.24	17.16	6.654	6.629	3.21	3.18	1.54	1.53
.3196	.3600	.4000	34.78	34.72	17.36	17.28	6.703	6.678	3.24	3.21	1.55	1.54
.3216	.3622	.4025	35.02	34.96	17.48	17.40	6.751	6.727	3.26	3.23	1.56	1.55
.3236	.3645	.4050	35.26	35.20	17.60	17.52	6.799	6.776	3.28	3.26	1.57	1.56
.3256	.3667	.4075	35.50	35.44	17.72	17.64	6.848	6.825	3.30	3.27	1.58	1.57
.3275	.3890	.4100	35.75	35.68	17.84	17.76	6.897	6.875	3.33	3.30	1.60	1.59
.3295	.3712	.4125	35.99	35.92	17.96	17.88	6.945	6.924	3.35	3.32	1.61	1.60
.3315	.3735	.4150	36.24	36.16	18.08	18.00	6.993	6.973	3.37	3.34	1.62	1.60
.3335	.3757	.4175	36.48	36.40	18.20	18.12	7.042	7.023	3.39	3.36	1.63	1.62
.3355	.3780	.4200	36.73	36.65	18.33	18.25	7.091	7.073	3.42	3.39	1.64	1.63
.3375	.3802	.4225	36.97	36.89	18.45	18.37	7.139	7.122	3.44	3.41	1.65	1.64
.3395	.3825	.4250	37.22	37.13	18.57	18.49	7.188	7.172	3.46	3.43	1.66	1.65
.3415	.3847	.4275	37.47	37.37	18.69	18.61	7.237	7.222	3.48	3.45	1.67	1.66
.3435	.3870	.4300	37.72	37.62	18.82	18.74	7.286	7.272	3.51	3.48	1.69	1.68
.3455	.3892	.4325	37.96	37.86	18.94	18.86	7.334	7.321	3.53	3.50	1.70	1.69
.3475	.3915	.4350	38.21	38.10	19.06	18.99	7.383	7.371	3.55	3.52	1.71	1.70
.3495	.3937	.4375	38.46	38.44	19.19	19.12	7.432	7.421	3.58	3.55	1.72	1.71

THE DETERMINATION OF WATER IN MOLASSES

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In the determination of moisture in molasses and similar products in air, the analyst is confronted with several difficulties; first, the formation of an external film; second, the effects of oxidation; and third, if the temperature is near 100 degrees Centigrade, loss of water of hydration. All the better methods aim to overcome the first two of these difficulties as far as possible by distributing the material in a thin layer. It would, therefore, seem that any method that would still further reduce the thickness of the layer of material would result in a still greater rapidity of drying and a closer approach to the total water present.

It is not necessary to speak of the history of the several methods that have been suggested. The better ones divide themselves into two classes: first, those that depend upon a thin distribution of the undiluted sample; and, second, those in which the sample is diluted before being dryed. In air drying at elevated temperatures the action of air upon the sample is a function of the time required and of the surface exposed.

To determine, if possible, the best working conditions, a number of experiments were undertaken.

Into two flat bottom platinum dishes, 85 mm. square, and 20 mm. deep, 1.9553 grams and 2.0637 grams of molasses No. 1 were introduced. The first was distributed as evenly as possible without dilution, while to the second a little water was added to aid distribution. Both were then placed in a large well ventilated water oven at about 98 degrees Centigrade, with the following results:

TEST I

Time of drying	Loss Undiluted Sample	Diluted Sample
2 hours.	19.49%	18.58%
3 hours.	20.70%	20.35%
4 hours.	21.16%	21.31%
5 hours.	21.50%	21.64%
6 hours.		21.88%
7½ hours.		22.31%

Samples have darkened and drying was discontinued.

Two other samples of the same molasses, undiluted, were dried in the same dishes in a hydrogen oven at 99 degrees Centigrade. These were spread as evenly as possible. The results follow:

TEST II

Time of drying	Loss C	D
3 hours.	21.70%	22.15%
5 hours.	22.85%	23.24%
7 hours.	23.51%	24.02%
9 hours.	17.58%	17.62%

The samples had darkened much by this time and were showing a marked increase in weight. The original weight of " C " was 2.0390 grams, and of " D ", 2.0002 grams.

Neither of these methods proved satisfactory under the conditions used. The results of Test I, though fairly concordant, are much too low, as evidenced by those of Test II, which are not concordant one with the other.

A portion of the same molasses was diluted with water to a content of molasses of 24.73%. This was dropped as evenly as possible upon prepared dry pumice, all weights being obtained by difference, in accordance with the method given on page 64, 2(a)(2) of Bulletin 107, (Revised) of U. S. Department of Agriculture. Circular Aluminum dishes, 90 mm. diameter and 20 mm. deep were used. They were dried in air at approximately

98 degrees Centigrade. " E " contained 1.8896 grams of molasses and " F," 1.0725 grams.

Results were as follows:

TEST III

Time of drying	Loss E	Loss F
2 hours.	22.67%	22.98%
3 hours.	23.52%	24.25%
5 hours.	24.37%	24.94%
7 hours.	24.93%	25.54%
9½ hours.	24.94%	25.54%

The results of Test III are not sufficiently concordant, but are probably nearer the truth than either Test I or Test II.

An effort was made to increase the surface exposed, to diminish the time required, and to exclude the action of air by drying portions of the diluted molasses on asbestos pads, in tubes through which a current of dry hydrogen at approximately 98 degrees Centigrade was passing. The pads were made from purified, long fiber asbestos, by suction, on filter paper, on a Buchner funnel; dried, and stripped from the paper. They measured 110 mm. in diameter and were as thin as could be handled conveniently. They were rolled, placed within the drying tubes, all dried, and tared.

3.2911 grams of molasses solution carrying 0.8600 grams of molasses No. 1 was dried to constant weight on such a pad. Time, 1 hour, 20 minutes. Loss, 26.63%. An additional drying of one hour gave a total loss of 26.35%. (Test IV).

After several months interruption, a number of tests were made of molasses No. 2.

Undiluted samples, the weights of which were determined by difference, were placed, dropwise, in a spiral on the aluminium dishes before described. The drops quickly coalesced. Sample " G " weighed 1.1480 grams, and sample " H ", 1.5218 grams. " G " was dried in a water oven at 98 degrees Centigrade while " H " was dried in hydrogen at the same temperature. The results follow:

TEST V

Time of drying	Loss G	 H
3 hours.	22.68%	22.50%
4 hours.	22.85%	23.40%
5 hours.	23.39%	

At which time the weights were practically constant.

It seemed reasonable that a paper coil such as is used in the determination of fat in milk by Adams' process would be a suitable material upon which to dry molasses. Accordingly, an aqueous dilution of molasses No. 2, containing 31.325% of molasses was prepared. Sufficient amounts of this mixture, ascertained by difference, were placed upon each of three coils of S. & S. paper 65 mm. x 565 mm. to give 1.9996 grams of molasses on "K," 2,3247 grams on "L," and 2.3973 grams on "M" (Test VI).

"K" and "L," dried in hydrogen to constant weight, which required 2½ hours, lost 23.58% and 23.54%, respectively. "M" required 3 hours drying in water oven at 98 degrees Centigrade to reach constant weight, and lost 23.68%.

From these tests the following conclusions seem justified.

First: All samples should be taken by difference.

Second: Drying the undiluted sample in air at 98 degrees Centigrade can be done only when particular care is taken to place the sample dropwise upon the dish.

Third: Drying a diluted molasses on pumice is tedious and yields low results.

Fourth: With a paper coil, as used in Adams' method for fat in milk, and dilution of the molasses to approximately 30% strength, the water can be determined in air practically as accurately as in hydrogen, and in less time than is required by the other methods tried.

All of our methods are largely empirical, not absolute. And it must be remembered that in all the above methods, the water of hydration is included in the loss. To avoid this, it will be necessary to dry at a lower temperature, preferably at about 70 degrees.

The best conditions for determining total water in molasses, as finally worked out are as follows:

Dilute the sample to an accurate dilution, approximating 30% of molasses. Distribute approximately 7 grams, weighed accurately by difference, as evenly as possible upon a dried coil of S. & S. filter paper " Adams' method " about 65 mm. x 565 mm., previously tared with a weighing bottle. Dry for three hours in a capacious, well ventilated water oven at 98 degrees Centigrade. Cool, weigh, and calculate loss as total water. Or dry to constant weight at 70 degrees Centigrade and calculate loss as mositure.

SOME NOTES ON SUGAR MANUFACTURE IN PORTO RICO

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The growth of the sugar industry in Porto Rico has been enormous during the past decade, the production of the Island now being more than seven times the fifty odd thousand tons annually made under Spanish rule.

As in Cuba, the old muscovado house with its imposing chimney, dignified masonry buildings and picturesque "batey" is now an abandoned ruin or so transformed as to be unrecognizable in the ugly but efficient modern sugarhouse which has grown out of it. New sugarhouses of presumably the latest design have been built in many places throughout the land, and where there were but two in the whole island in Spanish days, dignified by the name of "centrals," there are now some forty or more centrals producing raw sugar by modern methods.

In the fields, modern cultivation has done much to increase yield. Artificial fertilizers have been introduced to considerable extent, but the steam-plow has been the most important agent in rejuvenating the level lands along the coast, furrowing the rich loam to depths untouched by the primitive implements of early days and bringing to the roots what is practically virgin soil.

Sugar statisticians as a rule speak of Porto Rico as having reached practically the limit of its sugar production owing to the belief that but little land remains which is available for further cane cultivation. This may be true under present conditions, but on the south coast, the richest sugar district of the island—where the greatest fluctuation in yield occurs from scarcity of rain and inadequate irrigation, there are large tracts of land on the gentle upland slopes which when the present plans of the government irrigation scheme are carried out will materially swell the acreage of cane land. Moreover, there are thousands of acres of land on both the north and south coasts now pestilential swamps or saturated with magnesia and alkaline salts which need but dyking and draining to be as fertile as the best in the island. The fertility of such reclaimed lands is well known and have been corroborated by experiments made on these lands in Porto Rico on a small scale. If the government irrigation plans in southern Porto Rico are successfully carried out, there will be a large amount of irrigation machinery no longer needed which it has been suggested can be made valuable in developing a drainage scheme for these littoral lands. These will add much to the present acreage for cane and be a material aid in making the yield of the south coast especially more independent of climatic variations.

The highly intensive methods of cane cultivation practiced in Hawaii have been tried to considerable extent on the island but have not proved wholly applicable to advantage. Owing to the shorter growing period of West Indian cultivation, such heavy stands of cane do not reach full weight and maturity.

The numerous varieties of cane which have found habitat in the West Indies are well represented in Porto Rico, but of the few which have proved most desirable on the south coast the best seems to be the crystallina, being superior to the white cane in its tolerance of climatic changes. On the north coast, where there is much more rain, certain varieties of striped cane seem to be favorites. Some of the new seedling canes have shown much promise.

In the wetter districts of the island, loss in sugar occurs from lack of care in keeping the ripened canes free from the ground when they become beaten down by the winds and rains. Such canes will often take root at the points in contact with the soil and become green again with consequent large sugar loss. This is prevented by raking trash under the prostrate canes and so lifting them off the ground, a well-known expedient but often neglected.

While in many of the sugarhouses, owing to the natural evolution of the industry, we find all stages of progress represented in equipment, the more important factories have been quite modernized by reputable sugarhouse engineers, and new ones have been built during the past decade from presumably the latest designs and according to the most advanced practice. In view of this, it might seem presumptuous to comment on the design of these factories were it not that there seems to be evidence, not only in the balance sheet but elsewhere, that many sugarhouses are by no means as efficient as they should be, due allowance being made for " bad years " and the like. It is somewhat difficult to summarize in few words the causes which contribute to this inefficiency, but the writer's experience shows that in general they can be brought under three heads: (1) Lack of proper facilities in bringing cane promptly from field to mill; (2) Lack of comprehension of the proper relation of the different parts of a sugarhouse to the design as a whole; (3) Carelessness (or ignorance) in working out details of design, which may appear to be unimportant but which are vital for efficient running.

The large sugar loss in cane after cutting, provided it is not ground at once, is well known to sugar chemists, tests of Phipson, for instance, having shown sugar losses of nearly three per cent. in the first twenty-four hours after cutting, eight per cent. in the second day, twenty-one in the third and thirty-two in the fourth. In Porto Rico, great losses occur from this cane deterioration after cutting. In the smaller factories this is due to neglect to work out the problems of transportation and handling cane. Money is spent freely on sugarhouse machinery often to replace old but efficient apparatus by some new type of more popular design or of reputed greater efficiency which if devoted to improving the antiquated system of cane transportation would go much further to increase the yield. In the larger houses, the handling of cane is better attended to, but it is far more difficult of satisfactory solution owing to the complexity of the local conditions affecting such large territories and particularly, in many cases, because the impossibility of completely controlling transportation through the sugarhouse management. In this matter of transporting and handling cane, apparently the Hawaiian sugar planters have done much better than the West Indian.

Certainly, a considerable percentage of the low purity of the cane juices of Porto Rico, particularly in the Southern districts where such purities should be quite abnormal, is due to the change in condition of the cane after leaving the fields.

In the following notes on sugarhouse details, no claim is made for novelty in the ideas advanced. Indeed, they are, for the most part, established principles of good engineering; yet, many of them, are ignored to a singular degree in most houses of recent build where no cost has been spared to obtain the best.

In general layout of the plant there is often a remarkable ignorance of local conditions. Boilers and mills are situated so that the prevailing winds, which blow with great constancy in one direction, carry the dirt and heat into and through the entire house, making neat work impossible. Frequently, for the same reason, pans and other steam apparatus are so placed as to make working at them almost unendurable, all of which could have been obviated in most cases by use of a little intelligence and at no extra cost of construction if considered in the original design. Often mills and boiling apparatus are placed in what are practically separate and unrelated buildings, the boiling-house being lofty and cramped and of a design suitable for a Northern refinery, but out of place in a tropical sugarhouse where land cost is negligible, easy supervision of plant is important. Conditions in the West Indies make low buildings desirable on general principles.

The boiler plants in most sugarhouses have been greatly improved in recent years, and besides the ordinary reliable type of multitubular boiler there are now in use many water-tube boilers which are designed with sufficient water space to satisfactorily meet the rather severe requirements of sugarhouse practice, emergencies arising where for a time the fuel supply is cut off or greatly straitened while the usual steam consumption continues. Few realize the advantage of ample boiler capacity, although a recognized principle of good engineering practice. A spare boiler or two is not a bad investment as some of the larger houses have learned, and many of these have some furnaces specially designed for burning coal or wood when such becomes necessary, as a bagasse furnace is a very poor coal consumer.

The proper conservation of the immense quantity of hot condensed-water from heaters and evaporating apparatus is very incompletely worked out in many sugarhouses, especially the smaller ones. In many houses the storage tanks are too small so that much runs to waste, or badly placed and left unused so that litter, pieces of cane from the mills and other dirt, contaminates the water.

One of the most unpleasant and expensive accidents which can happen in a sugarhouse is to get sugar into the boilers through leakage into some steam space of evaporating apparatus or heater. Every sugarhouse engineer has had such experience and is familiar with the cause, a joint gives way or a steam coil splits; the leak may be so small as not to be noticed; when the steam is turned off, and the apparatus is not running, there is a vacuum in the coil, the sugar is drawn in and later goes with the condensation water into the boiler-feed. The result is that the boilers prime dangerously, the slides and valves of pumps and engines are often so gummed as to require taking them down for cleaning; the boilers have to be blown down, and the whole plantation is brought to a standstill for half a day or more.

It is a very simple matter in designing a sugarhouse to arrange the main pipe-lines carrying the condensation water from the various apparatus so that they are collected at some central point, well-lighted and in plain sight, and at such place have traps with sight-glasses so that the condition of the water in each pipe can be seen at a glance. If such a station is systematically watched, any leak can be detected in time and quickly traced to its source. I have seen but one fairly satisfactory arrangement of this kind in a Porto Rican sugarhouse. No doubt there are several, but the usual way is to lead the tail-pipes to some open tank, often an old boiler, which owing to the nuisance of the escaping vapor is usually situated outside of the factory where it is not likely to have much surveillance. The propriety of equipping all steam traps and tail-pipes of individual coils with sight-glasses or pit-cocks where they are easily seen and accessible would seem obvious, but it is a detail which is not considered usually.

Many forms of bagasse furnaces which work well in Hawaii and other countries fail in Porto Rico owing to the difference in the ash. In the West Indian sugarhouses the furnaces make immense masses of clinker, a veritable glass, which clogs the grates and makes it necessary to remove the fire entirely and give each furnace a thorough cleaning at least once a day. Many furnaces are poorly designed for such cleaning. On this account, the step-ladder grates, such as are used in Hawaii, do not work well in Porto Rico at least without considerable modification of design to allow for the removal of clinker.

In planning steam lines, often very little consideration is given to the use of steam when starting the house and in "liquidating." But one or two of the largest sugar houses in Porto Rico are equipped with duplicate apparatus so that continuous running is possible. In all the others a stop of twelve hours or more every week or so is necessary to overhaul machinery and particularly for cleaning the heating surfaces of heating and evaporating apparatus. A well-designed factory should have valves on its main steam lines so placed that as different sections of the house are closed down corresponding portions of the steam and exhaust system can be cut off. In many houses this is impossible and a large and quite needless waste of steam is the result owing to the condensation, requiring the continuance of a large part of the boiler battery which otherwise could be laid off and fuel saved. Boilers are often cut off at such times in an attempt to save fuel with no gain as steam cannot be kept up and the work in consequence hobbles along for many hours, stopping from time to time to regain pressure for a fresh start. Intelligent design of pipe lines together with a little foresight in planning ahead systematically, so as to have the volume of thin liquors in process reduced to the minimum at closing time, would often save bills for extra fuel which would throw much light on certain phases of cost of production, did such items appear correctly on the factory reports.

Often this is equally true in working up of low-grade sugars in the centrifugals, owing to lack of intelligent design in steam supply. If the cost of production of such sugars were worked out separately, they would often be found needlessly expensive on this account.

Low steam troubles which at times occur unavoidably in the best regulated sugarhouses can be often much mitigated if condenser and other main water pumps as well as dynamo and centrifugal engines have their exhausts arranged with open by-passes to relieve back pressure in such emergencies and so enable working when it would be impossible otherwise. This is a small detail, comparatively inexpensive, but which saves fuel in emergencies and like fire insurance, is handy at times.

Cane mills have undergone much elaboration in recent years. The coupled type, with twelve rollers and crusher which has reached a high development in Hawaii, is being extensively introduced in Porto Rico. These mills have been specially designed for the extremely hard and dry New Caledonia cane which has largely surplanted the Lahaina cane in Hawaii, and with maceration with juice on the second and third mill and hot water on the fourth, these equipments have given remarkably high extraction under such conditions. These mills have also shown great efficiency in Porto Rico on dry, ripe cane, but under the conditions existing at many sugarhouses their work actually measured is no better than the nine-roller mills with crusher when the latter are properly adjusted. This is because of the nature and condition of the cane which is very generally received, which is soft with a tough, stringy fibre not giving high extraction with these mills. The writer has more than once had the opportunity to make critical tests of the work of a twelve-roller mill as compared with that of a nine-roller mill, working side by side for weeks at a time on the same average cane where every effort of experienced men was directed in getting the best out of each mill. According to theory, the twelve-roller mill ought to have done the better work, but it simply did not. This is no denial of what such mills can undoubtedly do under certain conditions, but is a warning to many in Porto Rico who are replacing good nine-roller mills by the twelve-roller type at great expense, that greater yield can be expected from improvement in cane than in present change of mill equipment.

Some of the larger houses have adopted methods of continuous defecation, claimed to be advantageous because the volume of liquor in process is less than by the old method of open defecation and so the house is more easily liquidated. In one of these processes, the most of the " mud " (cachaza) is settled in large, closed tanks with conical bottoms, the air and gases which interfere in the settling being removed by connecting the upper part of the vessel with the vacuum apparatus. The older, open defecation leaves little to be desired for most houses if it is properly designed and worked. Very frequently it is not.

The modern open defecator is not designed as a juice-heater. It is a very extravagant apparatus for such purpose. Its sole object is to produce a powerful convection in the juice already raised to the boiling point, and to furnish efficient means of separating by decantation the coagulated matter which has been thrown to the surface as a scum by the convection. Such defecators use but little steam. This necessitates juice-heaters of ample capacity in two or more units, so as to allow cleaning without interruption. The defecators proper should be broad and shallow, the diameter at least twice the height. They should have large heating surface in coils at the bottom and have decanting pipes fitted with hoods so that they are automatically stopped running by the scums, allowing nothing but clear juice to pass. Such defecators have been designed and used for more than twenty years in some successful Cuban sugarhouses; yet we rarely see this type in Porto Rico. Another important but vital detail often overlooked is to have proper facilities for keeping the heating surfaces clean by washing with condensed water or, preferably, raw, unlimed juice.

The scums from open defecators, moreover, are much more compact, there is less work for the filter-presses to do and less sugar in the filter-cake. We often hear suggestions to put more juice through the filter-presses, or even put all of the juice through. With properly defecated juice this is entirely unnecessary and wasteful. In any process, decantation is always more economical where applicable. So too, secondary filters, sand filters and the like, are unnecessary with proper defecation system. The modern high-extraction mills make much fine bagasse (" bagacilla ") which is not effectively removed by the mill machinery designed for the purpose. This fine material is not thrown into the scums by the settling methods of defecation and consequently passes into the evaporating apparatus, if not removed by filtering the decanted juice again or by screening, and does much mischief by clogging the apparatus, especially of the drip-feed type.

Filter-press plants have been much improved in recent years and in most houses are equipped with efficient pressure regulators on the pumps. Most houses have not yet learned that the most efficient method of washing filter-press cake, if done in the presses, is by hot soft-water by gravity pressure from an upper floor tank, although this is extensively practiced in European beet-houses. Many run filter-presses too slowly so that it is a matter of several hours to fill a press, which causes souring. Low sugar percentage in the cake is often from this cause rather than from actual removal of the sugar. One or two sugarhouses have made considerable progress in the problem of handling the press-cake for a fertilizer, but as a rule, work of this sort has been very crude.

Many sugarhouses have replaced the standard type of evaporator by the drip-feed film evaporator owing to its greater evaporating efficiency, when clean, and the small volume of residual liquors which have to be worked off in liquidating. There are, however, disadvantages to this type of apparatus. Its efficiency is apt to fall off rapidly owing to the fouling of heating surfaces in spite of elaborate arrangements designed to prevent this. If the juice is not perfectly screened, the distribution plates may get clogged in places and corresponding evaporating areas cut out. There are no sight-glasses by which such troubles can be quickly located. The time saved in liquidating such apparatus is lost in cleaning. Caustic potash which need be used only in special cases for cleaning apparatus of the standard type is absolutely necessary for the preliminary washing of drip-feed evaporators. The foaming of the viscous caustic solution carries it to all parts of the heating surface and so softens the scale on the under side of the pipes not reached effectively by a boiling acid solution, which does not prevent stalactitic growths of scale. This makes the cleaning of such apparatus expensive and tedious because a washing, acid treatment and then a second washing has to be given afterwards, using steam not only for the boiling but for driving the circulating pumps which in large effects use a hundred horse-power or more.

In many houses the principal steam waste is in the pan-room. Proper sugar boiling, especially for molasses sugars, is greatly facilitated by having constant steam pressure, and this pressure should be low so as to ultilize all of the exhaust at a back pressure of 5-7 lbs. As there is not enough exhaust for all the juice heating, boiling and evaporating of the house, the pressure has to be maintained by live-steam injection into the exhaust system. In European beet-sugar houses, the plan recommended is a feed into the juice heater regulated by hand according to the indications of the gauge. Most Porto Rican sugarhouses have no regulation for keeping the exhaust pressure constant but use what excess is left from the evaporating apparatus in the pan coils, making up the deficiency with live steam. Sometimes in skillful hands, this arrangement works fairly well, but often the boiling is irregular and wasteful of steam.

Automatic regulation of the back-pressure by a reducer-valve opening into a recipient or juice-heater is in use in some houses. This arrangement has been used in Cuba for twenty years or more with fairly good results, and in the writer's experience is the best. Such systems are rarely carried out with intelligent consideration of some of the details necessary for good work. Some reducing valves are beautifully made and work well till some bit of scale in the pipes quite stops their working. Such are not suited for sugarhouses. No reducer can be relied upon to deliver steam within less than two or three per cent. variation on the initial pressure, so the proper way to reduce steam to practically constant low pressure in sugarhouse practice, which usually is from about 100 lbs. to 7, is to reduce in two stages, say by one reducer to about 40 lbs. and then pass the steam through a second reducer set for the constant pressure required. I know of but one sugarhouse with such an arrangement, although it is a well-known practice in factory engineering.

Some of the largest Porto Rican sugarhouses are using electric power, usually the three-phase system, for conveyor motors, centrifugals and the like. This tends to cut down the supply of exhaust steam and in future designs may lead to adoption of the Continental method of taking steam for the pans from a specially designed multiple effect. The previous paragraphs refer, of course, to present conditions.

Many vacuum-pans in use in sugarhouses will not work effectively with low-pressure steam. Quite recently, the writer has had experience with such pans in three Porto Rican sugarhouses.

These pans were modern, being quite new and the product of a well-known manufacturer. They made excellent sugar, when they had sufficient steam pressure and would be well suited for refinery practice where pressures of 60 lbs. were used. It was impossible with any of these pans to make a strike of sugar without 35 lbs. of steam and have the pan boil in reasonable time and make sugar efficiently. Such pans are wasteful for sugar houses, as perhaps can be best illustrated by the condition in one of these houses in Porto Rico, just referred to. This is a small but quite modern house, designed and built in the past five years. Grinding at the rate of about 450 tons per day, with the single engine of the nine-roll mill making about forty revolutions, the exhaust of the house was just sufficient for juice heaters and triple-effect evaporator, but conditions were changed when grinding at full capacity of 600 tons with the engine running a few revolutions more and the exhaust of the house correspondingly increased. Although the evaporator used more steam, there was an excess of exhaust. This could be utilized in the pans only while concentrating the charge of syrup. As soon as graining started, it was necessary to use live steam. The result was a big steam loss, often for hours, while the exhaust relieved itself over the roof.

There is no excuse for installing such pans as there are others of equally well-known makes and of equal capacity which will boil a strike of sugar in five hours or less with five pounds of steam. There are such in Porto Rico and many in Cuba of identical design which have done such work for more than twenty years. It is not a matter of greater heating surface so much as its arrangement and the design of the pans, which are low and broad. It is only in the more recent editions of the standard works of the Dutch engineers on sugar manufacture that we find reference to the superiority of such pans notwithstanding twenty years or more practical experience with such in the West Indies.

When a pan-room is properly designed to use steam at constant low pressure, live steam is only used for boiling in case of emergencies or in at the close of liquidating, when there is little exhaust and it may be more economical owing to excessive condensation or radiation to shut out live steam from the low-pressure system.

There are often other defects in design of such arrangements outside of those mentioned. Few engineers seem to give proper attention to the special difficulties of properly removing condensation from low pressure coils. Often the traps are not adapted for low pressure when these are used instead of siphons which, when properly arranged and fitted, are best, or two or more coils are connected on one discharge pipe, there being no check-valves to prevent backing up and "water-logging." Further, how many pans are fitted with pit-cocks in the discharge-pipes of the coils, or other similar devices by which the pan-man can quickly ascertain whether all coils are working properly? Very few pans have proper connections so that time can be economized by graining a charge large enough for two boilings in one pan which can then be "cast over" to a second pan, a very useful expedient in many cases and far preferable to "cutting" a finished strike.

Most Porto Rican sugarhouses are equipped with crystallizers, which are usually worked by cooling through radiation, the jackets being rarely used. Often the capacity of these crystallizers has no special relation to that of the pans, strikes being dropped one on another helter-skelter, the sole criterion of work being a low-purity molasses irrespective of the quantity. Some of the houses work more intelligently. Few have facilities for properly treating first molasses for reboiling. Usually any kind of a tank with a steam-pipe and water connection goes. Apparatus designed for this purpose pays well.

Centrifugal equipments are as a rule good. A few houses use the larger machines, but these are not advisable unless the equipment is big enough to have such machines used exclusively for first sugars. In the majority of the houses, all centrifugals have to be arranged to take care of seconds at times, and such sugars only purge best in the smaller machines, 30 to 36 inch, and such are generally used.

Electric power is being introduced in the larger Porto Rican houses, and this has been applied to centrifugals in various ways, sometimes by a motor as a prime mover, or by individual motors direct driving or connected by belting. The latter seems by far the simplest, especially where old installations are to be changed to electric drive, as all that is necessary is to remove the jack shaft and drive each machine with an individual motor placed back of it and connected with a quarter-turn belt. This arrangement has been seen by the writer in successful operation in a large New York refinery.

We hear much about the laziness and inefficiency of the Porto Rican laborer. The writer has had considerable experience with such labor and has found that picked men have proved excellent workmen. Without doubt the physical energy of the Porto Rican laborer is less on the average than that of the northerner but even this is not universally true, as anyone can observe who has seen a gang of roustabouts loading a steamer where each man carries singly 300 lbs. sugar bags on his head all day up steep gangplanks and for many yards. There are many laborers who have been taught to work systematically on the old estates and are easily trained to do good work in the modern sugarhouse. As a rule, the writer has found the Porto Ricans poor mechanics, although there are occasional notable exceptions. The Porto Rican workman of the better class has different habits and ways of living than the American, but it does not follow that the former's manner of living is necessarily so inferior at all points or that it is good business to make the Porto Rican conform in all respects to Northern ways; yet, many seem to think this. It is on this account that the native laborer works much better under native foremen, and the writer has found some of the latter of good executive capacity, faithful and efficient.

One of the difficulties which some of the larger sugarhouses have had in keeping efficient labor has been due to lack of intelligent consideration of the human element either as such or as a part of the business machinery. Many sugar estates are communities by themselves some distance from large settlements and are therefore obliged to house and often board their laborers. This entails many responsibilities on builders and management which are rarely given the attention their importance requires even when considered on purely business lines and viewing the laborer as merely a necessary adjunct to the machinery. For the purpose of obtaining the maximum efficiency of labor, if for no other reason, it would be good business for the larger estates at least to employ a capable sanitary engineer to deal with these problems on broad lines. It is generally understood that we have much to learn from the British colonies in taking care of labor intelligently.

As to chemical control in Porto Rican sugarhouses, the more important ones have dealt with this very well and most centrals have well-equipped laboratories and employ efficient chemists. Owing to the usual cane-contracts, in which the cane is paid for according to the estimated yield of the sugarhouse, as calculated from the sugar content of the cane when delivered by the planter, an elaborate system of laboratory testing is necessary, some of the larger centrals receiving cane from 50 or more separate plantations. This requires much book-keeping, which is frequently given to the laboratory assistants to the detriment of other important laboratory work. The chemical control of the factory tends to suffer, samples being taken in a perfunctory way, with no special care to insure their being representative. Indeed, the majority of houses spend freely for laboratory equipment and make but little provision for insuring proper sampling. If organization and facilities for this are lacking, of course much of the laboratory work is quite worthless, especially if the yield and extraction were calculated exclusively from analyses made on such samples as has been the practice in Java and Hawaii. In Porto Rico, usually such figures are based on actual weights or measurements of cane, juice and products in process, most factories having more or less crude facilities for making such measurements.

The Dutch chemists and engineers have given more attention to control measurements than in the West Indies. For instance, in many houses in Java, the efficiency of each effect of the evaporators is measured and the condition of the apparatus followed daily. It is very easy to do this with any evaporator whose heating surface is known by attaching suitable sampling traps and determining the Brix of the liquors passing through the evaporator. The writer has already referred to the usefulness of recording-gauges for steam and vacuum (in his book on the polariscope) and has had personal experience of their value. He will only reiterate here that it pays to go to the expense of installing such apparatus properly with pipes tight and properly trapped and to have them located in the office or laboratory not exposed to the dirt, heat and vibration of the factory. Otherwise it is better not to use such gauges at all as they will be worse than useless.

But a few words need be added on the methods of sugar boiling in Porto Rico, as while in general they are on the same lines, the quality of the work done varies much. The larger sugarhouses, most of them, follow the scheme of boiling developed by the Dutch chemists and outlined in the papers of Prinzen Georligs, namely, boiling firsts from pure juice, sometimes reducing the purity of these massecuites by boiling in molasses liquors after graining, if the original purity is much above 80; making " 1-2 sugars by building the first molasses into a syrup grain, the massecuite being made of 74-75 purity; and finally boiling in the molasses from this second strike on grained juice, making massecuites of 59-60 purity for the crystallizers. These crystallizer sugars usually have been made to polarize 90-94 and have been shipped for firsts, but recently owing to a higher standard being demanded by the refiners, they are worked back to a much greater extent into 96 sugars by remelting or direct mixing, no houses to the writer's knowledge being equipped with proper apparatus to work these back in any considerable quantity into the first massecuites as is done in Java, apparently. In Java they are boiled closer and left a shorter time in the crystallizer giving sugars of 80 or less, which are worked back into the first massecuites in the mixer. Most of the sugarhouses, large and small, which are equipped with crystallizers follow this general plan of boiling more or less closely, depending on facilities of the house and the intelligence of the sugarboilers. The largest houses have learned the necessity of having men of experience, trained in raw and refinery work, for sugar boiling and so, employing the best obtainable, do excellent work in the pan-room in consequence. There are many native sugar-boilers who can do good work if directed. These understand the manipulation of the pan well enough and make good sugar, but are lacking in that ability to plan work for greatest capacity with most economy and in mechanical knowledge which comes from the training and experience of the man who has worked for years both in refinery and sugarhouse.

The one criterion of good work in many houses seems to be to get a final molasses of 30 purity or thereabouts, no attention being paid in most houses to the quantity. The Javan process, as carried out in Porto Rico, works very well with juices of certain quality, but it is questionable in some cases whether more sugar cannot be made by conducting the boiling so as to obtain a molasses of about 57 purity and then make a blank strike. The final molasses would have a purity but little under 40 if at all, but there would be much less of it and the actual sugar lost would be less. Such a method which is by no means novel but is carried out successfully in some places, and follows the logical course of concentrating the impurities into comparatively small bulk rather than distributing them through a greater volume in order to induce crystallization at the expense of good sugar liquors. Certainly the Javan process as carried out in many houses gives no improvement on yield over the method on the older plan. Obviously, too, the measure of efficiency is shown by the quantity of sugar lost in the molasses rather than by its purity, a datum which few houses have correctly.

Summing up—The Porto Rican sugarhouses while up-to-date in equipment and equal to the average anywhere, still could be greatly improved in efficiency if engineers would make a more thorough study of local conditions and working requirements, especially those which can be met only by close study of details. A sugarhouse is an organism in a sense, and not merely a collection of machinery of calculated proportions. This is why the card-files of the central office may show two houses identical as far as rated capacity is concerned as figured out for each individual piece of machinery, and capital invested and yet the respective work of the two houses may be quite different. Labor efficiency, in most cases, also depends to a large extent on engineering problems which must be worked out locally, not in a New York office.

These notes taken from the writer's own experience are set forth merely as suggestive of some of the problems worthy of attention of sugarhouse engineers and managements.

AN ELECTROLYTIC APPARATUS FOR USE IN INVERT SUGAR DETERMINATIONS

By B. B. Ross

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A number of years ago the writer described a method for effecting the electroyltic estimation of copper in connection with invert sugar determinations (Jour. An. and Appl. Chem. VII, 83) and at that time gave a number of results showing its accuracy and ease of execution in actual laboratory practice.

The process referred to was a modification of a method originally proposed by Formanek (Ztschr. Zucker-Ind. in Boh., 1890, 178) and involved the electrolytic deposition of the reduced copper from a dilute solution in nitric acid, whereas the electrolytic method generally in use at that time required that sulphuric acid in excess should be added to the nitric acid solution of the copper, the nitric acid being expelled by evaporation in a platinum dish.

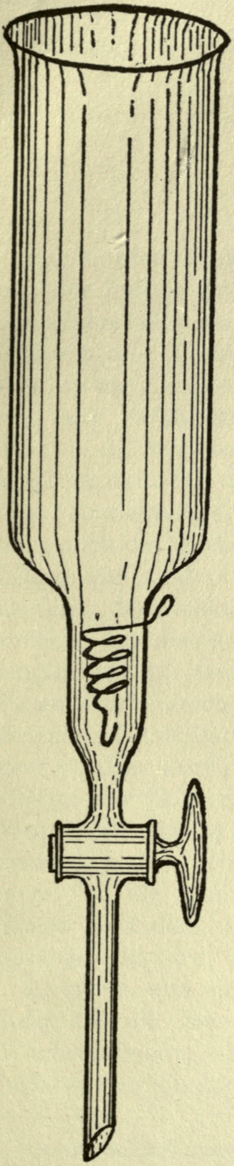
One of the chief advantages of the modified method was that it was not necessary to dissolve the precipitated cuprous oxide on the filter, while the long tedious washing necessary to free the asbestos filter of copper was also obviated, the filter and precipitate being simply transferred to a beaker containing a flat platinum spiral which served as an anode, while the cathode was a platinum cylinder suspended by a heavy platinum wire from an electrolytic support. About 200 c. c. of very dilute nitric acid containing about 4 c. c. of acid of 1.42 Sp. gr. per 100 c. c. were introduced into the beaker and the electrolytic process was at once begun, the cuprous oxide in close proximity to the anode being gradually oxidized and brought into solution, while a steady and regular deposition of copper on the cathode was at the same time taking place.

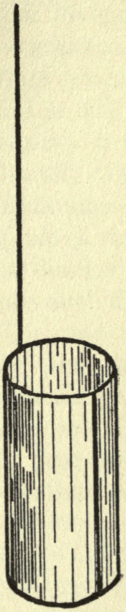
In carrying out this method in more recent years, the writer has made use of a special apparatus, which has very greatly simplified the execution of this process, a filtering tube of special construction having been devised for use in connection with the modified electrolytic method above described. This funnel tube, as will be noted from the accompanying figure, is provided with a ground glass stop cock and with a platinum spiral, one end of which passes through the constricted portion of the tube.

The alkaline cupric solution, properly diluted, is heated to boiling and an amount of invert sugar solution insufficient to reduce all of the copper is run in, the precipitation being effected in the usual manner. An asbestos filter is arranged in the lower portion of the filtering tube, which is connected with a filtering flask, and the precipitated cuprous oxide is brought upon the filter and thoroughly washed with hot water, as is the custom.

The stop cock is then turned at right angles and the funnel tube is filled about three fourths full of dilute nitric acid of the strength above mentioned. A platinum cylinder, such as is shown in the figure, is immersed in the dilute acid and serves as the cathode, while the platinum spiral, also shown in the figure, is used as the anode. A current yielding not more than 1 c. c. per minute of electrolytic gas should be employed in order to secure the most satisfactory deposition of copper. The liquid is drawn off and the cylinder washed in the usual way, preparatory to drying and weighing.

By the employment of this apparatus, the transfer of the filter and contents to another vessel is obviated and the manipulation essential to carrying out the electrolytic method is reduced to a minimum. Numerous tests of the solution left in the funnel, on the completion of the electrolysis, showed the liquid to be free from copper, while results given in the original article demonstrated the accuracy attainable by the use of this method.





EINFLUSS DER BELICHTUNG AUF DAS WACHSTUM DER SAMENRÜBE

VON F. STROHMER

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Bekanntlich hängt die Entwicklung der Pflanzen nicht nur von der Zufuhr der zu ihrem Wachstum notwendigen Mengen von Nährstoffen ab, sondern auch von den anderen Vegetationsfaktoren, wie Wärme und Licht, welche in das Minimum gekommen, so wie jene das Wachstum beeinträchtigen. Es ist ja schon eine alte Erfahrung, dass Lichtmangel die quantitative Produktion der organischen Substanz der Pflanze herabsetzt. Bei der Zuckerrübe ist das Studium des Einflusses der Belichtung auf ihre Entwicklung jedoch von besonderer Bedeutung, als ja das licht auch die Quelle der Zuckerbildung ist und daher durch die Menge der Lichtzufuhr nicht nur die Quantität sondern auch die Qualität der Zuckerrübenernte beeinflusst wird. Wie und in welcher Art dieses bei der gewöhnlichen Zuckerrübe, also der einjährigen zur technischen Verarbeitung bestimmten Zuckerrübenpflanze geschieht, habe ich in einer gemeinsam mit H. Briem und O. Fallada durchgeführten Arbeit[1] dargetan und dort gezeigt, dass durch Lichtmangel vor allem das Wachstum der Blätter der Zukkerrübe in auffallender Weise auf Kosten der Wurzelentwicklung gefördert wird und dass ferner die Zusammensetzung der Wurzeltrockensubstanz durch Lichtmangel in einer für die technische Verarbeitung derselben ungünstigen Weise verändert, besonders aber der Zuckergehalt derselben herabgesetzt wird.

Es schien nun von grossem Interesse, den Einfluss der Belichtung auf die Entwicklung der Zuckerrübe in ihrem zweiten Wachstumsjahre, also auf die Samenrübe zu studieren und zu untersuchen, ob auch bei dieser der Lichtmangel das Wachstum

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[1] Oesterreichisch-ungarische Zeitschrift für Zuckerindustrie und Landwirtschaft, XL. Jahrg. 1911, page 11.

der oberirdischen Teile begünstigt und hiedurch der Samenertrag eventuell gesteigert werden kann und ob ferner durch die verschiedene Belichtung die innere Qualität des geernteten Samens beeinflusst wird. Zu diesem Behufe wurden von mir Versuche und zwar ebenfalls in Gemeinschaft mit H. Briem und O. Fallada ausgeführt und zwar wieder wie unsere eingangs erwähnten Untersuchungen auf der Wohanka schen Rübensamenzuchtstation in Uholičky. Zu denselben wurden drei gleichschwere Mutterrüben I, II and III von schöner Form, mit dem gleichen Gehalte von 18.0% Zucker in der Rübe, ausgesucht und jede mittelst eines Schnittes in Zwwi gleiche Hälften zerlegt. Der Schnitt wurde selbstverständlich auf jener Rübenseite geführt, wo keine Seitenwurzeln waren, so dass von jeder Rübe gleichwertige Hälften a und b resultierten. Die einzelnen Rübenhälften kamen am 20. April, 1910, auf einem Samenrübenfelde vollkommen gleichmässiger Beschaffenheit zum Anbau und zwar so, dass die Hälften Ia. IIa und IIIa volle $\frac{3}{4}$ des Tages von der Sonne beschienen waren, während die Hälften Ib, IIb und IIIb daneben unter Bäume gepflanzt wurden, wo sie vollstän dig in Schatten wuchsen.

Bekanntlich war die Sommerwitterung des Jahres 1911 in Mitteleuropa und daher auch in Oesterreich eine sehr trockene, also für den Versuch, in Bezug auf Ertrag eine ungünstige. Da aber bei demselben alle Vegetationsfaktoren bis auf den zu prüfenden-das Licht-die gleichen waren, so muss sein Resultat doch als brauchbar bezeichnet werden. Den Witterungscharakter am Versuchsorte charakterisieren nachstehende Zahlen:

	April	Mai	Juni	Juli	August
Mittlere Temperatur C	8.61	13.94	17.06	20.93	20.6
Maximal Temperatur C	13.87	19.2	22.7	26.35	26.1
Minimal Temperatur C	3.64	8.1	10.8	14.84	14.8
Niederschlagsmenge mm	9.0	30.2	15.1	38.9	36.3
Regentage:	8	13	10	4	6

Infolge der grossen Trockenheit, wurden die Pflanzen notreif und mussten dieselebn am 10. August 1911 geerntet werden, wobei wir jede Pflanze samt der Wurzel aus dem Boden zogen. Von der in dem genannten Jahre in Böhmen stark auftretenden

Blattlausplage blieben jedoch die Versuchskulturen vollständig verschont.

Nachdem die geernteten Pflanzen lufttrocken geworden waren, wurden sie in Wurzeln, Stengel und Blätter und Samen zerlegt, wobei unter Samen die vollständig reinen Samenknäule zu verstehen sind. Hiebei wurden erhalten in Gramm:

Rübe:	I		II		III	
Hälfte:	a	b	a	b	a	b
Samen:	98.0	25.0	106.0	28.0	23.0	1.4
Stengel und Blätter:	134.0	57.0	132.0	69.0	71.0	26.6
Wurzel:	85.0	55.0	92.0	58.0	62.0	14.0

Hiezu wollen wir bemerken, dass sich das Fleisch der Rübe III schon beim Zerlegen in die beiden Wurzelhälften nicht ganz gesund erwies und die von derselbein herrührenden Pflanzen im Wachsteum stets zurückblieben; der Einfluss der Beschsttung respektive des Lichtmangels, machte sich jedoch auch bei dieser Rübe in derselben Weise geltend, wie bei den gesunden Pflanzen, dass nämlich auch bei der Samenrübe durch verminderte Lichtzufuhr das Produktionsvermögen sehr bedeutend herabgesetzt wird und dass diese Produktionsverminderung besonders stark im Ertrage an Rübensamenknäulen zum Ausdrucke kommt; denn bezeichnet man diesen Ertrag bei den belichteten Pflanzen mit 100, so wurden bei den beschatteten Rüben

I	25.5
II	26.4
III	6.1

Rübensamenknäule geerntet. In diesen Zahlen kommt auch deutlich die Tendenz zum Ausdruck, dass der Samenertrag umso besser ist, je kräftiger die ausgesetzte Mutterrübe war. In Bezug auf das Verhältnis von Wurzelgewicht zum Gewicht der produzierten Menge oberirdischer Pflanzenteile, ist jedoch der Einfluss des Lichtmangels bei der Samenrübe, wenn man von der kranken Pflanze III absieht, ein geradezu umgekehrter, wie bei dem Wachscum der Rübe in ihrem ersten Wachstumsjahre, freilich hat hier die Wurzel auch andere Funktionen zu erfüllen als bei der Samenrübe.

Die Lichtwirkung auf das Produktionsvermögen der Samenrübe macht sich jedoch nicht nur in der Erhöhung des Gewichtes der geernteten Samenmenge geltend, sondern auch in der Grösse der einzelnen Knäule, denn auf 1 Gramm entfielen Knäule bei

Rübe:	I		II		III	
Hälfte:	a	b	a	b	a	b
	78	94	74	84	90	111

Die Knäule der belichteten Rüben waren also schwerer, demnach in dieser Beziehung qualitativ besser als die beschatteten und war die am häufigsten vertretene Knäulgrösse bei

Rübe:	I		II		III	
	a	b	a	b	a	b
zwischen mm	3½–4	3–3½	3–3½	3–3½	3–3½	3–

Um zu erfahren, ob die vershciedene Lichtzufuhr auch die innere Qualität der Samenknäule beeinflusst hatte, wurde auch die Keimfähigkeit der geernteten Samen bestimmt und hiebei gefunden:

Rübe:	I		II		III[1]
Hälfte:	a	b	a	b	a
Von 100 Knäulen waren keimfähig					
nach 7 Tagen:	50	66	59	53	52
nach 14 Tagen:	50	69	63	54	53
Keime von 100 Knäulen					
nach 7 Tagen:	73	98	92	73	59
nach 14 Tagen:	80	103	98	76	60

Ein eindeutiger Unterschied in Bezug auf Keimfähigkeit zwischen den Samen der belichteten und unbelichteten Mutterrüben

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[1] Wegen der geringen Samenmenge wurde die Untersuchung auf Keimfähigkei tbei der Rübe III b unterlassen, der Samen jedoch zum Anbau gebracht.

lässt sich demnach nicht erkennen und ist die Qualität sämtlicher Samen eine minderwertige, was gewiss inder trockenen Witterung, unter welcher sie erwachsen waren, seine Ursache hat. Wenn sich nun auch kaine durch die verschiedene Belichtung bedingte verschiedene Keimfähigkeit der Samen erkennen lässt, so ist es doch nicht ausgeschlossen, dass die Nacykommen der belichteten und beschatteten Mutterrüben, also dic entsprechenden Fabriksrüben, sich untereinander qualitativ unterscheiden. Um in dieser Richtung Klarheit zu gewinnen, wurden die geernteten Samen im laufenden Jahre an zwei verschiedenen Orten und zwar in Niederösterreich und in Ungarn angebaut, mit welchem Erfolge, kann selbstverständlich gegenwärtig, wo das Wachstum der Rüben nicht abgeschlossen ist, noch nicht gesagt werden; es sei jedoch bemerkt, dass der Aufgang der verschiedenen Samen ein vollständig gleichmässiegr war. Wenn demnach der Versuch auch noch nicht vollständig abgeschlossen ist, so glauben wir dennoch, dass die hier mitgeteilten Beobachtungen bezüglich des Einflusses der Belichtung auf das Wachstum der Samenrübe bereits die Beachtung der Interessenten verdienen.

INVERSION VON ROHRZUCKERLÖSUNGEN MIT TELST CHLORAMMONIUM

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Schon vor längerer Zeit haben wir dargetan,[1] dass anzunehmen ist, dass Chlorammonium in einer wässerigen Lösung nicht als solches vorhanden ist, sondern vom Wasser in NH_3 und H Cl dissoziiert und deshalb Rohrzucker beim Erwärmen mit solcher Lösung invertiert wird. In dieser Beobachtung schien uns ein Weg für die korrektere Ausführung der Rohrzuckerbestimmung in unreinen Zuckerlösungen mittelst der sogenannten Inversionsmethode gegeben zu sein. Es ist bekanntlich bei der zuletzt genannten Methode eine Fehlerquelle darin gelegen, dass die direkte Polarisation in neutraler, die Inversionspolarisation dagegen in saurer Lösung ausgeführt wird; verschiedene schwer entfernbare Nichtzuckerstoffe, namentlich solche stickstoffhaltiger Natur, aber in neutraler lösung ein anderes optisches Drehungsvermögen aufweisen als in saurer. Hiedurch muss naturgemäss das Resultat der Untersuchung nach genannter Methode, welche eben für inhre Richtigkeit die optische Unveränderlichkeit des Nichtzuckers durch die Inversion voraussetzt, beeinflusst werden. Wäre die vollständige und glatte Inversion einer Rohrzuckerlösung mittelst Chlorammonium durchführbar, so könnte hiedurch die Möglichkeit gegeben sein, sowohl die direkte als auch die Inversionspolarisation in neutraler Lösung auszuführen und könnte so die oben erwähnte Fehlerquelle vielleicht umgangen werden.

Um die Inversionsbedingungen des Rohrzuckers für Chlorammoniumlösungen kennen zu lernen, wurden nun von uns eine Reihe von Versuchen vorgenommen. Bei denselben kamen

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[1] Oesterreichisch-ungarische Zeitschrift für Zuckerindustrie und Landwirtschaft, XXXV. Jahrg. 1906, p. 168.

nach Mohr geaichte Gefässe und folgende Lösungen zur Verwendung:

Rohrzuckerlösungen. Solche die wenn nichts anderes bemerkt ist 13.024 g reinen Kristallzucker von 99.8% Polarisation zu 50 cc bei 20° C gelöst enthielten.

Chlorammoniumlösungen verschiedener Konzentration wobei von einer solchen ausgegangen wurde, welche in 30 cc genau 0.332 g NH_4Cl enthielt und demnach einem Zehntel jener Menge H Cl äquivalent war, wie sie bei der gewöhnlichen Inversion zur Verwendung kommt.

Die Versuche führten wir dann in der Weise aus, dass wir 50 cc der Rohrzuckerlösung mit 30 cc der Chlorammoniumlösung in einem 100 cc Kölbchen mischten, in unten angegebener Weise in einem Wasser- oder Chlorkalziumbade erhitzten, dann rasch abkühlten worauf bei 20° C auf 100 cc aufgefüllt und nach gründlichem Durchschütteln und Filtrieren im 200 mm Rohr im Apparat mit Ventzkeskala polarisiert wurde. Bei diesen Versuchen ergaben sich die in Tabelle I verzeichneten Resultate:

TABELLE I

Versuch-snummer	50 cc. Zuckerlösung mit g. Zucker	30 cc. Chlorammoniumlösung mit g. NH_4 Cl	Inversions—		Auf 100 füllte Aussehen	cc. aufge- Lösung Polarisationsgrade
			Temperatur C	Dauer Minuten		
1	13.024	0.332	20	30	farblos	+ 49.9
2	13.024	0.332	20	60	farblos	+ 49.9
3	13.024	0.332	69	5	farblos	+ 49.9
4	13.024	0.332	69	30	farblos	+ 45.1
5	13.024	0.332	110	60	farblos	+ 31.5
6	13.024	1.99	20	30	farblos	+ 49.9
7	13.024	1.99	100	60	farblos	+ 37.5
8	13.024	1.99	100	120	gelblich	+ 19.1
9	13.024	5.00	100	60	farblos	+ 22.1
10	13.024	5.00	100	120	gelb	+ 13.1
11	13.024	5.00	110	60	gelb	+ 3.6
12	13.024	10.00	100	60	gelb	+ 19.5
13	6.512	5.00	100	60	gelblich	+ 11.4
14	13.024	gesättigte Lösung	110	30	lichtgelb	+ 6.5

Aus den Zahlen der Tabelle I ist nun ersichtlich, dass durch Behandeln von Saccharose mit Chlorammonium in wässeriger Lösung jene invertiert werden kann und dass die Grösse dieser Inversion mit der einwirkenden Menge des Chlorammoniums wächst und ebenso durch Erhöungh der Einwirkungsdauer und der Einwirkungstemperatur gesteigert werden kann. Die Ergebnisse zeigen aber auch, dass sich keine für die analytische Praxis brauchbare Kombination dieser Reaktionsfaktoren ausfindig machen lässt, bei welcher die Inversion der Saccharose eine glatte und vollständige wäre und bei welcher sich nicht auch schon Zersetzung des bereits gebildeten Invertzuckers einstellen würde. Da somit das gesuchte Ziel nicht erreicht wurde, versuchten wir ob sich nicht die Reaktion durch Anwendung von Katalysatoren beschleunigen liesse und wurde deshalb dem Reaktionsgemisch vor dem Erwärmen eine kleine Menge Zinkstaub oder Platinmohr zugesetzt, wobei sich die in Tabelle II verzeichneten Resultate ergaben:

Tabelle II

Versuchsnummer	50 cc. Zuckerlösung mit g. Zucker	30 cc. Chlorammoniumlösung mit g. NH_4Cl	Inversions—		Auf 100 cc. aufgefüllte Lösung	
			Temperatur C	Dauer Minuten	Aussehen	Polarisationsgrade
KATALYSATOR: ZINKSTAUB						
15	13.024	5.0	100	60	farblos	+ 21.5
16	13.024	10.0	100	60	farblos	+ 10.2
17	6.512	5.0	100	60	gelblich	+ 11.4
KATALYSATOR: PLATINMOHR						
18	13.024	10.0	100	60	gelb	+ 20.4
19	13.024	10.0	100	120	dunkelgelb	+ 1.9

Wie die Zahlen der Tabelle II zeigen, liess sich demnach auch durch Verwendung von Katalysatoren das Ziel nicht erreichen und wurde deshalb versucht das Reaktionsgemisch ganz schwach anzusäuern, ein Vorgang durch welchen wir jedoch unseren ursprünglichen Plan verlassen mussten und den wir nur deshalb noch verfolgten, um die Reaktion von Chlorammonium auf Zucker noch weiter kennen zu lernen. Bei diesen Versuchen wurde der Chlorammoniumlösung mittelst Salzsäure eine solch schwachsaure Reaktion gegeben, dass sie in 50 cc Lösung durch 1 Tropfen 1/10 n-Lauge wieder aufgehoben wurde. Bei den diesbezüglichen Versuchen erhielten wir die in Tabelle III verzeichneten Werte:

TABELLE III

Versuchsnummer	50 cc. Zuckerlösung mit g. Zucker	30 cc. Chlorammoniumlösung mit g. NH_4 Cl	Inversions—		Auf 100 füllte Aussehen	cc. aufge-Lösung Polarisationsgrade
			Temperatur °C	Dauer Minuten		
20	13.024	10.0	100	30	farblos	+ 11.0
21	13.024	10.0	100	60	gelb	— 6.0
22	6.512	10.0	100	75	gelb	+ 0.0
23	6.512	10.0	100	90	gelb	— 3.5
24	6.512	10.0	98	120	gelb	— 4.5
25	13.024	gesättigte Lösung	110	30	tiefgelb	— 8.1

Wie die Tabelle III ergibt, wurde demnach auch durch Ansäuern der Chlorammoniumlösung keine vollständige und glatte Inversion des Rohrzuckers erzielt und war dies auch bei der Kombinierung von Ansäuerung und Verwendung eines festen Katalysators (Platinmohr) nicht der Fall, wie die Ergebnisse der Tabelle IV beweisen:

TABELLE IV

Versuchsnummer	50 cc. Zuckerlösung mit g. Zucker	30 cc. Chlorammoniumlösung mit g. NH_4 Cl	Inversions—		Auf 100 füllte Aussehen	cc. aufge-Lösung Polarisationsgrade
			Temperatur °C	Dauer Minuten		
26	13.024	10.0	100	60	gelb	+ 18.0
27	13.024	10.0	100	120	dunkelgelb	— 1.8

Nach verschiedenen weiteren Versuchskombinationen wurde die weitgehendste Inversion erreicht, wenn 50 cc Zuckerlösung enthaltend 13.024 g Saccharose mit 30 cc einer gesättigten Chlorammoniumlösung zum Aufkochen gebracht wurden. Diese Lösung ergab nämlich nach dem Abkühlen und Auffülen bei 20° C auf 100 cc im 200 mm Rohre eine Polarisation von —13.2° Ventzke. Die Lösung war aber gelb gefärbt, was auf eine Zersetzung bon gebildeten Invertzucker hinweist. Bei den Versuchen, in welchen Katalysatoren zur Anwendung kamen, wurde das Maximum der Inversion nicht sogleich erreicht, sondern war dieselbe nach dem Abkühlen der Lösung auf 20° C noch eine langsam fortschreitende, so beobachteten wir bei:

Versuch 18	Unmittelbar nach dem Auffüllen:	+ 20.4° Ventzke
	10 Minuten nach dem Auffüllen:	+ 19.4° Ventzke
	15 Minuten nach dem Auffülen:	+ 19.0° Ventzke
	4 Stunden nach dem, Auffülen:	+ 18.8° Ventzke
	50 Stunden nach dem Auffüllen:	+ 18.8° Ventzke
Versuch 19	Unmittelbar nach dem Auffüllen:	+ 1.9° Ventzke
	10 Minuten nach dem Auffüllen:	+ 0.2° Ventzke
	3 Stunden nach dem Auffüllen:	— 0.8° Ventzke
	50 Stunden nach dem Auffüllen:	— 0.8° Ventzke
Versuch 22	Unmittelbar nach dem Auffüllen:	± 0.0° Ventzke
	1 Stunde nach dem Auffüllen:	— 1.8° Ventzke
	4 Stunden nach dem Auffüllen:	— 1.8° Ventzke
Versuch 23	Unmittelbar nach dem Auffüllen:	— 3.5° Ventzke
	4 Stunden nach dem Auffüllen:	— 3.7° Ventzke
	50 Stunden nach dem Auffüllen:	— 3.7° Ventzke
Versuch 24	Unmittelbar nach dem Auffüllen:	— 4.5° Ventzke
	4 Stunden nach dem Auffüllen:	— 6.5° Ventzke
	60 Stunden nach dem Auffüllen:	— 6.8° Ventzke
Versuch 25	Unmittelbar nach dem Auffüllen:	— 8.1° Ventzke
	7 Minuten nach dem Auffüllen:	— 9.5° Ventzke
	1 Stunde nach dem Auffüllen:	—10.9° Ventzke
	4 Stunde nach dem Auffüllen:	—11.2° Ventzke
	24 Stunde nach dem Auffüllen:	—11.2° Ventzke
Versuch 27	Unmittelbar nach dem Auffüllen:	— 1.8° Ventzke
	10 Minuten nach dem Auffüllen:	— 4.0 °Ventzke
	1 Stunde nach dem Auffüllen:	— 5.4° Ventzke
	48 Stunde nach dem Auffüllen:	— 5.5° Ventzke

Aeusserst auffallende Resultate fortschreitender Inversion ergab eine Lösung, welche durch dreiviertelstündige Behandlung von 50 cc einer halbnormalen Zukkerlösung mit 30 cc einer ganz schwach angesäuerten, gesättigten Chlorammoniumlösung bei 110° C erhalten wurde. Dieselbe zeigte:

unmittelbar nach dem Auffüllen bie 20° C	—11.6° V
2 Minuten nach dem Auffüllen bei 20° C	—12.5° V
4 Minuten nach dem Auffüllen bei 20° C	—13.2° V
6 Minuten nach dem Auffüllen bei 20° C	—13.6° V
8 Minuten nach dem Auffüllen bei 20° C	—14.0° V
10 Minuten nach dem Auffüllen bei 20° C	—14.3° V
12 Minuten nach dem Auffüllen bei 20° C	—14.5° V
15 Minuten nach dem Auffüllen bei 20° C	—14.7° V
20 Minuten nach dem Auffüllen bei 20° C	—15.1° V
25 Minuten nach dem Auffüllen bei 20° C	—15.2° V
30 Minuten nach dem Auffüllen bei 20° C	—15.4° V
35 Minuten nach dem Auffüllen bei 20° C	—15.55° V
40 Minuten nach dem Auffüllen bei 20° C	—15.7° V
45 Minuten nach dem Auffüllen bei 20° C	—15.8° V
50 Minuten nach dem Auffüllen bei 20° C	—15.85° V
55 Minuten nach dem Auffüllen bei 20° C	—15.90° V
60 Minuten nach dem Auffüllen bei 20° C	—15.9° V
24 Stunden nach dem Auffüllen bei 20° C	—16.5° V
48 Stunden nach dem Auffüllen bei 20° C	—16.5° V

Nach 24 Stunden war demnach in diesem Falle die vollständige Inversion der Saccharose erreicht; da die Zahl 16.5 jedoch die normale Inversionsdrehung der reinen Saccharose überschreitet, so scheint hiebei auch eine geringe, konstant gebliebene Zersetzung von Dextrose stattgefunden zu haben, welche auch die gelbe Farbe der Lösung bedingte. Diese Annahme scheint auch durch den nachfolgenden Versuch ihre Bestätigung zu finden, wobei eine gleichstarke Zuckerlösung in gleicher Weise, jedoch anstatt dreiviertel Stunden eine ganze Stunde lang mit ganz schwach angesäuerter gesättigter Chlorammoniumlösung behandelt wurde und wobei sich ergab:

Unmittelbar nach dem Auffüllen:	—13.2° V
7 Minuten nach dem Auffüllen:	—15.4° V

15 Minuten nach dem Auffüllen:	— 16.3° V
1 Stunde nach dem Auffüllen:	— 17.3° V
2 Stunde nach dem Auffüllen:	— 17.3° V

Die Lösung wurde hiebei allmählich ganz dunkelgelb.

Nach dem Dargelegten haben demnach die Versuche uns nicht zu dem gesteckten Ziele geführt, wenn wir dieselben hier dennoch mitgeteilt haben, so geschah dies darum, weil sie vielleicht einen oder den anderen der Fachkollegen vom Betreten eines Weges abhalten, der ungangbar ist und auch deshalb, weil sie unsere Kenntnisse über die Inversion des Rohrzuckers immerhin vermehren dürften.

Zum Schlusse wollen wir nur noch erwähnen, dass uns die Resultate der Versuche 1, 2 und 3, welche zeigen, dass Chlorammonium in den dort angegebenen Mengen das Resultat der direkten Polarisation nicht beeinflussten, veranlasst haben zu prüfen, ob auch die Inversionspolarisation durch Neutralisation der zur Inversion verwendeten Salzsäure mit Ammoniak oder Natronlauge ebenfalls unbeeinflusst bleibt.

Zu diesem Zwecke wurde je dreimal das halbe Normalgewicht reinsten Kristallzuckers in gewöhnlicher Weise invertiert und nach der Inversion (a) direkt, (b) erst nach Neutralisation mit Ammoniak und (c) erst nach Neutralisation mit Natronlauge, wobei Phenolphtalein als Indikator zur Verwendung kan, mit Wasser auf 100 cc aufgefüllt und im 200 mm Rohre polarisiert. Hiebei beobachteten wir:

Neutralisiert mit:

Direkt	Ammoniak	Natronlauge
a	b	c
— 16.3	—16.5	—16.4

Bei Wiederholung des Versuches mit einem anderen Kristallzucker:

a	b	c
— 16.3	—16.5	— 16.25

Ferner wurden je dreimal 75 cc einer wässerigen *Asparaginlösung*, entsprechend einer Drehung von —0.38, mit 5 cc Salszäure wie gewöhnlich bei der Inversion behandelt und nachhor (a) direkt mit Wasser aufgefüllt, (b) erst nach Neutralisation mit Ammoniak und (c) nach Neutralisation mit Natronlauge, wobei wiederum Phenolphtalein als Indikator zur Verwendung kam, und schliesslich im 200 mm Rohre polarisiert. Hiebei ergaben sich °V:

a	b	c
+4.3	±0.00	±0.00

Der gleiche Versuch wurde mit einer *Glutaminsäure* lösung, von welcher 75 cc einer Drehung von +0.20 entsprachen durchgeführt und erhalten °V:

Nach Neutralisation mit:

Direkt	Ammoniak	Natronlauge
a	b	c
+1.5	—0.1	—0.1

Diese Beobachtungen deuten einen Weg an, auf welchem es vielleicht möglich ist, die Fehlerquellen der Inversionsmethode wenigstens einzuschränken und die weiter durchstudiert, dieselben möglicherweise genz beseitigen lassen und behalten wir uns weitere diesbezügliche Studien vor. Wie wir aus einer der jüngsten Publikationen E. Saillards,[1] die uns jedoch erst nach Abschluss unserer Studien bekannt wurde, ersehen, sucht derselbe zur Lösung der Frage einen ähnlichen Weg einzuschlagen.

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[1] Journal des fabricants de sucre 1912, Nr. 21.

SUGAR BEET SEED GROWING IN THE UNITED STATES

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The production of sugar beet seed in the United States involves the same general principles that are embraced in the production of sugar beet seed in other countries. In considering this question, therefore, it will be best to go over the principles which have to do with the growing of beet seed in general and to note the special factors which influence beet seed growing in the United States, in so far as they differ from the factors governing this industry elsewhere. In this connection it should be said that the growing of beet seed in this country is still in an experimental stage and probably will not develop for many years into a commercial proposition which shall be capable of supplying the home demand, at least not until the soil and climatic conditions in the various localities have been thoroughly tested and found suitable for the establishment of this new industry on a safe basis. Even then it will be wise to develop the industry gradually, for the reasons that will be apparent as we study its requirements. For many years a more or less general idea has prevailed both in this country and abroad that high grade sugar beet seed could not be grown in the United States. However work along this line is under way in several of our sugar beet centers where it will be thoroughly tested for the reason that there exists in the minds of many of the beet sugar producers of this country a feeling that the beet sugar industry will never be on a secure footing with all the possibilities of development of which it is capable until we are no longer dependent upon foreign countries for our seed supply. This feeling exists without any prejudice against the foreign grown seed or against the man who grows it, but simply for the reason that so long as we must rely upon the importation of beet seed for the production of our crop, the beet sugar industry in this country will be dependent upon the success or failure of the seed crop in other countries and upon the various changes in our trade relations that may arise from time to time with the present seed producing countries. The adverse conditions which prevailed last year in nearly all the beet seed producing countries of the old world resulted in a shortage of the seed crop which increased the selling price several fold, and made it almost impossible for this country to get a supply of good seed adequate for its needs. Another partial failure of the seed crop in the near future would so deplete the world's supply of beet seed that the beet sugar industry would be badly crippled, if not entirely destroyed, in certain sections for the time being at least.

Another reason for the production of home grown beet seed still more potent than any of those mentioned is to be found in the laws of plant growth and development. If we plant the seed from a single beet root grown from any of the so called varieties now in use, we shall obtain a large number of types on strains as indicated by the habit of growth and texture of both leaf and root and in their ability to manufacture and store sugar. In order to make the greatest progress in sugar beet sugar production we should select the type or types best adapted to a given locality until we get a pure type of the strain or strains selected. This will require careful selection through several generations, but until we get these pure strains possessing the desired characters upon which to base our future breeding and selection we cannot hope to get the highest results from the standpoint of tonnage and quality of the roots. Having secured the pure strains desired, we are then in a position to re-combine the strains that possess the characters most desirable or to continue the pure strains as such if they possess the characters that are most desired. Following the laws of plant growth as influenced by environment we shall find that certain types or strains produce the best results in a given locality, while other types or strains are better suited to other localities. For this reason it is advisable not only that the seed to be used in producing a given crop be grown in the country where the crop is to be produced, but also that the various sections of that country, especially if the climatic conditions are widely different, should have each its own strain of seed. It is apparent therefore that sugar beet growing will not reach its highest plane of development in this country until we are able to produce our own seed in accordance with the principles of selection, breeding, and adaptation to environment.

In looking over the varied conditions of soil and climate which prevail in the several sugar beet sections of this country, one cannot help being impressed with the fact that we have in many places soil and climatic conditions which seem to be of the best for the growing of sugar beet seed. In accordance with the foregoing considerations it stands to reason that beet seed growing in the United States, and especially in the sugar beet centers, will be best adapted to our needs, from the standpoint both of tonnage and quality. This is the natural law with reference to other crops, and there is no reason to believe that the same law does not hold in regard to sugar beets. It is entirely possible that beet seed of satisfactory quality and yield might be grown in this country entirely outside of our present sugar beet centers. It seems desirable, however, to confine our efforts, for the present, to those localities where sugar beets are now grown commercially, for the reason that such localities present better facilities for the selection of suitable roots, and furthermore, all discarded roots can then be put through the factory, thereby avoiding serious loss.

In considering the advisability of entering into the growing of sugar beet seed commercially, a number of factors upon which the success or failure of the enterprise depend should be carefully noted. These are in the main climate and soil and the personality of the individual upon whom the details of the work must rest. This latter factor, in the judgment of the writer, is the one of greatest importance, because the individual who grows the seed, or who is entrusted with the details of the work, must be a close observer, one who is capable of taking infinite pains in all the details, and one who is absolutely honest with himself and with the public. In regard to the soil it may be said that a dark, rich, loamy soil is the best for the production of beet seed. Such soils are found in practically all of the sugar beet localities in this country. The climatic conditions are more complex and should be carefully considered before undertaking such an important work on a large scale. The elements of climate which have a direct bearing upon seed production are Temperature, Precipitation, and Wind. Both winter and summer temperatures are to be considered for the reason that beet seed requires two growing seasons for its production. The roots grown one season must be kept over winter and planted out the next season. It is important that the roots remain dormant during the winter. To this end the roots should be kept just as close as possible to the freezing point without being frosted. It is possible for the temperature to fall several degrees below freezing point without injuring the beets. The summer temperature is equally important since a too high temperature at the time the seed is setting will cause more or less of it to blast, so that the crop will be a failure or a partial failure. Rain at harvest time tends to give the seed a dark color which impairs its selling quality as the trade demands a bright seed. If the rains at harvest time are frequent, or even if the atmosphere is continuously damp, the seed not only turns dark but it tends to mold, a condition which may injure its germinating quality. The roots should have plenty of moisture while the seed is forming in order to produce good plump seed. High winds after the seed stalks have formed, and especially after the seed has set, may break down the seed stalks or break off the branches, thereby reducing the yield of seed. This difficulty may be overcome by the use of windbreaks. Any one of these climatic elements may be the limiting factor to exclude the possibility of profitable beet seed production in a given locality. It should be noted that there are other limiting factors such as diseases, insect pests, and other agencies which may so affect the buds that seed stalks fail to form, or they may prevent the formation or development of the seed. These factors are not confined to any locality nor to any country, but the ability to control them must be reckoned with in considering the establishment of so important an industry.

If one has convinced himself that the chances for success in beet seed growing are reasonably sure it will still be wise to start the work on a small scale. This will enable one to study the soil, climatic conditions, and other limiting factors in relation to seed production, and at the same time give him an opportunity to look closely after all the details and to adapt himself to his new line of work so that he can safely increase his business from year to year with a minimum chance of failure. Having decided to undertake the production of sugar beet seed, the first step consists in selecting suitable roots as seed beets. In the selection of roots attention must be given to size, shape, and quality. Size may or may not be an important factor, depending upon the conditions under which the beets were grown. If the roots are grown close together in poor soil, or with an abnormally small amount of moisture, the size is not of any considerable importance. On the other hand, if the roots are small under favorable conditions of growth, that is if they are inherently small, they should be avoided since selection along this line would tend to produce a strain of beets of low tonnage. Attention should also be given to the relative size of the top. Tops that are abnormally large at the expense of the root growth are not desirable for seed production. The shape of both root and crown are important factors in the selection of seed beets. The roots should be of good length and should not taper too suddenly. On the other hand, they should carry their size well down toward the middle part of the root and should then taper gradually to a well formed single point. The root should be so twisted that the sutures, and consequently the feeding roots, present a spiral appearance. This gives the beet a chance to draw its food supply from all directions around the root. The crown should not be elongated, but should be nearly flat, and practically flush with the surface of the ground. This will tend to keep the crown-tare down to a minimum. The crown should not be abnormally broad in proportion to the size of the root, but should be well supplied with buds for the production of seed-stalks.

Having selected the roots with reference to size and shape, the next and most important consideration is that of quality, which embraces both sugar and purity. In general the purity of the individual root is neglected for the reason that no satisfactory method has been devised for the determination of the purity of a single root without rendering it unfit for seed production. By purity is meant the proportion of sugar to the total solids in the juice and purity is closely related to the maturity of the beet. The importance of producing beets with a high co-efficient of purity lies in the fact that one part of the salts taken up from the soil by the beet root will keep about four parts of sugar from crystallizing and forming commercial sugar. In actual work the purity is checked up from time to time by an analysis of several of the seed roots as a composite sample, thereby getting juice enough to make a purity test. The sugar content of the roots can and should be determined for each root to be used for seed production. This is done by taking a core out of each beet starting at the shoulder and extending diagonally through the root and subjecting it to a polariscope test. Each beet seed growing farm should therefore have a testing laboratory equipped with suitable apparatus for making sugar and purity determinations. It is customary for beet seed growers to fix upon some satisfactory sugar content and to discard all roots showing a lower sugar content than the one fixed upon. While the sugar content of roots does not seem to be a fixed characteristic of the beet in the sense that color, shape, and habits of growth are fixed characteristics, yet the tendency in the beet roots to store sugar is of the highest importance and should receive the most careful attention. To this end the individual who undertakes the production of beet seed should be thoroughly conscientious and reliable, so that he will without any hesitation discard those roots that are not strictly up to the standard. It would be absolutely useless to undertake the growing of beet seed unless the proper equipment can be provided and utilized in such manner that the quality of the roots shall constantly improve or at least shall not deteriorate.

Having selected the roots with reference to the above named factors, the next step consists in storing the roots so that they will keep in a perfectly sound condition until the following spring without starting a new leaf growth. In putting the beets away in the fall the leaves should be removed without injuring the buds. In some instances the roots are stored in root cellars, but it is a common practice, and one that has been found very satisfactory, to silo the beets in the open. To do this the beets are piled on a well drained spot in the field and then covered with earth or preferably with sand. All spaces between the roots should be filled with the sand to retard evaporation, and to prevent field mice from wintering in the beet piles, where they would do considerable damage to the roots and especially to the dormant buds. In any case the roots should be put into the storage cellar or silo in a perfectly fresh and crisp condition. If they are allowed to wilt they do not keep well in the silo, and as a rule do not thrive when planted out for seed. As indicated above, the silo should be covered with just enough dirt to keep the roots from freezing without causing them to heat. This covering will differ in the various beet seed growing localities and indeed in the same locality from year to year. It is therefore a wise plan to cover the silo lightly at first and to increase the covering from time to time as the weather becomes more severe.

The roots should be planted out in the spring as early as the soil and weather conditions will permit. This will be several weeks earlier, usually, than the seed itself can be planted with safety. The ground should be plowed deep and firmed down to a good bed. It should be marked out in checks so that the roots, when planted, will stand in rows each way in order that the beets may be cultivated both ways. The beets should be from two and one half to three feet apart each way so that the tops will have plenty of room and so that the cultivator can be run between the rows without breaking down the seed stalks. In planting the roots it is best to take them from the silo and drop them at the points where they are to be planted, then take a long spade and force it perpendicularly into the ground to a depth as great as the length of the root, pushing the spade forward and crowding the beet root into the open space just back of the spade. The root should be held in place and the spade withdrawn. The dirt should be firmly packed around the root, the top of which should be just flush with the top of the ground. The soil at the time the roots are planted should be moist but not wet. The field should be kept free from weed and should receive frequent cultivations to conserve the moisture. Especial pains should be taken to see that the beets are well supplied with moisture at the time the seed is forming, otherwise the yield and quality of the seed will be greatly reduced. After the seed has formed, the water, if under control, should be withheld in order to allow the seed to ripen. No special attention need be given to the pollination of the flowers as that takes place naturally by the action of the wind and insects. The flowers produce a great abundance of pollen, so that the atmosphere in a beet seed field, at pollination time, is filled with the yellow powder. As the seed begins to ripen it assumes a yellowish tinge, which eventually changes to a light brown color when it is ripe. The seeds near the attached ends of the stems and branches are the first to ripen while the distal or free ends of the branches frequently have immature florets at harvest time. The seed should be harvested just before it begins to shatter. Harvesting is accomplished by cutting off the seed stalks close to the ground and piling them in small piles until they are thoroughly dry. They are then pitched onto a rack and hauled to a suitable place for threshing. If the seed shatters when hauled it is best to spread a canvas in the bottom of the rack; otherwise some of the seed of the best quality will be lost. In the older beet seed countries the seed is threshed by means of a special machine, but in this country it is put through an ordinary threshing machine, or is tramped or pounded out on a level floor. It is then cleaned by putting it through a fanning mill which takes out the lighter material. After this it is made to fall upon a canvas belt six or eight feet in length and several feet wide, which is inclined at the proper angle and is constantly rotated toward the high end so that the seed as it falls upon it is carried by its own weight down into the receiver, while the broken stems and branches are carried over by the canvas and discarded. The seed is then spread in some suitable place to dry. Some seed firms have artificial dryers, but the seed can be spread upon a clean floor and stirred from time to time until it is thoroughly dry, when it can be sacked without danger of molding. The standard generally adopted for marketable sugar beet seed specifies that the moisture content shall not exceed fifteen per cent., and that the impureties shall not exceed three per cent.

There are only a few pests that are troublesome to seed beets. The disease especially to be dreaded is the "curly top." It is never advisable to make any selections for seed beets in fields where there is any appreciable number of curly top beets, since it has been observed that beets may be affected with curly top without showing symptoms of the disease until the roots have begun their second year growth. Such roots produce little if any seed and in fact often fail to throw up seed stalks at all. Likewise roots that are in the least affected with root rot or crown rot should be discarded and not placed in the silo. Even if they go through the winter without any apparent development of the rot, they will usually decay the second year, and the labor of selecting, testing, siloing, and planting them is lost.

Leaf spot is as a rule not a serious menace to beet seed growing. It should be prevented, however, by growing the seed in a field not infected with the fungus since the spores may become attached to the rough coats of the seed and in this way be spread to localities not hitherto infested with it. In some parts of the West the Jack Rabbit is the worst enemy of the seed beet. Since the beet roots are planted out early in the spring they furnish a favorite feeding ground for this animal. It would therefore be useless to try to grow beet seed in certain localities until the Jack Rabbit is exterminated, or until some inexpensive method is found whereby his ravages may be prevented.

When beet seed of good quality has been produced in commercial quantities, it is important that its reputation as a seed, up to the standard in germination and capable of producing roots of good tonnage and quality should be established. This reputation must be founded upon actual facts and should be capable of demonstration to practical growers. To this end it should be thoroughly tested in comparison with standard sugar beet seeds. These tests should be made by growers of unquestionable reputation who will give the seed a fair test. When the reputation of the seed has become established so that there is a demand for it every effort should be made to maintain and if possible to improve that reputation with each succeeding crop. Enough has already been done to prove that the limiting factors may be overcome and that beet seed of good quality can be grown in this country at least in limited areas. It remains to be shown to what extent these areas can be increased, and with what success new areas may be developed.

OBJECTIONABLE NITROGENOUS COMPOUNDS IN SUGAR CANE JUICE

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During the past few years the question of the so-called "objectionable" nitrogen in the sugar beet has attracted considerable attention in sugar circles and a great number of papers have appeared on this subject. By objectionable nitrogen is meant the nitrogen of those compounds which are not removed during the process of manufacture and hence accumulate in the molasses. The problem has been attacked in two different ways, first by determining nitrogen in its different forms in all the products of the factory from the juice on to the final molasses; and second by isolating from some of these products the different individual compounds which either contain objectionable nitrogen or are during the manufacturing process converted into such substances. While great advances have lately been made in these lines of work in the beet sugar industry, our knowledge of the objectionable nitrogenous compounds in the cane is practically the same as in 1899, when van Lookeren Campagne[1] wrote that as far as the nitrogenous constituents of the cane are concerned, very few definite data can be given as regards individual compounds. Even about the quantity of nitrogen in its different forms contained in cane factory products very little is known, excepting the cane itself, cane juice and molasses. The cane contains about 0.05% of total nitrogen, and about one half of this is objectionable nitrogen;[2] in cane juice we have about 0.04% of total nitrogen with 60% of objectionable nitrogen,[3] In final molasses the total nitrogen rises to 0.4–0.6%.[4]

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[1] Archief v.d.Java Suikerind., 1899, p. 751.

[2] Louisiana Agr. Expt. Sta., Bull. 91, p. 5.

[3] Louisiana Agr. Expt. Sta., Bull. 91, p. 28.

[4] Louisiana Agr. Expt. Sta., Bull. 91, p. 93.

The compounds containing objectionable nitrogen may be divided into four groups, viz., (1) Nitrates; (2) Organic nitrogenous bases; (3) Aminoacids and (4) Amids of aminoacids.

(1) The nitrogen in the form of nitrates amounts to about 17.77% of the total nitrogen found in cane juice, or 0.007% as calculated on the juice itself.[1]

(2) The quantity of nitrogenous bases is exceedingly small. Of the xanthin group of bases Shorey isolated guanin from Hawaiian sugar cane juice.[3] Its quantitative determination gave 0.0026%. Shorey also found very small quantities of lecithin in cane juice which upon decomposition yielded both cholin and betain.[4] While the presence of the three bases named is interesting from the physiological point of view, it is of no import for the sugar factory on account of the small amount of these bases.

(3) The nitrogen in the form of aminoacids amounts in cane juice, according to Browne, to 30.53% of the total nitrogen.[1] The aminoacids that have so far been reported to be present in cane juice, are leucin and glycocoll, both isolated by Shorey[5] from the precipitate produced by mercuric nitrate, after removal of the lead precipitate. Winter[6] tested cane juice for aspartic acid by means of ammoniacal lead acetate, but with negative results. Shorey recovered only a very small quantity of leucin so that it could be identified only by its appearance under the microscope and by Scherer's reaction. Glycocoll was however reported by Shorey to be present in considerable quantity in the juice of cane of all stages of maturity and from locations ranging in altitude from 400 to 1500 feet above sea level. Shorey classes glycocoll among the acid amids, whereas the writer, in accordance with the classification generally adopted, places it among the aminoacids. Shorey gives principally the following facts to prove the identity of the substance isolated by him. It was not optically active; its nitrogen content after drying at 110° C. was 18.69%; it

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[1] Louisiana Agr. Expt. Sta., Bull. 91, p. 28.

[2] Louisiana Agr. Expt. Sta., Bull. 91, p. 93.

[3] Jour. Am. Chem. Soc., vol. 21, p. 809.

[4] Jour. Am. Chem. Soc., vol. 20, p. 113.

[5] Jour. Am. Chem. Soc., vol. 19, p. 881; vol. 20, p. 133.

[6] Ber. Versuchsst. West Java, 1, p. 39.

gave a condensation product with benzoylchloride (hippuric acid), after heating the substance with alkali, there remained in the residue oxalate and sometimes small quantities of cyanide. This was the first instance that glycocoll had ever been obtained from any plant juice, and the discovery was of the greatest interest, especially as Maxwell[1] had under the same circumstances found, not an aminoacid, but an acid amid, viz., asparagin, without, however, identifying his substance by physical and chemical tests. Shortly after Shorey's publication, van Lookeren Campagne[2] expressed serious doubts about the exactness of Shorey's observations and conclusions. It seems to the writer that the substance isolated by Shorey cannot have been gylcocoll, because it contained water of crystallization, and because it split off one half of its nitrogen upon distillation with alkali. These latter facts point to the probability that the substance was really an amid of some aminoacid. The question of its identity must however remain an open one until further researches shall have been made with Hawaiian cane.

(4) The nitrogen in the form of amids of aminoacids makes up 24.07% of the total nitrogen in the cane juice.[3] So far we have been very much in the dark as to what acid amids occur in the sugar cane. It has been mentioned above that Maxwell reported to have isolated asparagin from the mercuric nitrate precipitate, but without giving tests to prove his assertion. He also suggested that glutamin might be present at the same time. Went[4] tested sugar cane microscopically for asparagin, with negative results. This does not prove anything either way, since asparagin is not precipitated by alcohol in a crystalline form when large quantities of sugars and gummy matter are simultaneously present.

As may be seen from the foregoing, our knowledge of the aminoacids and acid amids which make up over one half of the total nitrogen of the cane, is still extremely meagre. In fact, none of the different substances reported, asparagin, glutamin, glycocoll and

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[1] Louisiana Agr. Expt. Sta., Bull. 38, p. 1380.
[2] Archief v.d. Java Suikerind., 1899, p. 751.
[3] Louisiana Agr. Expt. Sta., Bull. 91, p. 28.
[4] Archief v.d. Java Suikerind., 1896, p. 533.

leucin, has been definitely identified. This question was therefore taken up again by the writer, and it was found that the mercuric precipitate from sugar cane juice contains principally asparagin, besides small quantities of glutamin and of tyrosin.

These investigations were carried out in two different places. The first of these, the Agricultural Experiment Station in Tucuman, Argentine Republic, lies within the temperate zone, while the second, the Experiment Station of the Porto Rico Sugar Producers' Association, is in the tropics. The methods used were practically the same in both places. In Tucuman 25 liters of cane juice from mixed purple and striped cane, old ratoons, were worked up, in Porto Rico about 150 liters of juice from plant cane of the variety Demerara, No. 117. The canes were in both cases fully mature under local conditions. The juice was quickly neutralized with sodium hydroxide and precipitated with a slight excess of a concentrated solution of neutral lead acetate. The filtrate from this was, in Tucuman, precipitated with a water solution of mercuric nitrate, and in Porto Rico with one of mercuric acetate[1]. The precipitate was filtered off, washed, decomposed with hydrogen sulphide, the mercuric sulphide removed by filtration, the filtrate neutralized with ammonia and boiled down in vacuo as quickly as possible, until crystallization began. A large mass of crystals was obtained after standing for some time; they were collected on a Buchner funnel, washed with 50% alcohol and recrystallized three times from water. The last crystals were finally washed with 95% alcohol, then with ether, and were dried at room temperature. In the first series of experiments there were obtained 6.12 grams of pure substance (I), in the second 20 grams II. The crystals were very well formed, of a brilliant luster, colorless and odorless, very hard, and had no pronounced taste. They were somewhat soluble in cold water, readily in hot, insoluble in alcohol and in ether. They did not give a red, but a brownish coloration with ferric chloride. When Nessler's reagent was added to a solution of the substance, the liquid remained quite clear, but on boiling, a precipitate slowly formed, showing that ammonia was being split off. Upon heating

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[1] See Neuberg & Ishida, Z. Ver. D. Zuckerind., 1911, p. 1113.

to constant weight at 105° C., the substance No. I lost 12.03% of its weight, and No. II lost 11.98%. The total nitrogen was found, by Kjeldahl's method to be 18.4% in No. I, and 18.72% in No. II. In order to ascertain whether the substance contained an acid amid group, it was distilled with baryta water, the volume being kept constant by adding water as needed through a separatory funnel, so that the amino nitrogen would not be attacked. In the first 250 cc. of the distillate there was obtained 9.00% of nitrogen, in the next 125 cc. 0.27%. The next 250 cc. gave altogether only 0.11%. It is thus seen that one half of the nitrogen is in the form of acid amid nitrogen. In another experiment the substance was boiled with 10% hydrochloric acid under reflux for two hours; an excess of magnesium oxide was then added, and the ammonia distilled over under a vacuum at about 45° C. 8.94% nitrogen were recovered in this way, again approximately one half of the total. In substance No. II, 9.13% nitrogen were obtained by distillation with baryta water. (Nitrogen in asparagin, calculated, 18.66%).

These data prove that the substance is asparagin. This conclusion was corroborated by a series of analyses which Dr. L. M. Dennis was kind enough to have made at the laboratories of Cornell University, with the following results:

Water of crystallization, 12.11%; 12.07%; 11.92%; average 12.03%.

Air dry substance, Carbon 32.29; 32.73%; 32.65%; average 32.56%. Hydrogen 6.33%; 6.96% 6.94%; average 6.74%.

Substance without water of crystallization, Carbon 36.32%; Hydrogen 5.97%.

The theoretical values for asparagin are: Water of crystallization 12.00%; air dry substance, carbon 32.00%, hydrogen 6.67%; substance without water of crystallization, carbon 36.36%, hydrogen 6.06%.

The conclusions drawn from the writer's figures were thus confirmed by an independent investigator.

The asparagin from cane is the 1-modification, as may be seen from the figures below. The determinations with substance No. I were made at 15° C., those with No. II at 28° C. The specific rotation for the D-line was found to be:

	No. I	No. II
Water solution, 1%		—6.0
Water solution, 1.5%	— 5.2	
Water solution, 3%		— 5.4
Water solution, 1%, plus 1/10 vol. conc. HCl		+ 30.4
Water solution, 1.2%, plus 1/10 vol. conc. HCl	+ 29.0	
Water solution, 3%, plus 1/10 vol. conc. HCl		+ 27.3
n/2 Sulphuric acid, 1.2%	+ 34.7	
Water solution, 1%, plus 1/10 vol. 35% H_2SO_4		+ 30.1
Water solution, 3%, plus 1/10 vol. 35% H_2SO_4		+ 27.7
Water solution, 0.5%, plus 1/10 vol. lead subacetate	+ 65.9	
Water solution, 1%, plus 1/10 vol. lead subacetate		+ 53.2
Water solution, 3%, plus 1/10 vol. lead subacetate		+ 20.5

These figures agree well with those for 1-asparagin obtained by other observers. The specific rotation seems to vary with the concentration, the temperature and the proportional quantity of acid or lead subacetate added.

Two portions of 0.15 gram each were dissolved in water and titrated with N/10 sodium hydroxide, using phenolphtalein and cochineal resp. as indicator, at 15° C. There were used 2.3 cc. of alkali with phenolphtalein, and 0.15 cc. with cochineal as indicator. These figures also agree well with those obtained by Degener.[1]

The mother liquor from the asparagin was in both series of experiments boiled down further under a vacuum until crystals began to form again, and then allowed to stand. In both cases a mixture of two kinds of crystals ensued. In the investigation carried out at Tucuman a small quantity of beautiful needles interspersed with prisms was obtained. The prisms were removed mechanically as far as possible; they turned out to be asparagin. The needles were recrystallized twice from 60% alcohol, washed with strong alcohol and ether, and air dried. Under the microscope the crystals had the characteristic appearance of glutamin

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[1] Deutsche Zuckerind., 1897, p. 65.

as described and illustrated by Sellier.[1] The substance did not lose weight at 105° C., and therefore contained no water of crystallization. The nitrogen determination according to Kjeldahl gave 19.51% against the theoretical 19.18%. The specific rotation for the D-line in a 1% solution at 15° C. was + 4.3; by the addition of 1/10 volume of concentrated hydrochloric acid the rotation increased to + 31.3. In the presence of basic acetate of lead it was found to be left handed. The substance was therefore d-glutamin.

In the second series of experiments carried out in Porto Rico, the mother liquor from the asparagin was again boiled down in vacuo until crystals began to separate anew, and was then allowed to stand. A fine crystalline mass resulted which was thrown on a Buchner funnel and washed with a small quantity of 50% alcohol. As it was still very dark colored it was boiled out with 95% alcohol and then recrystallized from water. Upon cooling a dense mass of very fine silky white needles separated out which under the microscope appeared arranged in bundles. The filtrate from these crystals contained asparagine which was easily identified. The silky needles were found to be almost insoluble in cold water, but they dissolved readily in hot water. They were recrystallized three times, finally washed with alcohol and with ether, and air dried. They did not contain any water of crystallization and melted at 242° C. Judging from these properties the substance was thought to be tyrosin. The two characteristic tests with Millon's reagent and with Moerner's reagent (1 part formaldehyde, 45 parts water, 55 parts concentrated sulphuric acid; green coloration) were both positive. Finally a nitrogen determination was made which gave 7.56%, against 7.73% theoretical. It is thus seen that the substance was tyrosin. Unfortunately there was not enough material with which to decide whether it was the l- or the d-modification.

The mother liquor resulting from the mixture of tyrosin and asparagin was boiled in vacuo to a syrup and then placed in a desicator over calcium chloride. After two days beautiful needles had formed throughout the dark brown mass. Besides these a

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[1] Bull. Ass. Chim. Sucr. Dist., vol. 27, p. 190.

small quantity of a different kind of crystals was present. These were however soluble in cold 80% alcohol, whereas the needles did not dissolve. These latter were recrystallized three times from 60% alcohol. They were identical with the glutamine crystals obtained in Tucuman, by boiling down the mother liquor from the asparagin. They were more soluble in water and in dilute alcohol than asparagin. With Nessler's reagent they yielded a brown precipitate much more quickly than asparagin. The nitrogen determination by Kjeldahl's method gave 19.38%, against 19.18% theoretical. One half of this nitrogen was split off as ammonia by boiling with hydrochloric acid and distilling with magnesia under a vacuum. The glutamin obtained was again the dextrorotatory modification, the specific rotation for the D-line at 28° C. of a 0.6% solution being about + 6, and in the presence of hydrochloric acid + 35.5.

The last mother liquors obtained in Tucuman and in Porto Rico still seemed to contain more crystallizable substances, but it was found impossible to purify them sufficiently for identification.

As regards the quantity of the three substances isolated, asparagin was by far the most abundant. The glutamin recovered amounted to only 1.6% of the asparagin, and the tyrosin to only 0.5%. It is probable however, that the cane juice contains a larger proportion of glutamin than would appear from these figures, because glutamin is very easily decomposed and lost during the different processes of its isolation.

From the plant physiological point of view the results of this investigation show that the sugar cane does not materially differ from other plants in the nature of those substances which are considered the intermediate stages between the inorganic nitrogenous compounds and the plant proteids. It appears from the researches of Shorey that under certain conditions some other amid which differs from asparagin may take the place of asparagin and glutamin.

Under the conditions obtaining in the process of sugar manufacture from cane, asparagin and glutamin are not removed, but a part of the asparagin and a still greater part of the glutamin are broken up with the result that aspartic and glutamic acids accumulate in the molasses along with the undecomposed asparagin and glutamin. These amids are largely responsible for the ammonia that is given off from the juices during the process of evaporation. This conclusion is corroborated by the results of Browne[1] who found that the quantity of acid amids in cane juice is only slightly smaller than that of the aminoacids, while in final molasses the aminoacids preponderate very largely. The acid amids and aminoacids found in the mercuric precipitate undoubtedly must be classed as objectionable nitrogenous compounds and as molasses formers in the light of Prinsen Geerligs's theory of molasses.

It is now well known, and it has been shown again in this investigation that asparagin in dilute solution and in the presence of subacetate of lead may have a specific rotation about equal to that of sucrose, so that each per cent. of asparagin would cause a plus error of one per cent. of sucrose. Glutamin under the same conditions is laevorotatory, but its rotation to the left is much smaller than that of asparagin to the right. Thus the glutamin will partly neutralize the error due to the presence of asparagin. The proportion between asparagin and glutamin probably varies with different conditions, as age and variety of the cane, climatic conditions and so forth, and the total quantity of both is usually well below 0.1%. Thus it appears that under ordinary conditions the amids present in cane juice will not perceptibly affect its polarization. Only under abnormal conditions may the error caused by their presence be large enough as not to be negligible. Such a case may at times happen in those countries where the cane is cut in an immature state, and where it may therefore contain a comparatively large quantity of amids, owing to the well establised fact that young cane contains a larger amount of amids than mature cane.

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[1] Louisiana Agr. Expt. Sta., Bull. 91, p. 14.

GENERAL INDEX TO THE TWENTY-FOUR VOLUMES OF ORIGINAL COMMUNICATIONS

Volume	Section	
1	I.	Analytical Chemistry.
2	II	Inorganic Chemistry.
3	IIIa	Metallurgy and Mining.
4	IIIb	Explosives.
5	IIIc	Silicate Industries.
6	IV	Organic Chemistry.
7	IVa	Coal Tar Colors and Dyestuffs.
8	Va	Industry and Chemistry of Sugar.
9	Vb	India Rubber and other Plastics.
10	Vc	Fuels and Asphalt.
11	Vd	Fats, Fatty Oils and Soaps.
12	Ve	Paints, Drying Oils and Varnishes.
13	VIa	Starch, Cellulose and Paper.
14	VIb	Fermentation.
15	VII	Agricultural Chemistry.
16	VIIIa	Hygiene.
17	VIIIb	Pharmaceutical Chemistry.
18	VIIIc	Bromatology.
19	VIIId	Biochemistry including Pharmacology.
20	IX	Photochemistry.
21	Xa	Electrochemistry.
22	Xb	Physical Chemistry.
23	XIa	Law and Legislation Affecting Chemical Industry.
24	XIb	Political Economy and Conservation of Natural Resources.