COMMON COMMODITIES AND INDUSTRIES

PERFUMERY

E. J. Parry

THE RAW MATERIALS OF PERFUMERY

(La Parfumerie Moderne)

FIG. 1.

CARTING LAVENDER FLOWERS

Frontispiece

PITMAN'S COMMON COMMODITIES
AND INDUSTRIES

THE RAW MATERIALS OF PERFUMERY

THEIR NATURE, OCCURRENCE AND EMPLOYMENT

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PREFACE

THIS little work is intended to deal with the raw materials employed in the manufacture of perfumes. The whole art of perfumery has been so revolutionized by the aid of Synthetic Chemistry that a popular account of this particular branch of perfumery may be found of interest.

E. J. P.

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THE RAW MATERIALS OF PERFUMERY

CHAPTER I

INTRODUCTORY

PERFUMERY, as known to most people, is an art; but as known to the expert perfumer, it has become elevated, if not to the level of a science, at least to the level of a scientific art.

For, in the modern developments of the art of perfumery, the very highest branches of chemical research have been called in, and it is no exaggeration to say that the last thirty or forty years of organic chemical research have entirely revolutionized the old conceptions of the art of Perfumery.

This will, however, be developed in a later chapter, especially when we come to consider the synthetic perfumes. The use of perfumes goes back to very distant ages, and entered into the mystic rites of nearly every form of religious worship. Thus we read of their use on the altars of Zoroaster, and in the rites of the followers of Confucius: they were used in the Temple of Memphis as well as in those of Jerusalem.

It has, indeed, been said that the history of Perfumes is, in some sort, the history of civilization. A good sized volume would be necessary to deal with the historical aspect of the subject, so that it will here only be possible to pass under rapid review and in bare outline a few aspects of the antiquity of the subject.

In Egypt, that most ancient of civilizations, perfumes were well known at a very early date. In the reign of Cheops, the builder of the great pyramid, we read of their use in funeral and religious ceremonies, and we all remember that when Joseph was sold by his brethren he was taken by merchants carrying spices and perfumes into Egypt. De Rougé has translated a poem called Pen-ta-our found engraved on one of the walls of Karnak, in which Rameses II, who was anterior to the Exodus, is made to exhort the god Ammon to give him the victory in battle, saying "I have enriched thy domain and I have sacrificed thirty thousand oxen to thee, with all the sweet smelling herbs and the finest perfumes." Many other examples of the repute in which perfumes were held by the Egyptians might be quoted, but the above must suffice for our purpose.

The Hebrews before their captivity in Egypt were a pastoral people, who were more or less free from luxurious tastes, and knew little about perfumes, and cared less. When they left Egypt, however, they took away with them many of the arts cultivated by their captors, amongst which was the indulgence in perfumes. But although the Hebrews in the early days neither used perfumes in their religious ceremonies, nor on their persons, they must have known of the commercial value of such substances, because in the 1644 edition of the Bible (Diodati) we are told that Joseph was sold by his brethren "to a company of Ishmaelites who came from Galaad; and their camels were laden with precious drugs, and ladanum resin, which they were carrying to Egypt to sell." The building of the altar upon which Aaron was to burn perfumes, after the return from captivity is too well known to need description, and the books of Exodus and Numbers will furnish many examples of the Hebrew use of perfumes for ritualistic purposes, and in the Book of Proverbs we find the personal use accentuated in such verses as "I have perfumed my bed with myrrh, aloes and cassia."

And if the history of almost any of the older Asiatic nations be studied, it will be found that almost every one of them was well acquainted with the use of perfumes, either for ceremonial or personal purposes, more often for both.

When we turn to the luxurious civilizations of the Greeks and Romans, we meet with the use of perfumes on every side. Let us take just one or two examples of their knowledge of the Art, and we can then pass on to the real purport of this little work. Apollonius, in a work which he wrote, entitled *A Treatise on Perfumes*, thus speaks of the principal perfumes in use amongst the Greeks. "The best orris comes from Elis or Cyzique; extract of roses from Phaselis, Naples and Capua; saffron from Sicily and Rhodes. The finest essence of nard is made at Tarsus, and extract of vine leaves at Chypre and Adramyttium. The perfume of marjoram and the apple blossom comes from Cos. Egypt is celebrated for its essence of Chypre, and those from Phoenicia and Sidon are the next best."

And so we might go on indefinitely. We cannot read a Greek or Latin poet nor even a historian without continually coming across references to the use and abuse of perfumes, and, if our readers wish to see to what an extent the use of perfumes became a "fine art" under the luxurious Greek and Roman civilizations, they may read with advantage, such articles as that on "Baths" in Smith's classical *Dictionary of Greek and Roman Antiquities.*

Having touched upon the antiquity of the Art of Perfumery, we may now proceed to deal with modern perfumery and perfume materials.

CHAPTER II

PERFUME MATERIALS IN GENERAL

There are so many hundreds of raw materials used by perfumers in the manufacture of their products, that it will here be possible only to deal with them in classes, with a special examination of a very few of the most important. In order to combine these substances so that the result may be a successful perfume, it is not only necessary for the perfumer to have a very considerable practical knowledge, which is gained only by long experience, but, if the best results are to be achieved, he must have some scientific knowledge of the chemical characteristics of the various constituents of his raw materials, so that he may not blend together antipathetic substances, but may be sure that his perfume is, so to speak, harmonious and free from discords. Broadly speaking he has the following groups of bodies from which he may draw for the manufacture of his wares—

1. Materials of purely vegetable origin.
2. Materials of purely animal origin.
3. Artificial substances, which are either simple substances synthesized by chemical processes, or may be mixtures of such substances with some constituents of a natural perfume material.

All these substances are of the highest importance to the perfumer, and although forty years or so ago, he had only classes (1) and (2) to rely on, it is not an exaggeration to say that to-day many of the articles embraced by class (3) are absolutely essential to the successful modern perfumer.

We will now briefly examine the characters of the three categories of substances just enumerated.

It is correct, within narrow limits, to say that vegetable perfume materials consist in the main of "essential oils" or as they are often termed "volatile oils." It is true that they are not always *used* in the form of essential oils, nor can they always be obtained in that form. It is also true that the essential oils are often accompanied by resinous matter, so that the odoriferous body is known as an "oleoresin" or as a "balsam." But, broadly speaking, it is true to say that the vegetable perfume materials are almost entirely essential oils in some form or other. They may be, and often are, of so delicate a nature that they will not withstand the ordinary process of extraction of essential oils, so that they have to be prepared in some other manner, and presented to the manufacturing perfumer in some other form, such as a flower pomade; of these and similar products we shall speak in the sequel. For the moment, we need only say that they are by far the most important of the materials used in the manufacture of perfumes.

The second class of products referred to above is that which embraces those of purely animal origin, such as musk, ambergris, castor and civet. These products are, in the natural form, hardly recognizable as "perfumes," except, perhaps musk, although to most people natural musk has a somewhat disagreeable odour. Civet, for example, is a substance with a foul and very objectionable odour. It is only in a state of intense dilution that the virtue of these bodies as perfume materials appears. In such dilute solution, they not only modify the odours of other perfume materials, but they also have a very remarkable fixative value, that is, they render the more volatile substances present in the perfume much less fugitive and much more lasting.

The evolution of the third group of perfume materials referred to above constitutes a veritable romance of organic chemical research. Starting from either some substance which occurs naturally in a plant, or from one of the coal tar products, the organic chemist has succeeded in building up a number of synthetic perfumes which are to-day absolutely necessary in successful perfume manufacture. In some of these cases the artificial body so built up is absolutely identical with the principal constituent of the natural perfume which it imitates. Such, for example, is the artificial methyl salicylate. Now, as the essential oil of wintergreen contains about 99·5 per cent. of methyl salicylate, it is easy to understand that the pure 100 per cent. synthetic product is for all practical purposes, identical with the natural plant product. In the same way synthetic benzaldehyde made from coal tar is practically identical with natural essential oil of almonds. Vanillin, made by a complicated process from oil of cloves, is identical with the crystalline substance which is present in vanilla beans, and to which the beans owe their characteristic odour and flavour. But in this case the natural substance does contain small amounts of other bodies which modify the odour of the vanilla bean, so that artificial vanillin is not quite identical in odour with natural vanilla beans. It is, however, so near a match for the beans, that it is used as their substitute in an enormous proportion of the chocolate consumed, and it would require a connoisseur to recognize the difference between chocolate flavoured with the natural and the artificial substances. If we turn to synthetic musk and synthetic violet, however, we find that the artificial product is quite different from any constituent of the natural product. In such cases the synthetic product only claims to produce a musk-like odour or a violet-like odour. But in spite of this, this class of body represents the corresponding odour so well, that they are used in enormous quantities as substitutes for the natural bodies. For example, the vast majority of the violet perfumes used by the public contain a synthetic body known as ionone, which is manufactured by a complicated process from essential oil of lemon-grass or verbena. Many violet perfumes, indeed, especially the cheaper varieties, contain no true violet product at all. Preparations of ionone, however, so well represent the violet perfume that the public are quite satisfied with the result. Then again we have the mixed type of perfume, consisting of some synthetic or artificial product, and some natural substances mixed together. Examples of this are artificial oil of neroli, and artificial Otto of Rose. The chemist can make a substance called methyl anthranilate from coal tar. This body has a characteristic neroli odour, and is actually present in natural neroli oil. But it is only by diluting it with a number of other bodies, some synthetic, some extracted from various plants, that an oil closely resembling true oil of neroli can be obtained. In the same way, the chemist manufactures a complicated body called phenyl-ethyl alcohol, also from coal tar. By mixing this with geraniol, citronellol and other bodies which can be extracted from various plants, and several other synthetic products, an oil is obtained which is a very passable imitation of Otto of Rose, and serves well for the manufacture of cheap rose perfumes. It is true that in this particular case, as in some others, the artificial product is not as fine in odour as the natural product, which it imitates rather than coincides with, but this type of product is largely and successfully employed in the manufacture of cheaper perfumes than would be possible if the much more expensive natural Otto of Rose were employed.

In the succeeding chapter, the plant substances above referred to will be studied in more detail.

CHAPTER III

PLANT PERFUME MATERIALS

WITHOUT going into minutiae of detail we may broadly divide this group of bodies into five classes as follows—

1. Essential oils.
2. Pomades.
3. Concretes.
4. Balsams, etc.
5. Plant substances other than the above.

As the essential oils are volatile in a current of steam, it is obvious that in order to separate them from the inert non-volatile matter of the plant tissues, a process of distillation is the ordinary method by which they are obtained. At the same time, it cannot be too strongly insisted that the less an essential oil is heated, the better is its quality. Hence, if distillation be the process employed for the preparation of the oil, the most scientific method should be employed, and the lowest possible temperature should govern the distillation. As a matter of fact it is very rarely the case that any choice is left to the manufacturer, and he is compelled to distil his essential oils. In a few cases he is able to resort to a cold process of expression such as is the case with lemon, bergamot and orange oils, but in most cases, where distillation would destroy the delicate essential oil, he is forced to resort to the preparation of the perfume material in some other form, such as a pomade. In order to illustrate this group of perfume materials, which are exceedingly numerous we shall describe a few of the perfume plants in detail. These examples will suffice to illustrate the whole group which contains, amongst others, the following essential oils which are amongst those most commonly used by the manufacturing perfumer—

Almond	Cloves	Marjorame
Aniseed	Eucalyptus	Orange peel
Bay leaf	Geranium	Patchouli
Bergamot	Lavender	Roses
Cassia	Lemon	Sandalwood
Cedar wood	Lemon-grass	Vetivert
Cinnamon	Linaloe	Ylang-ylang
Citronella		

The above are, of course, merely a few examples to indicate the scope of the vegetable world to which the perfumer turns for the preparation of his raw materials.

Lavender. Few perfumes are so popular amongst those of delicate and refined taste as the old-fashioned lavender water. The exact composition of this perfume differs with the individual manufacturer, but it is essentially a solution of oil of lavender in alcohol, with small amounts of other ingredients to slightly modify or "round off" the lavender perfume, and traces of some fixative substance. The essential oil of lavender, however, is the main ingredient, and it is essential to success that the best oils should be selected for the purpose of manufacturing the perfume. It is, of course, absolutely necessary that in this, as in every case of an alcoholic perfume, only the finest spirit should be employed.

France is essentially the home of the lavender plant. Italy and Spain produce small quantities, and a small amount is cultivated in England. The oil distilled from the English grown plants differs very considerably from that obtained from French plants, and the English oil invariably commands a higher price than foreign oil. In the author's opinion the best lavender waters are prepared from a mixture of the two oils.

The lavender plant grows wild in about twenty of the French Departments. It is a strong and robust plant withstanding cold of an intense nature, and well adapted to the general conditions of French soil and climate.

For many years two species of the plant were

FIG. 2.

AN OLD STILL HOUSE AT MITCHAM

described under the common name *Lavandula officinalis*. Jordan separated the two species and renamed them, as follows—(1) *Lavandula delphinensis*, is found in the highest regions and yields an essential oil very rich in esters, which are amongst the principal odoriferous constituents of the oil ; (2) *Lavandula fragrans*, which is frequently, but not always, found associated with its sister plant, and which yields a more penetrating oil.

The spike lavender is a quite different plant—*Lavandula latifolia*—and yields the oil of spike lavender, which is quite different from the ordinary oil of lavender. But this particular plant and *Lavandula fragrans* are very easily hybridized, and the resulting bastard lavender yields an essential oil which has properties intermediate between those of the oils from the two parents. The bastard lavender plants often get mixed with the pure species, and to that extent cause the resulting essential oil to be of less value.

M. Leopold Lamothe describes the lavenders in the Drôme district, where he sees great possibilities for cultivation of hitherto unproductive land, in the following manner—

(1) The *coarse lavender* or *bastard lavender*, growing at the foot of the mountains. It grows to a large size, sometimes a metre in circumference. It yields a coarse essential oil. According to G. Chatenier, it is a hybrid of spike or *Lavandula latifolia* and of *L. officinalis* var. *fragrans* (see below). Botanically, it is thus described : plant 5 to 7 decimetres in height, stout woody stems, with numerous branches, erect, often divided at the summits into erect spreading shoots. Leaves, straight, oblong, obtuse, narrowed towards the base, with edges turned in below at the end, green on both faces. Spikes generally coarser than in the parent with verticillasters more or less far apart. Oval bracts, lanceolated or lanceolated and more or less longly acuminated, green before the anthesis, almost equal to the calix. Numerous bracteoles, straight and greenish. Calices of a blueish-grey. Pollen scarce and poorly developed. Ovaries generally sterile.

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FIG. 3.

CUTTING LAVENDER

This variety is fairly common in the neighbourhood of Nyons.

(2) The *medium lavender*, which is met with in the vicinity of the first, and always at a higher elevation. It is an intermediate variety created, no doubt, by the climate. According to Jordan it is the *Lavandula fragrans*, a subdivision of the species *L. officinalis* D. C., with very numerous slender and stiff branches; leaves very erect, very narrow and very much rolled up, and dense spikes. It is very widely distributed and is met with on nearly all the arid slopes and on the low hills of the arrondissements of Die, Montélimar and Nyons. The oil produced from it is deficient in fineness.

(3) Lastly, the *fine lavender*, which yields the best essential oil, grows at the highest altitude. Jordan classifies it as the second subdivision of the species *L. officinalis* D. C. and calls it *L. Delphinensis* Jord.; it has strong stems with flexuous branches, oblong leaves, lanceolated, spread out and erect, and loosely arranged spikes. It inhabits the high districts of Lus-a-Croix-Haute, Valouse, Ballons, Teyssières and Vesc.

There are a number of other species of lavender found in France, but we need not deal with these here.

The lavender harvest commences about the middle of July, and in many cases the flowers are distilled in a very crude manner over a naked fire, in a small portable still which has not undergone any modification for centuries. It is very common for the small peasant to hire the still from the nearest town, for which he pays a sum of about 20 francs for the season, and which he sets up in some spot where he can obtain water for the condenser and wood for his fuel. The flowers and water in the still are heated over the naked fire, and are, obviously, liable to be burnt, even when most carefully distilled. Further, in the attempt to economize in fuel, the warm water is not always emptied out of the still, and as this is full of salts of lime, there is a rapid accumulation of lime salts in the interior of the still, which, at an elevated temperature react with the esters present in the oil, and decompose a portion of them into free acids and free alcohols, which cause a corresponding deterioration in the odour value of the oil.

The following summarizes the advice given to the small peasant distiller by M. Gattefossé, one of the largest distillers of lavender oil in the South of France.

(1) Cut the flowering spikes when flowering is at its maximum, for the plant then contains the very highest percentage of esters ; and let the harvest be as quick as possible, if possible within a week.

(2) Choose, by preference, the morning and the evening of a day without wind, and as cool as possible, since wind and heat dissipate a good deal of the perfume.

(3) If it should come on to rain, or if it be foggy, cease harvesting and wait for warm weather to repair any damage done to the plants.

(4) If the flowers cannot be taken at once to the still, store them in a closed shed, so as not to allow them to dry, and so lose some of their perfume.

(5) Do not allow any fermentation to take place, as this spoils both the quality of the oil and its yield.

(6) Set up the still near a plentiful supply of water for condensation purposes.

(7) Use pine wood, by preference, as fuel, as this burns steadily on account of the resin it contains.

(8) Watch the still carefully, and empty it, water and all, after each charge, so as to prevent the accumulation of lime salts.

(9) If possible, replace the old-fashioned still by the most modern one you can obtain.

(10) Leave the oil, when distilled, for several months before you offer it for sale, when it should be as clear as crystal.

(11) Get the distillate tested for its percentage in esters.

Apart from this system of peasant distillation, there has been a considerable advance in the methods adopted by the larger distillers, and in the larger centres of the industry, a rapid system of carrying the flowers to modern distilleries has been arranged. These modern distilleries contain apparatus for steam distillation, thus avoiding the risk of burning the plants and the oil, which is involved in the use of open fires, and the quality of the oil produced at such distilleries is very much better than that of the peasant distilled oil.

Lavender oil is a pale mobile liquid very soluble in alcohol, and owing its odour to several constituents, the principal of which is the ester, linalyl acetate. It is customary to value lavender oil according to its ester content, but this is not always a true basis of valuation, as oils grown, for example on the Italian frontier, containing about 30 per cent. of esters, are often of finer odour than the sometimes rank oils containing 40 per cent. grown in other districts. English lavender oil rarely contains more than 10 per cent. of esters, and owes its characteristic odour to other bodies, more than to its linalyl acetate.

The principal causes which influence the amount of esters present in a French lavender oil are the following—the relative proportions of the various types of flowers distilled ; the amount and character of chemical manure employed ; the amount of sunlight the plants get ; the weather during the harvesting ; the time between

FIG. 4.

LAVENDER STILL.—(GATTEFOSSÉ—VIAL PATTERN) gathering the flowers and their distillation ; the altitude at which the plants grow ; and, indeed, many other minor circumstances, which have some influence on the development of the plant.

Most lavender oils have characters which fall within the following limits—

Specific gravity = 0·870 to ·892
Optical relation = –5° to –10°
Esters 28 to 45 %
(English oil under 10%)

Adulteration of the oil is very common, chiefly with the much less expensive spike lavender oil, and artificial esters prepared chemically, which are practically odourless, and are only added to deceive the analyst and make the oil to appear to have a higher ester percentage than it really has.

The Rose. The Rose has often been described as the Queen of Flowers. It certainly is second to none in its popularity amongst manufactured perfumes, and the well known "Essence of White Rose" is always a favourite with ladies. It is necessary to here remark that the word *white* is a misnomer, as nearly all the rose perfume is distilled from *red* roses. The perfume of the rose will serve to illustrate more than one process used for the manufacture of raw materials for the perfumer.

The essential oil of the rose, better known as Otto or Attar of Rose, is produced principally in Bulgaria, but a fair amount has, in the past five years, been distilled in France, and French Otto of Rose is becoming a distinct competitor of the Bulgarian commodity. France, however, has long been a very considerable contributor to the world's output of rose perfume. For years past she has distilled a small quantity of the Otto, and has produced practically the world's supply of Rose Water, and has also manufactured a very large quantity of Rose Pomade, without which most of the best "Essence of White Rose" would never have been manufactured. A very short history of the rose perfume will not be out of place.

The red colour of the red rose is due to one of the following causes (at least so we are told in very old authorities !)—

(1) The blood of Venus, drawn by a thorn upon which she trod when Mars was pursuing her in a fit of righteous anger.

(2) A drop of nectar spilt at a feast of the gods by Cupid.

(3) The sweat of Mahomet, as the Turks affirm.

Be this as it may, classical authors have devoted much space to the glory of the rose, and classical literature is full of praise for the flower and its perfume.

Herodotus in his *History* states that the odour of the rose was sought after by drinkers as a remedy against headache caused by over-indulgence. Horace, too, recommends an unsparing use of roses at the commencement of a feast, and during the decadence of the Roman Empire, the Romans used to soak rose leaves in their wine before they drank it. It is probable that the first use of Rose Water, as distinct from the petals, was in Egypt, and the species of rose the Egyptians used was almost certainly *Rosa Damascena*. It was between 1582 and 1612 that the oil or Otto of Rose was discovered. The discovery has been described in two separate histories of the Grand Moguls, one by Mohammed Achem and the other by Mannuci, a Venetian physician. The latter tells us that at the wedding feast of the princess Nour-Djihan with Djihan-Guyr, the amusements and luxurious appointments were on a very extravagant scale. Circling the whole of the gardens, a canal was dug which was filled with rose water. Whilst her newly-made husband and she walked along the borders of the canal they perceived an oily substance floating on the surface. It was skimmed off and found to be the most delicious perfume they had ever smelt, and the manufacture of Otto of Rose commenced in Persia about 1612, and in 1684 the distilleries of Shiraz were well known and working on a large scale, producing what they termed the *Aettr Ghyl*, literally the "fat of the flower." Through the Turks the manufacture was introduced into Europe, and it is probable that the first otto was distilled in Bulgaria, then part of the Turkish Empire, about 1690.

In France, up till five years or so ago, a small quantity of Otto of Rose was manufactured from the red rose, *Rosa centifolia*, but was entirely consumed in the country itself. French roses were almost entirely used for the manufacture of Rose Pomade (which is an altogether different type of product from the essential oil, and which will be discussed in a later chapter) and of Rose Water. To-day, however, numerous other roses, such as the "Rose d' Hai" are used for distillation purposes, and a certain amount of French Otto of Rose distilled from the so-called mixed garden roses, is available for the requirements of other countries. Roses, as flowers, were exported before the war to all the capitals of Europe, and directly the season for cut flowers was over, millions of roses were wasted in the South of France, because no one thought that they would yield an otto which would be able to compete with the usual type of this product. A number of the more scientific cultivators, however, carried out a number of experiments and new roses were introduced, the chief object of the rose grower being to improve the odour, rather than the appearance, of the flower. The type of still was also improved, and the result has been that a type of still is now used which ensures the maximum yield and the finest otto. It is probable that 10,000 to 20,000 ounces of French otto is, up to the present, the maximum annual production, but it is possible that in the near future this may increase substantially.

Apart from French otto, the world draws its supply from Bulgaria (with a small amount made in some of the Turkish provinces).

The greater part of the Bulgarian Otto of Rose is distilled by small peasants who have their rose gardens throughout the valleys of the greater Balkans and Sredna-Gora. The area under rose cultivation is included between the 24th and 26th degrees of longitude E., and the 42nd and 43rd degrees of latitude N. The geological formation is principally syenite, the decomposition of which has produced a very workable soil which has become very fertile. The roses flourish best on sandy sun-exposed slopes, with a south or south-eastern aspect. The principal districts in which the flowers flourish are : (1) the department of Stara-Zajora, including the cantons of Kazanlik, Nova-Zagora, and Stara-Zagora ; (2) the department of Pazardjik, chiefly the canton of Pechtera ; (3) the department of Philippopoli including the cantons of Karlovo, Tchirpan Novo-Selo and Brezovo.

The flowers are gathered in the early morning just before the sun rises, and the picking should cease by 10 to 11 o'clock unless the day be cloudy, when it continues all day. If the gardens are near a small town, a local distillery usually exists, to which the flowers are carted, and they should be distilled on the same day as they are picked. In the case of a few of the larger centres modern distillation plant exists, and very fine otto is distilled. The bulk of the otto, however, is distilled by the peasants in very primitive stills. The distilleries—apart from the few large modern ones above referred to, are primitive wooden sheds, with the stills in rows as illustrated (Fig. 5). There are copper alembics from 3 to 5 ft. in height, resting on furnaces built on bricks. They hold about 10 to 15 kilos of rose flowers and 70 to 100 litres of water. The distillation water, from which the otto has been separated contains dissolved perfume, so it is returned to the still and used in the distillation of a fresh batch of flowers. A well tended garden of an acre will yield about 100 lbs. of flowers every day for three weeks, and 1 lb. of otto is the average yield from 3,000 lbs. of the flowers. The roses cultivated in Bulgaria are of two varieties, the red and the white rose. As a matter of fact, the red rose is the only one which is really cultivated, the white rose, which is of more vigorous growth, being used for hedges between the plantations.

The essence of otto is a pale yellow liquid which sets to a jelly like solid at a temperature of from 18° to 24° C., due to the deposition of crystals throughout the whole mass. It consists of two well defined portions, namely the liquid portion which contains the whole of the odour of the oil, and the solid portion, known as the stearoptene, which is odourless. Sometimes this stearoptene is removed by large distillers, and the resulting oil sold at a correspondingly enhanced price, as "stearoptene-free" Otto of Rose. As a matter of fact, the stearoptene is only so slightly soluble in alcohol that it is usually thrown out by admixture with spirit, and then separated by filtration.

Bulgaria usually exports from 30 to 60 per cent. more "Otto" than she distils. This is due to the enormous amount of adulteration which takes place, and really pure Otto of Rose is the exception rather than the rule. The principal adulterant is rectified

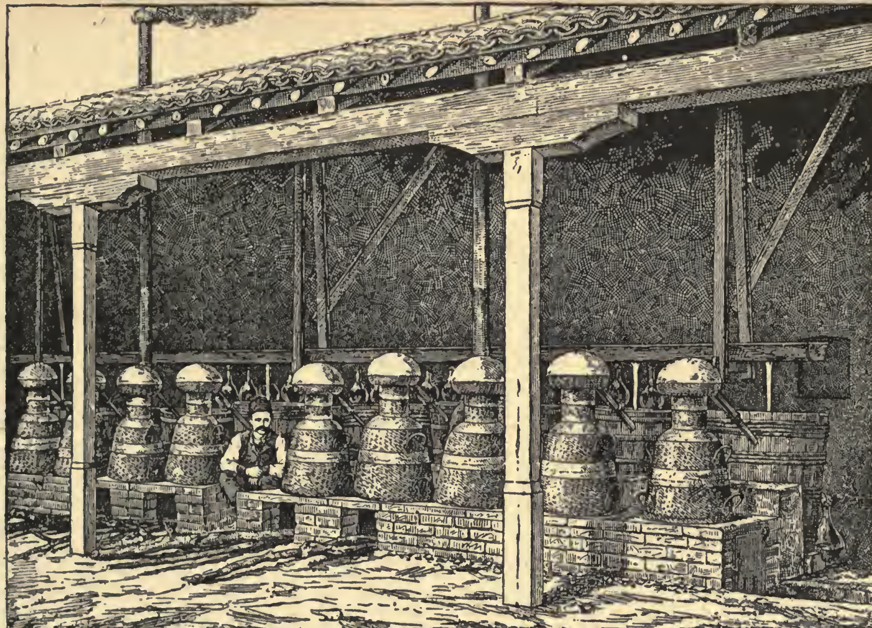

Fig. 5.

NATIVE DISTILLERY OF OTTO OF ROSE (BULGARIA) geraniol, which has a sweet rose-like odour, and is obtained either from citronella or palmarosa oils.

Genuine Bulgarian Otto of Rose has the following characters—

Specific gravity at 30° C	= 0·850–0·860
Optical rotation	= –1° to –4°
Congealing point	18° to 24°
Total alcohols calculated as geraniol	= 70–75%.

Otto of Rose is used on a fairly large scale for perfuming the highest grades of soap, and for the manufacture of handkerchief perfumes. It is used also in certain high-class confectionery and to a not inconsiderable extent for perfuming certain types of tobacco. In the manufacture of essence of "white" rose it is frequently associated with a very little sandalwood oil, and almost always with traces of an animal fixative agent.

Bergamot Oil. Our Italian friends produce the world's supply of Oil of Bergamot, one of the essential constituents of Eau de Cologne. This favourite perfume was first made in Italy, the secret being taken to Cologne, where a manufactory was started by a German, who later had many competitors. Now, as the whole of the perfume materials in Eau de Cologne are either of Italian or French origin, except perhaps traces of other materials, it is obviously ridiculous that people should think that the Germans have a monopoly in the manufacture of the best quality. The principal ingredients in this perfume are the essential oils of neroli, bergamot, lemon, rosemary, and traces of various other oils according to taste, such as lavender, rose and cinnamon.

Bergamot oil is one of the few essential oils which are spoiled by distillation; hence, it is produced by an expression process. It is obtained from the peel of the bergamot fruit, *Citrus bergamia*, the principal centre of the industry being in Southern Calabria, which is practically the only province of Italy where the bergamot tree is cultivated. There are extensive plantations in and round about Reggio, Melito, Gallico, Avangea, Sancta Catarina, S. Lorenzo Palizzi, and Staiti.

The greater part of the oil is expressed from the peel by machinery in the following manner. The machine consists of a wheel with pegs which revolve a drum with bars, ending in a bowl. The last-named is a kind of plate about 6 to 8 ins. in diameter, provided with copper points about ¼ in. long, and fitting closely into a cylinder, the bottom of which constitutes a similar plate, on which the ripe fruits are placed. By its weight the drum presses the fruits, and the two sets of copper points tear the rind, and the liquid which escapes is collected in a receiver placed at the lower end of the machine. This liquid is filtered through filter bags suspended in metal cases, so as to protect the oil from being oxidized by the air, and the filtered mixture of water and oil is allowed to settle and the oil is then drawn off. It should be dried by contact with a little sodium sulphate, as water acts somewhat deleteriously on bergamot oil.

A certain amount of bergamot oil is also obtained by the older process known as the sponge process, which is the usual process by which the oils of lemons and orange are manufactured. In this process the operator takes a fruit in his hand and with three rapid strokes with a large knife, cuts off practically all the peel in three pieces. The peeled fruit is then used for pressing the juice from. The slices are then passed along to a second workman, seated on a stool with a pan at his feet. With an ordinary sponge he presses each piece of peel by the edge, so as to bring the convex peel into a flat surface. By this pressure which is very slight, the oil glands are broken and the oil is absorbed by the sponge, which is from time to time squeezed over the pan to recover the oil. One man can obtain about 25 to 27 ounces of oil per day by this method. Bergamot trees flourish best on well-watered, low-lying lands, and are frequently cultivated amongst the lemon and orange trees. The harvest is gathered in November and December and early in January. The oil is of a green colour—sometimes a brown-green, due to the green colouring matter of the peel, and not, as used to be said, to the presence of copper. It owes its beautiful odour almost entirely to the 35 to 42 per cent. of linalyl acetate which it contains. As would be expected, this oil, being pressed from the peel and not distilled, contains a little non-volatile matter which it dissolves out of the peel. The pure oil has the following characters—

Specific gravity	= 0·880 to 0·886
Optical rotation	= + 8° to + 20°
Esters	= 35 to 45%.

Ylang-ylang Oil. Ylang-ylang is, of course, a very favourite perfume. The principal ingredient used in its manufacture is the essential oil of Ylang-ylang.

The oil is derived from a plant which grows in several parts of the world known as *Cananga odorata.* The oil known as Ylang-ylang is the finest variety, and is produced principally in Manila, whilst the oil produced in Java and several other places is known as Cananga oil. The difference between the oils is not due in any way to any botanical difference between the trees, but to the climatic and soil conditions, and to some extent to the care with which the flowers are sorted and selected.

The tree is a native of Ava and Tenasserium, and is fairly widely distributed throughout Southern Asia. When wild the tree grows to a considerable height, but the flowers have little or no odour.

When cultivated the tree does not grow to such a height, and the flowers have a delightful perfume.

It is in Manila that the best oil is distilled, but even there, many different qualities are produced. The industry is an important one in Java, and also in the French colony of Réunion, where the cultivation of the Ylang-ylang has made great progress. The trees attain a height of 40 to 65 ft., and are very elegant and ornamental. The flowers are produced at the base of the leaves, and are in bunches of two or three on a short stem. The oil is of a very delicate nature, and requires very careful distillation. It owes its odour to a number of substances, amongst which are esters of benzoic acid, and para-cresol methyl ether. The oils vary considerably in their physical and chemical characters, and are sometimes adulterated with fatty oils, such as olive oil.

We will now turn to a series of essential oils which form a very important group, both from the perfumer's point of view, and from that of the merchant. There are a number of oils known as the "Grass oils," distilled from members of the natural order "Gramineae," grown in various parts of the world, more especially in India, Ceylon, Burmah, and Java, although cultivated to some extent in many other places. These grass oils furnish some of the most important raw materials to the manufacturing perfumer. Those that we shall deal with are the following—(1) Palmarosa and ginger-grass oils, (2) Lemon-grass oil, (3) Vetivert or Cus-cus oil, (4) Citronella oil.

Palmarosa and ginger grass oils were for many years regarded as many different qualities of the same oil, ginger-grass oil being regarded as an adulterated palmarosa oil. This, however, is now known not to be the case. Both oils appear to be the product of the same species of grass, Cymbopogon Martini. There are two kinds of this grass, known in India as Motia and Sufia, the former yielding palmarosa oil, and the latter ginger-grass oil. It is, however, probable, that much of the ginger-grass oil of commerce contains some of the more esteemed palmarosa oil, in order to improve its own poor odour. The two grasses may, perhaps, be regarded as varieties. There is a fairly big demand for palmarosa oil, and the output of the two oils is probably about 150,000 pounds per annum.

Palmarosa oil was formerly commonly known as Turkish geranium oil. on account of the fact that it usually arrived here *viâ* Turkey, and was, at one time, largely, and still is, to some extent, used in Turkey as an adulterant of Otto of Rose. It is an almost colourless, or pale yellow oil, with a geranium like odour, but without the delicate perfume of the geranium. The essential difference between palmarosa oil and geranium oil is that the former consists, in the main, of free geraniol, whilst geranium oil owes its sweet odour to geraniol contained in the form of esters, principally as geranyl tiglate. The grass from which the oil is distilled is known locally as Rusa grass. At present the principal places of production of the oil are Pimpalner, Akrani, Nandurbar, Shahada and Talada, all situated in Khandeish. It is also prepared on a smaller scale in the districts of Nagpur, Sagar, Jubbulpur, Karnul and Ajmere. It is produced in more or less primitive stills, although a certain amount of modern stills are now in use. Pure palmarosa oil has the following characters—

Specific gravity	= 0·887 to 0·900
Optical rotation	= −3° to +6°
Refractive index	= 1·4720 to 1·4765
Geraniol	= 75 to 90%

It is quite soluble in 3 volumes of 70 per cent. alcohol.

It is used as a cheap perfume of the rose-geranium type, and also for the commercial preparation of pure geraniol, which is of far sweeter odour than the palmarosa oil itself. Palmarosa oil is exported from Bombay in pots containing 100 to 200 lbs. each.

Ginger-grass oil differs in odour from oil of palmarosa in that its alcoholic constituents consist of a mixture of geraniol and dihydrocuminic alcohol. Its characters are as follows—

Specific gravity	= 0·900 to 0·950
Optical rotation	= −30° to + 50°
Refractive index	= 1·4775 to 1·4950

It is only suitable for use as a cheap perfume, in soap and similar preparations. Lemon-grass oil is an oil which enjoys a considerable employment in the perfume industry. It is commonly known as verbena oil, on account of its odour being very similar to that of the true vervain or verbena oil, which is but rarely found in commerce. Both oils owe their typical perfume to the presence of a large percentage of the aldelyde citral, and lemon-grass oil, in addition to being used as a perfume itself, is the source of the citral which forms the only raw material from which ionone, or artificial violet perfume is manufactured. The bulk of the lemon-grass oil of commerce is derived from the grass Cymbopogon flexuosus, the less soluble oils being apparently derived from Cymbopogon citratus. The former grass yields an oil which is soluble in 3 volumes of 70 per cent. alcohol, and is known as "soluble" lemon-grass oil, whilst the latter yields the so-called "insoluble" oil, which is not soluble in 3 volumes of 70 per cent. alcohol. It is probable that a small amount of the lemon-grass oil of commerce is derived from other, lesser known species, such as Cymbopogon pendulus, but the quantity of this is practically negligible. The bulk of the lemon-grass oil of commerce comes from India, but Ceylon and Java produce a certain amount, and various other parts of the world are responsible for small shipments from time to time. Uganda has sent over some shipments of oil to this country, which were of quite good quality, and the West Indies took up the industry some fifteen years ago. The West Indian oil appears to have been distilled from a different variety of the grass, and it was found to contain a considerable amount of the so-called olefinic terpene myrcene. This body is very easily oxidized into an insoluble compound, and although the oil usually left the West Indies as a quite soluble lemon-grass oil, by the time it reached this country it was insoluble; and, further, it was found that the citral underwent rapid oxidation, so that the actual citral value of the oil rapidly diminished. These defects caused the oil to be unable to compete with the East Indian variety, so the distillation in the West Indies was practically abandoned. Comparisons of the lemon-grass oils from Ceylon, India, Uganda, and Bermuda were made in 1911 in the laboratories of the Imperial Institute.

It appears that the grasses used in Ceylon for distillation are of a mixed character, some oils being of the insoluble variety, whilst others appear to be distilled from mixtures of different grasses. The Uganda oil was of the insoluble type, and was undoubtedly distilled from Cymbopogon citratus, and contained from 64 to 75 per cent. of citral. The Bermuda oil only contained 40 per cent. of citral, and could not compete with the East Indian oil, whilst the Montserrat oil was a soluble oil containing 74 per cent. of citral. The lemon-grass oils from India which were examined were as follows—

(1) Tyrna lemon-grass oil, a deep yellow oil, having the usual odour of lemon-grass oil.

(2) "Cochin lemon-grass oil," a deep-yellowish-brown oil, which had a fine lemon-grass odour rather more pungent than that of the preceding and following samples.

(3) "Mariani lemon-grass oil," a golden-brown oil having the usual odour of lemon-grass oil.

(4) "Ceylon lemon-grass oil," a deep-yellowish-brown oil, with the usual odour of lemon-grass oil.

	No. 1.	No. 2.	No. 3.	No. 4.
Specific gravity at 15°C. / 15°C.	0·9021	0·9053	0·9140	0·9058
Optical rotation in 100 mm. tube at 20° C.	−0°20	−0°39′	−0°5′	−0°6′
Citral by sodium bisulphite method, *per cent.*	72·5	84·5	73·0	76·0
Solubility in 70 % alcohol	Not completely soluble to a clear solution even in 10 volumes of alcohol.	Soluble to a clear solution in 2 volumes. Further addition of alcohol produced a slight turbidity.	Did not give a clear solution even in 10 volumes of alcohol.	As No. 3.
In 80% alcohol	Soluble in 0·7 volumes. The addition of more alcohol caused turbidity which did not disappear on further dilution.	Soluble in 0·8 volumes to a clear solution. A large excess of alcohol produced turbidity.	Soluble in 1 volume, but became very turbid on further dilution.	Gave an almost clear solution with 1 volume of alcohol, but became very turbid on further dilution.
In 90% alcohol	Soluble in quantities up to 1 volume but became cloudy on the addition of more alcohol, and did not again become clear.	Soluble in all proportions although an excess of alcohol produced slight turbidity.	Gave a clear solution up to 1 volume of alcohol, but became turbid on further dilution.	Remained clear up to the addition of 1 volume of alcohol, but then became turbid and did not clear on further dilution.

Only one of the present samples, the "Cochin lemon-grass oil," belonging to the group of "soluble" lemon-grass oils, the remaining three oils all being insoluble in 70 per cent. alcohol.

These four oils all contained a satisfactory amount of citral, but the "Cochin" oil was particularly rich in this constituent, containing 84·5 per cent. Most lemon-grass oils of commerce contain from 70 to 75 per cent. of citral. If, therefore, the "Cochin" grass grows well and gives a good yield of leaves, it will be desirable to encourage its cultivation rather than that of the other varieties.

Lemon-grass oil owes its perfume value almost entirely to its citral, which gives it a very powerful odour, which is slightly modified by the presence of small amounts of other constituents. It owes its monetary value when purchased for ionone manufacture entirely to its citral, as it is usually sold on its citral value, the oil being graded as 70 to 75 per cent., 75 to 80 per cent., and so on. It is used in the preparation of all perfumes of the verbena type, and in small quantity when a fresh lemony odour is required to round off other predominating perfumes. We now come to a very valuable perfume oil known in commerce as vetivert oil. The plant which yields vetivert oil is known locally as cus-cus or khas-khas, and was up till recently described as Andropogon muricatus, but is known now to be Vetiveria zizanoides. The oil is not distilled from the leaves, but from the roots.

These roots are known in Bengal under the name of khas-khas, meaning in Hindustani, "aromatic roots," from which the name cus-cus is easily traced. The plant is a perennial tufted grass growing to a good height, and is found all over the country near the Coromandel coast, Mysore, Bengal, Burma and the Punjaub. It is also found in Réunion and Mauritius and in the West Indies. The leaves themselves are practically odourless, whilst the roots have a strong, agreeable odour. On distillation, the first fractions passing over are much more volatile and lighter than those which come over with difficulty towards the end of the distillation. These light and heavy oils can be separated by using a steam-jacketed still with steam at a pressure of about 10 lb., until no more oil comes over. The heavy oil is then obtained by passing steam at a higher pressure direct into the retort. The oil distilled in Europe is usually, if not always, a single distillate, and the fractionated oils are scarcely commercial articles. The yield of oil is a matter of much disagreement. According to Piesse, 100 lb. of oil yield about 9 or 10 oz. of oil, whilst Watts states that only 2 oz. are obtained. Other observers give from ·2 to ·4 per cent. Probably about 1 per cent. is the usual average. Some of the oil (which is entirely used for high class perfumery) as found in commerce is adulterated, frequently with a fixed fatty oil.

The oils distilled in Europe from the roots imported from India has the following characters—

Specific gravity	= 1·015 to 1·045
Optical rotation	= + 24° to + 36°
Refractive index	= 1·5200 to 1·5275

The oil distilled in Réunion is now an article of commerce on a fairly large scale, and differs somewhat in its physical character from the above. A pure Réunion oil will usually have the following values—

Specific gravity	= 0·990 to 1·015
Optical rotation	= + 20° to + 25°
Refractive index	= 1·5130 to 1·5260

Vetivert oil is a thick, viscous, brown liquid, with a heavy penetrating odour, of the character usually associated with the idea of Oriental perfumes. It is intensely penetrating and in addition to its odour value, has a distinct value as a fixative. It owes its odour to an alcohol named vetivenol and a sesquiterpene or mixture of sesquiterpenes known as vetivene. It blends well with oils of the type of orris root oil, and with cassie flower oil, and is very useful in the preparation of perfumes of the Oriental type. The last of these grass oils to be described is Citronella oil. This oil is distilled on an enormous scale, and is used for perfuming the cheapest variety of household soaps and similar inexpensive products. Substantially there are two varieties of the oil, the common, and cheaper, being the oil distilled in Ceylon, whilst the finer oil is typified by the Java distillate which is closely resembled by that distilled in Burmah. The odour value of Citronella oil depends, in the main on two substances, geraniol and citronellal. The principal causes of the difference between the odours of the Ceylon and the Java oils are as follows :

(1) The Ceylon oil is almost exclusively distilled from the variety of Cymbopogon nardus known as Lenabatu grass, whilst that distilled in Java is obtained from the variety known as Maha Pengiri.

(2) The Ceylon oil is, with the exception of a small mount, usually known as "estate oil," almost invariably adulterated with petroleum.

(3) The Ceylon variety contains more geraniol than citronellal, the total of the two constituents present in commercial oils being about 55 to 58 per cent., whereas the oils of the Java type contain more citronellal than geraniol, the total amount of the two constituents being from 80 to 90 per cent. The Java type of oil is suitable for better class work than the Ceylon oil, and fetches a correspondingly higher price.

Neither oils are used to any extent in the preparation of expensive, high-grade perfumes, but both find very extensive employment in cheap perfumery.

The above short descriptions of plant essential oils are sufficient to indicate the general nature of the source of this important group of raw materials for perfumery.

It is to be noted that these oils occur in the most varied portions of the plant ; in some plants it is the flowers, in some the leaves, the wood, the bark or the root, which yield the perfume bearing material. Different methods of distillation are necessary to meet the varied characters of the oils, since the boiling points of the various constituents differ within very wide limits.

We may now leave the essential oils proper and turn to the group of raw materials manufactured from plants known as pomades. There are a number of plants which flourish principally in the South of France, which yield perfumes of so delicate a nature that they are very considerably damaged by exposure to any elevated temperature, and which have to be treated by a cold or practically cold process. The process used is really an extraction by means of a non-volatile, odourless solvent which becomes saturated with the perfume of the flowers, and which is then sold as a pomade when the solvent is a solid, or as a perfumed oil when it is a liquid. The solvents employed are usually the finest lard in the case of pomades and olive or fine mineral oil in the case of the perfumed oils. As these solvents are practically insoluble in alcohol, the finished pomade or perfumed oil can be shaken thoroughly with spirit, when the delicate perfume is now removed from the fatty solvent, and passes to the spirit, which is now a spirituous perfume either ready for use, or ready for the addition of other substances such as essential oils and fixatives, when a compound odour is required. Some flowers, when picked, contain all the perfume which can possibly be obtained from them ; others have the power of elaborating more perfume material as fast as that already present is removed by the solvent, provided the life of the flower be prolonged. These and other considerations decide exactly what process shall be used in their extraction.

Before describing the processes and for extracting perfumes by means of non-volatile solvents, we may shortly deal with the principal flowers of the South of France which are treated in this manner.

Jasmin. The flowers of the Jasmin are obtained from *Jasminum grandiflorum*, the shoots of which are usually grafted on to the stems of *Jasminum officinale*. This perfume is almost always extracted by the enfleurage process, but the actual essential oil has been prepared and found to be composed principally of benzyl acetate linalyl acetate, benzyl alcohol, linalol, and small quantities of other substances. It is an oil of specific gravity 1·008 to 1·018, and an optical rotation of $+ 2°$ to $+ 4°$. Jasmin flowers contain only a portion of the perfume which they are capable of yielding, fresh oil being developed by the flowers as the solvent fat removes what is originally present. The harvest is from July to October, and is one of the most important in the South of France. During the last twenty years the cultivation of jasmin has increased very largely. Mild weather is essential to a good crop, and sharp frosts cause a considerable loss to the cultivator.

Violet. The usual natural violet perfume is extracted from the flowers as a pomade. We say *natural*, since the greater part of the violet perfume of commerce is artificial, and will be described under synthetic perfumes, of which ionone, the representative of violets, is one of the most important. Two kinds of violets are grown in the South of France, the Parma violet, and the Victoria violet. Both are harvested in February or March. Autumn rains and mild weather in

January and February are very favourable to the obtaining of a good crop of both these flowers. The harvest of violet flowers, however, cannot be said to be on the increase, as the natural perfume is suffering severely from the competition of the artificial product. A certain amount of a perfume of a distinctive character is now being made from the green leaves of the violet plants.

Tuberose. Like the Jasmin flower, the Tuberose flower develops more perfume, as the non-volatile solvent extracts that which is already formed. The flowers of *Polianthes tuberosa* are very delicate, but, again like Jasmin, the actual essential oil has been isolated in a pure condition. Hesse succeeded in isolating 0·8 kilogram of the oil from the enfleurage pomade obtained from 1,000 kilograms of the flowers. It is a heavy oil of specific gravity 1·007, containing a ketone which has been named tuberone and benzoic and allied esters.

The cultivation of this flower is rather a delicate matter, and the results are always somewhat uncertain. The harvest is gathered in August and September, but of late years climatic conditions have usually been unfavourable, and the cultivation of this flower cannot be described as an expanding industry.

Rose. The French rose industry has been referred to under Otto of Rose. It is, however, in reference to the pomade industry that French roses have their greatest importance. The most remarkable development of the French rose industry during the past fifty years is the impetus given to it by Graveraux and Cochet-Cochet, who by crossing the well-known red rose, *Rosa damascena* with *General Jacquimont*, and then crossing this hybrid with *Rosa rugosa*, obtained a new rose which they named the Rose d'Hai. This rose is a free bloomer, and yields a fair perfume, and is being largely cultivated in the South of France. The annual harvest of rose leaves in France averages from 2,000,000 to 3,000,000 kilograms. In addition to the above described flowers which are treated with non-volatile solvents, others are the jonquil, hyacinth, mignonette, narcissus, cassie, mimosa, carnation, and several others.

The processes known as maceration or enfleurage are carried out in the following manner. A quantity of the most highly refined neutral fat, lard preferably, if a solid fat be required, olive oil by preference, if a liquid fat be used—is heated in a pan on a water bath, in the maceration process, and the freshly gathered flowers—obviously only those which will stand the temperature—are thrown in, and the whole well stirred for from twelve to forty-eight hours. When the whole of the perfume has left the flowers, the fat is strained off into a fresh pan and a new lot of flowers added. This process is repeated ten or twelve times until the fat is sufficiently rich in perfume, when the process is finished, and we have the pomade or perfumed oil. There is always a tendency for flower petals to decompose by a process of fermentation, and it is a matter of common experience that the shorter the time of contact between the flowers and the fat, the more delicate is the odour of the pomade. Hence numerous devices are resorted to in order to reduce the time of maceration. One of the most successful of these is the following. The fat is heated to about 70° in a reservoir from which it flows in a slow stream through the macerating chamber which consists of a long tank in which the flowers are suspended in wire-work baskets. From time to time the basket nearest to the reservoir is taken out and emptied, and all the other baskets moved forward and a fresh basket added at the other

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FIG. 6.

POMADE MANUFACTURE (ENFLEURAGE)

end of the row. A constant movement of the fat and the flowers in opposite directions is thus attained, and the period of maceration is much reduced. Where the flowers are so delicate that they will not stand the heat of the maceration process, the process of enfleurage is employed. It is a slow and expensive process, and the yield is generally very small. Enfleurage pomades, are, in consequence generally very expensive. A number of rectangular wooden frames about 24 ins. by 36 ins., with a strong glass bottom, known as "chassis," are piled one on the other, and on each is spread a thin layer of the finest neutral fat. Each frame requires from 6 to 8 ozs., both surfaces of the glass being spread with the fat. The freshly gathered flowers are spread on the upper surfaces of the chassis and left there from twelve to seventy-two hours, according to the nature of the flower. The layers of the fat on the upper surfaces become impregnated with the perfume by actual contact with the flowers and the under surfaces absorb any perfume which may be volatilized from below. When the flowers have completely lost their perfume, they are replaced by fresh ones, and so on until a very concentrated pomade is obtained. Chasis à huile are used when liquid fat is employed, and consist of similar frames with wire netting bottoms on which cloth is spread. This cloth is soaked in the neutral oil, and the flowers strewn thereon. The complete process frequently occupies eight or ten weeks. The fat is then scraped from the glass, and the oil is pressed out of the cloths by means of hydraulic presses. The finished products, pomades or perfumed oils are sold as such to the manufacturing perfumer, but as their manipulation is somewhat troublesome, he usually prefers to have them dealt with by the French manufacturer, so as to allow the perfume to be presented to

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Fig. 7.

AGITATORS FOR EXTRACTING PERFUMES FROM POMADES him in a more easily usable form. To achieve this object, advantage is taken of the fact that the actual perfume material is readily soluble in alcohol, whilst the fatty solvent is not. The pomade or oil is therefore beaten up in machines called "batteuses" or beating machines with warm alcohol. These machines are, in substance, churning machines which bring the pomade or oil into intimate contact with the alcohol. A very small amount of the fatty solvent is dissolved by the alcohol, but this can be removed by cooling the alcoholic solution to –15° C., and filtering at that temperature. The fat or oil is never rendered completely odourless by this treatment, and is never thrown away, but is sold to soap makers as "corps epuisé" for soap perfuming. The alcoholic extracts are now ready for the market, and are sold under the name of "Triple Extracts" or "Quadruple Extracts," according to their degree of concentration. A very large amount of the bottled perfumes sold to the public consist of these triple extracts without any further treatment. When price has to be considered, they are very often diluted with more alcohol, before the public get them, and they are also used as bases in the manufacture of mixed perfumes by the addition of other odoriferous substances.

A few words must now be devoted to the so-called concretes or absolutes, which are also known under various fancy or trade names. The extraction of the perfume material of plant substances by means of a volatile solvent, which is afterwards recovered by distillation, is a very old process, having been employed in a more or less experimental manner as far back as the year 1835. It is, however, only during the past twenty or twenty-five years that the manufacture of this type of perfume material has been carried out on

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FIG. 8.

HYACINTHS READY FOR MANUFACTURE OF CONCRETE a commercial scale. The principle underlying the process is, of course, very simple. The oily and resinous portions of the plant, which are the perfume bearers, are dissolved out from the plant substance, leaving behind the greater part of the inert and inodorous substance. The volatile solvent is then distilled off and the perfume substance is left behind in the still. The choice of a solvent is a matter of the very greatest importance. It must fulfill the following conditions—

(1) It must dissolve the whole of the odour bearing substances present in the plant tissue.

(2) It must be neutral, without any chemical action on the perfume material which it dissolves.

(3) It should dissolve as little else besides the perfume material as possible.

(4) It must distil within such limits of temperature that the perfume material is not damaged by the heat necessary for distillation, nor should the perfume material be volatilized and so lost during the evaporation of the solvent.

(5) It must leave absolutely no odour behind when evaporated.

The process of extracting perfumes by means of a volatile solvent was invented by Robiquet, but its practical application was due to Massignon, who together with Naudin enabled the process to be carried out on a commercial scale, and the solvent to be recovered without undue loss. The most efficacious solvent, which fulfils all the above conditions is a very low boiling petroleum ether—that is, to all intents and purposes, a chemically pure low boiling "petrol." There are many different forms of apparatus used for the purpose of extracting perfumes by means of volatile solvents, but in principle they are all more or less based on the Soxhlet process of extraction, so well known in all analytical laboratories. The material to be extracted is packed in a suitable container, and the petroleum ether is admitted to it so that it permeates the whole mass, becomes charged with the perfume material, and then leaves through an orifice, whence it runs into a receiving vessel, which is exposed to a temperature sufficient to volatilize the solvent, which rises and is liquefied in a condenser and drops back on to the mass of material being extracted. A continuous process is thus maintained until the material is quite free from perfume, and only a small amount of solvent has been employed. This is recovered in a proper still, and the crude matter left behind now consists of the whole of the perfume material of the plant, together with any other non-perfume matter the petroleum ether has extracted. This inert matter consists chiefly of wax, fat and traces of colouring matter. Owing to the presence of wax, etc., these natural perfume products are usually semi-solid or even solid. It is for this reason that they are known as concretes. The extraction process is one of considerable difficulty and requires very great skill if it is to be carried out so that the resulting product faithfully represents the perfume of the plant and has not suffered any harmful alteration by the treatment involved. The plants which are usually subjected to this process are those where the amount of perfume material is so small that it could not be practicably obtained by any distillation process, but would be almost completely lost. These absolutes or concretes (or whatever fancy name may be given to them) therefore contain the perfume of the plant in an extremely concentrated form, and are therefore very expensive. The only practical disadvantages of this class of product is the fact that they contain the vegetable wax, which is quite odourless and quite insoluble in alcohol. But as the wax and the perfume are very closely associated, it requires a number of washings with alcohol to completely extract the perfume, a matter of the highest importance when the high price is remembered. The practical result is that the manufacturing perfumer has a great deal of work to do to extract the perfume from the concrete, loses a fair amount of alcohol in the process, and also loses a certain amount of the valuable perfume. Further he obtains the perfume in a state of very considerable dilution, owing to the large amount of spirit he has had to use How this is remedied is well described by Charabot in the following words—

"The period at which the extraction of perfumes by volatile solvents entered into the region of industrial realities, coincided exactly with the time of my first researches at the Sorbonne, in the laboratory of Charles Friedel, in the same laboratory where, first under the direction of Wurtz and subsequently under that of my illustrious and lamented Master, such a strenuous and glorious struggle had been maintained for the definite triumph of the splendid atomic theory, thanks to which organic chemistry has produced the marvellous results which are so evident to all. The industry of the artificial perfumes, on the morrow of the discovery of ionone, had just taken a new step in advance, and the synthetic products were beginning to claim their place in compositions of the finest quality. Perfumery then had need of natural raw materials, sufficiently powerful and consequently sufficiently concentrated, not to be dominated, crushed out of existence by the chemical perfumes. These latter were capable of imparting even to the most delicate compositions, valuable characters of originality and fixity, but only on the express condition that they can be sufficiently dominated by products derived from flowers, which are the only ones which can impart delicacy and sweetness. It was this necessity, accentuated still more by the tendency of fashion towards powerful and tenacious perfumes, which struck me, together with the inconveniencies involved by the first products obtained by means of volatile solvents. And thus my researches were directed towards the obtaining of the perfumes of flowers in the form of products both powerful and soluble in alcohol. They soon led to a satisfactory solution, and the preparation of products conforming with the desiderata mentioned above. Since then, we have been able to substitute for the first processes which I invented, methods which are more perfect because they have been deduced from the accumulation of acquired knowledge both on the composition of the odorous matters and on their successive states in the plant. And these methods, made appropriate to the treatment of each flower, have enabled us, by employing the solvents in a suitable manner, to leave the vegetable wax, the inodorous substance which is insoluble in alcohol, behind, and to extract solely and completely the odorous principles in the form of products entirely soluble in alcohol. These products, the absolute flower oils, are consequently extremely convenient to use, since it is only necessary to pour them into alcohol, to obtain a clear solution of any concentration that may be desired."

The exact methods by which the insoluble wax is got rid of vary with different manufacturers, but by dissolving the concrete in a solvent, and then adding a second solvent in which the perfume material is soluble, but the wax insoluble, most of the wax is precipitated. The liquid is then filtered, the solvent volatilized and recovered, and the treatment repeated. The perfume material is finally obtained as an oil free from wax, and soluble in alcohol. Rose, orange, jasmin, tuberose, cassie, mimosa, violet, mignonette, broom, oak moss and other similar perfume plants are typical of those which specially lend themselves to this process.

We will conclude this chapter by a brief reference to a few of the balsams and resins which are extracted from plants and which are used as raw materials for the manufacture of perfumery.

There are a certain number of resins and oleo-resins which find considerable employment in the perfume industry, some of which are solid substances free from liquid essential oils, whilst others are mixtures of solid resinous substances with a certain amount of essential oil which may be, and sometimes is, separated in the pure state from the oleo-resinous mixture. Of these we shall select a few for more or less extended description.

Opoponax. Opoponax has long been a name for perfumers to conjure with, and its popular perfume will probably still enjoy a very long life. The name of opoponax as applied to a perfume was clearly originally given to a product which was not true opoponax at all. True opoponax was correctly described by Flückiger and Hanbury in their Pharmacographia as having a penetrating, offensive odour, reminding one of crushed ivy leaves. The opoponax of perfumery is a resinous body of characteristic odour, resembling true opoponax in colour and appearance. It has a dull brown surface with white streaks here and there, and the pieces break with a dull fracture. The odour reminds one of a slightly perfumed bdellium—indeed, it has often been described as " perfumed bdellium." Its botanical source has now been settled with practical certainty by E. M. Holmes, who states that it is the resinous exudation of the stem of Commiphora Erythraeu, one of the plants belonging to the natural order Burseraceae.

The crude substance contains about 5 to 7 per cent. of essential oil having the characteristic opoponax odour. It is used in perfumery in the form of a tincture or alcoholic extract, but, of course, the "Essence of Opoponax" of commerce contains it only as a base, numerous other modifying perfume materials being also present.

Frankincense. This fragrant gum resin, also known as olibanum resin, is the product of two or more species of the tree Boswellia. The following description is taken from the author's handbook on *Gums and Resins*. It was known to the Greeks under the name Libanos, to the Romans as Olibanum, and to the Arabs as Luban, all of which are derived from the Hebrew word *Sebonah*, meaning milk. It has from time immemorial been regarded as one of the indispensable ingredients of incense for ceremonial purposes. E. M. Holmes gives the following amusing account by Cosmas, of the method adopted by the traders and the natives of the highlands of Abyssinia who collect the resin, but who do not understand the traders' language. "The gold caravan is usually made up of about 500 traders, with them they take a good quantity of salt and iron, and when they are close to the gold land, they rest awhile and make a great thorn hedge. They then kill the cattle, cut them up, and split their joints upon the thorns while they put out the salt and iron at the foot of the hedge. That done, they retire to a certain distance. Now up come the natives with their gold in little lumps, and each places what he considers sufficient above the beef, salt, or iron which he fancies. Then, too, they go away. Next return the merchants and inspect the price offered for their goods. If content they take away the gold and leave the flesh, salt or iron thus paid for. If not content they leave the gold and other things together and retire again. A second visit is then paid by the natives, and either more gold is added, or it is removed altogether according as the purchaser thinks worth while." The trade in frankincense appear to have been carried out in the same manner as that in the above description of gold trading.

The two trees which yield frankincense are *Boswellia carteri* and *Boswellia frereana*, the former yielding what the natives call male frankincense, and the latter yielding the female frankincense. The former appears to be that which usually reaches the London market. It occurs in fine, small tears, or in small lumps. It consists of a mixture of gum, resin and essential oil, the latter in very small quantity. It has a characteristic odour, and is the principal constituent of the incense burned for ceremonial purposes.

Ladanum. Ladanum, or labdanum resin is a product of the very highest importance in the perfume industry, being almost indispensable in the manufacture of those heavy perfumes with a somewhat "languorous" Oriental odour. The best method of using this perfume is in the form of something resembling the "absolutes" described above, the substance yielding about 15 per cent. to either acetone or petroleum ether, and on the evaporation of the solvent, the powerful, alcohol-soluble, perfume matter remains behind. Ladanum is a soft, sticky oleo-resinous substance, which is exuded by the glandular hairs of a small plant which is usually *Cistus Creticus,* but which may sometimes belong to another species. It is collected in Crete and Cyprus. It accumulates on the beards of goats and on the fleeces of sheep that browse upon the foliage, and is scraped off by combing the hair of these animals. As found in commerce it varies from a somewhat soft to a hardish mass easily softened by warming. Its odour is heavy and powerful, reminding one somewhat of ambergris. Cretan ladanum has been analysed by E. J. Emmanuel, who found it to contain the following—

Ether soluble resin	48%
Alcohol ,, ,,	17%
Essential oil	2%
Ladaniol	0·8%

Ladanoil was obtained in the form of white, sweet-smelling crystals, resembling, and possibly identical with, champacol, the odorous substance obtained from champacá wood. The essential oil is a liquid of specific gravity 0·950, containing acetophenone and other bodies not yet identified. The value of ladanum as a perfume depends on its extraordinary sweetness and its intense persistence, giving a very permanent character to other perfume materials. It is therefore used both as a fixative and an odour modifier, but care must be taken that it is only used in very small amounts, as otherwise it may overpower all the other odours and ruin the composition.

Storax. Storax or styrax is a balsamic substance which exudes from the bark of the tree *Liquidambar orientalis*, one of the natural order *Hamamelidiae*, chiefly found in the south-western portion of Asiatic Turkey. It is a pathological secretion, not exuding normally, but induced by damaging the bark by heating and bruising. The cambium layers are thus injured, causing the formation of numerous oil ducts into which the balsamic material flows, and whence it is discharged by way of the wounded bark.

Crude storax as thus obtained is a greyish-opaque liquid of very thick consistency, and having a very sweet and aromatic odour. This crude storax contains from 20 to 30 per cent. of water and organic dèbris, On standing the water separates, and the remainder can be dissolved in alcohol, filtered, the alcohol evaporated, and the residue carefully dried. This is the purified storax which is used in pharmacy and perfumery. It owes its sweet odour principally to cinnamic acid esters, which are frequently fraudulently removed, and the emasculated storax offered on the market as genuine storax.

American Storax. There is another variety of liquid storax, known as American Storax, which is the product of various species of *Liquidambar Styraciflua*, a tree flourishing high up in the mountains of Honduras, in Central America. The much esteemed secretion is known to the natives under the name Copalme. This fragrant balsam was discovered soon after the Continent itself, and whole shiploads of it were sent to Spain from Mexico for perfuming, incense, and medicinal purposes. Its use declined, however, and probably owing to the difficulty of collection the trade in it nearly died out. With the commencement of the Great War, however, a great scarcity of oriental products set in, and fresh sources of supply, or substitutes had to be sought for. Added to these difficulties, the oriental storax which was available on the market was so frequently deprived of its aromatic constituents, with the result that attention was again turned to the supplies of American Storax in Honduras. Although the tree is widely distributed throughout the Southern States of America, known as the sweet gum, the labour conditions did not allow its collection on a commercial scale. In Honduras, however, the conditions were more favourable, and good supplies were obtained during the war from this source. A slight excrescence appears on the bark of the tree which soon enlarges into a pocket in which the balsam is secreted.

It is said that only about one tree in every hundred square yards of forest is found to be worth tapping, owing to the age and other conditions of growth. The pockets usually contain from one to eight pounds of balsam each. Watermeyer gives the following analysis of an average sample of this American Storax.

Mineral matter	= traces only
Purified balsam	= 85%
Saponification value of Purified balsam	= 179
Acid value of Purified balsam	= 41

The balsam appears to be rich in cinnamic acid esters, and fairly low in free cinnamic acid.

Balsam of Peru. This valuable perfume balsam is an oleo-resinous secretion of the bark of *Myroxylon pereirae*, a tree flourishing in Western Central America, and found largely in the forests of San Salvador. The secretion is not a natural one, but is pathological, being induced by gently heating, and afterwards scorching the bark of the tree. The wounds so made are covered with cloths which are repeatedly changed and boiled with water, and the oleo-resin separated f om the water. Balsam of Peru is a dark reddish-brown liquid of great viscosity and of penetrating and sweet odour. A white variety, obtained from a different tree, or a different variety, is occasionally found, but the reddish-brown balsam is the only type found in commerce.

It contains 55 to 65 per cent. of a substance known as cinnamein, which, however, is not a definite chemical individual, but a mixture of esters of cinnamic and benzoic acids. It also contains a small amount of free aromatic acids and free alcohols, and a very small amount of vanillin. The alcohols combined with the cinnamic and benzoic acids to form the esters are principally benzyl alcohol and peruviol. Five samples examined by Dr. Preuss were found to have the following characters—

	Specific Gravity	Cinnamein	Ester value of cinnamein	Resin
1.	——	61%	240	20%
2.	1·1404	64·7%	260	18·1%
3.	1·1408	66%	260	16·8%
4.	1·1612	50·8%	249·8	28·4%
5.	——	37·7%	——	27·55%

Balsam of Peru is adulterated to a considerable extent, principally with an artificial Balsam made up to closely imitate the natural product. This causes a good deal of difficulty to the analyst who is called upon to examine a sample, and his difficulties are increased by the fact that the methods of preparation of the pure Balsam in San Salvador are very variable, so that pure samples have characters which vary within somewhat wide limits, so that standards for the natural product are difficult to set up.

Common American rosin is sometimes used as an adulterant, but this is fairly easy to detect.

Balsam of Peru is a very useful substance in the preparation of heavy odours of the oriental type, and is also possessed of good fixative properties. It is used in the form of an alcoholic solution.

Balsam of Tolu. This balsam, having a very fragrant odour, is also used to some extent in perfumery, in the form of an alcoholic tincture. It is the exudation from artificially made incisions in the trunk of the tree *Myroxylon Toluifera*, a tree indigenous to New Granada. When freshly prepared it is a soft, tenacious mass, becoming quite hard and brittle in very cold weather, or after being kept for a long time.

The Balsam contains benzyl benzoate, benzyl cinnamate, free benzoic and cinnamic acids, traces of vanillin and esters of a body called toluresino-tannol. It is

FIG. 9.
MYROXYLON PEREIRAE
(Peru Balsam Tree)

often adulterated with ordinary American resin, but more frequently by the abstraction of its valuable constituents.

Balsam of Tolu has excellent properties as a fixer, and is valued on this account, as well as for its sweet and persistent odour. The variations in the characters and composition are such as to cause considerable difficulty to the analyst in framing standards for the natural product, and in deciding whether a given sample is genuine or not. A pure Balsam of Tolu usually has characters falling within the following limits—

Specific gravity	= 1·090 to 1·110
Refractive index at 60°	= 1·5850 to 1·6020
Acid value	= 100 to 150
Saponification value	= 170 to 205

The total cinnamic acid present varies between 20 and 30 per cent.

Benzoin. Benzoin, or gum benjamin, as it is frequently called is a balsamic resinous matter obtained from various species of the Styrax tree, of which Styrax benzoin is the most important.

The trees which yield benzoin are found principally in Siam, Sumatra and Java. They do not appear to secrete any resinous matter of an aromatic character when allowed to grow in a normal manner, but when a wound is inflicted, sufficiently deep to injure the cambium layer, numerous resin ducts are formed as a diseased condition of the plant, in which the resinous secretion now commences to appear. This, like several other important perfume resins, may therefore be described as a pathological secretion. The trees are usually hacked to the proper depth with an axe, when the resin commences to accumulate beneath the bark, or to exude from the incisions. This secretion gradually hardens, and when it is quite solid it is collected and packed in boxes for exportation. Pure benzoin is a brownish to brownish-red solid substance occurring in large masses in which numerous white or nearly white tears or fragments are embedded. It is easily powdered, and in this form is used to a considerable extent as a constituent of incense and similar fragrant powders, and in the manufacture of burning pastilles. In liquid perfumes it finds employment in the form of an alcoholic tincture, and apart from a sweet penetrating odour, it possesses good fixative properties. Siam benzoin is one of the most highly esteemed varieties ; it is chiefly collected in the province of Luang Pratang, but it is not quite certain as to which species of the Styrax tree yields this particular variety. It occurs, not only in lumps, but sometimes also in the form of isolated tears. It is characterized by its very pronounced odour of vanillas, and by its comparative freedom from cinnamic acid. Sumatra benzoin is also a highly esteemed variety of the resin. It is undoubtedly the product of Styrax benzoin, and is produced on the island of Sumatra. It only occurs in the form of masses, and its odour recalls that of styrax rather than that of vanilla. It may be distinguished from Siam benzoin by boiling a fragment with dilute sulphuric acid and potassium permanganate, when a marked odour of oil of almonds is perceived, owing to the oxidation of the substances present in the Sumatra variety, which are not present in Siam benzoin. The cheapest variety of benzoin is that known as Palembang benzoin, which is obtained from a species of the Styrax tree whose botanical relationship is still uncertain.

The principal constituent of Siam benzoin is benzoic acid, partly in the free state and partly combined as esters. Vanillin is also present, in traces. In Sumatra benzoin about half the free acids consist of cinnamic acid. The principal adulterants of benzoin are vegetable débris and earthy matter. The following figures are typical of the three principal types of the resin—

SIAM BENZOIN.

Mineral matter	0·24 to 1·98%
Soluble in 90% alcohol . .	88 to 96·5%
Acid value	130 to 158
Ester value	42 to 69.

SUMATRA BENZOIN.

Mineral matter	0·4 to 1·96%
Soluble in 90% alcohol . .	90 to 94%
Acid value	98 to 140
Ester value	50 to 100.

OTHER VARIETIES.

Mineral matter	0·4 to 2·9%
Soluble in 90% alcohol . .	86 to 95%
Acid value	106 to 142
Ester value	50 to 90

In addition to the above described categories of natural plant perfume materials, there are a certain number of plant substances which are used in perfumery in a different manner from those in which the above described substances are employed. As a type of this class of body we may take the vanilla bean. No attempt is made to separate from these substances (of which the tonquin bean, or tonka bean, is another example) any definite active principle. They are used in the form of alcoholic extracts or tinctures made by macerating the plant substance in alcohol of suitable strength. The most largely employed of this class of substances is the vanilla bean. It is employed to an enormous extent in the flavouring of cocoa to make chocolate, but it is also used to a considerable extent in perfumery, the odour being sweet and persistent, producing an agreeable modification of the perfume of other constituents of a bouquet, and at the same time acting as a very useful fixative. The vanilla bean is the fruit of a climbing orchid, a native of South America. There are two species which are cultivated, *Vanilla planifolia*, the true Mexican vanilla, and *Vanilla pompona*, the West Indian vanilla. Vanilla is cultivated in many parts of the tropics, especially in Mexico, Seychelles, Réunion, Mauritius, Tahiti, Java, the Fiji islands, and the West Indies. It was used as a flavouring before the

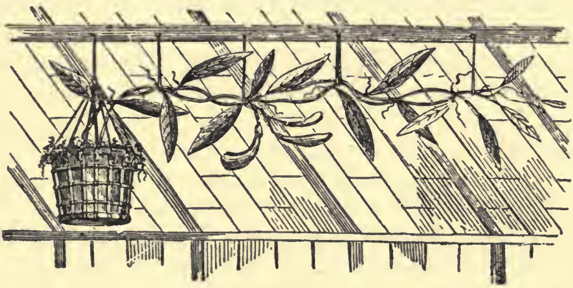

FIG. 10.
VANILLA

discovery of America, and was first brought thence to Europe by the Spaniards.

The plant requires a tropical climate, hot and moist with frequent but not excessive rains. In Mexico the flowers are fertilized naturally by bees and humming birds, but it is strange that in no other part of the world do the bees visit the flowers, or, if they do, they do not fertilize them. It is therefore necessary to fertilize the vanilla flower by hand, a somewhat delicate operation, but one which is soon learned successfully by the natives. As the flowers only remain open for one day, a large number of persons are required for this work at the flowering season, and women and children become very expert at it. The flowers open one by one on the stalk, but sometimes more than one are open at the same time. The best time to fertilize the flowers is from 8 o'clock in the morning till 1 o'clock in the afternoon. Fertilization is most successful on a day which has been preceded by a rainy day, but on which no rain is falling. An average worker can fertilize 2,000 flowers a day if the vines are fairly close together. He uses a small pointed stick, or splinter, the size and shape of a tooth-pick. He carries a number of these, and with them transfers the pollen to the stigma of the flower. When the fruits are gathered, they have to be dried and cured in order to turn them into the vanilla beans as we know them. In the fresh state they have little or no odour, the vanilla odour being developed by a process of fermentation during the drying and curing. By the use of hot water, stove heat, or sun heat, they are rapidly ripened uniformly throughout the pod. There are numerous methods adopted for the artificial curing of vanilla of which we will describe one, namely, the Mexican process. The pods are piled in heaps in a shed to protect them from the sun or rain, and in a few days, when they have commenced to shrivel, they are "sweated." In fine warm weather they are spread out on a woollen blanket and exposed to the sun. About midday the blanket is folded over them and the bundle left in the sun for the rest of the day. In the evening they are packed in air-tight boxes and allowed to sweat all night. This process is repeated for a few days, until the beans become dark coffee coloured. In cloudy weather they are cured in an oven at 140° F., instead of being exposed to the sun. After the sweating process is over the beans are spread out on matting every day for about two months to dry in the sun, and when completely dry are tied into the small bundles in which they are found in commerce. The total vanilla crop of the world is rather a variable quantity, sometimes falling to 350 tons, and at times rising to well over 500 tons. The vanilla bean owes its characteristic odour to a crystalline substance termed vanillin. The odour is, of course, modified to a slight extent by traces of other bodies, but vanillin is the dominant and characteristic odour bearer of the fruit. In fine quality beans, the vanillin is present in sufficient quantity to crystallize out on the surface of the beans, and give them a frosted appearance. This appearance is sometimes fraudulently imitated on beans of poor quality by soaking them for a few moments in a solution of benzoic acid in alcohol; when the alcohol evaporates the crystals of benzoic acid have the same general appearance as the vanillin crystals.

Piesse gives the following as the best method of preparing vanilla beans for perfumery purposes. "In order to obtain the perfume or essence, half a pound of vanilla pods are cut up small and put into one gallon of pure alcohol of a strength known as 60 over proof, giving the whole a shake up daily. The ingredients must remain together for four weeks, at which time all that is worth extracting will be found in the spirits, which may then be strained off clear and bright. It is then suitable as a flavouring agent, or, when blended with other scents, makes delicious perfumery. These, sold under the names of clematis, heliotrope, wallflower, etc., mostly contain half in bulk of vanilla extract."

The statement as to the presence of this large quantity of vanilla in the perfumes named is certainly not true of the perfumes of to-day.

The flavour and perfume of the vanilla bean is so highly esteemed that it caused chemists to investigate the nature of its odorous constituent very minutely in the hope of being able to manufacture it by synthetic means. The successful synthesis of vanillin is a romance in the history of organic chemistry, and will be dealt with when we turn to the discussion of the synthetic or artificial perfumes.

CHAPTER IV

ANIMAL PERFUMES

THERE are a few substances obtained from animal sources used in perfumery. It is not altogether correct to describe them as perfumes, as some of them, in the natural condition are objectionable in odour and, for example, in the case of civet, positively revolting. And even when diluted to such an extent that the revolting odour becomes tolerable, or even pleasant, their value, in general, depends more on the wonderful fixative value they have than on their actual odour. The animal perfume materials that will now be described are four in number, namely, civet, musk, castor and ambergris.

Civet. Civet is a glandular secretion of the civet cat, of which there are several species, and is a soft oily substance of the consistence of butter with a powerful faecal odour. It arrives in this country in horns, and upon opening these, the civet appears of a deepish brown colour, but if the surface be turned over, the under portion will be found to be of a pale yellowish colour, the brown colour of the surface being due to oxidation. Civet is used in the form of an alcoholic tincture or solution, in very minute quantities, when its very objectionable odour disappears, and the resulting product, mixed with various essential oils, etc., is far more persistent as a perfume than the same product made up without the civet.

Civet is a substance which has been known for hundreds of years, and which among the ancients was supposed to possess marvellous virtues. Avicenna, the famous Arabian alchemist, who lived about A.D. 980, writes of civet in his well known work on pharmacology. He states that it should be dissolved in oil of ben, and distilled in a copper vessel, when the distillation will be found to be a valuable remedy in cases of chills, tumours, epilepsy, rheumatism, etc. It was also used to a considerable extent in the manufacture of toilet powders, perfumes, ointments and soaps. But, frankly, we cannot understand why Benedick, in *Much Ado about Nothing*, should rub himself with civet to make himself attractive to Beatrice. To-day, it would be an excellent method of driving one's friends away.

The following account of the natural history of the civet cat is the most authentic and up-to-date account of the animal we have. It is due to Mr. C. Court Treatt,[1] by whom, also, the illustration we give was drawn.

Natural History. The civet cat tribe (Viverridae) is a division of the large group of carnivora, and is closely allied to the cat tribe, from which, however, it differs in several points of structure. The Viverridae are strictly confined to the Old World, both at the present day and probably in pre-historic times. Under the title of civet cat are placed zoologically not only those animals which produce the civet of commerce, but also several close-allied carnivors, such as ichneumons, palm civets, mongooses, genets, linsangs, etc. Although the members of this group bear the name of cats, they differ considerably from the cat family. The faces are longer, the bodies longer and thinner, and the legs shorter and stouter; the soles of the feet are hairy. With the exception of the Rasse, to be mentioned later, all the species of true civets possess an erectile crest of coarse long hairs running down the middle of the back.

[1] *Perfumery and Essential Oil Record* 1912, 73.

The fur is long, coarse and rough, marked at the throat with a black patch; the body striped and mottled with black; and the tail, which is long and stout, striped with alternate light and dark bands. All the true civets are characterized by the possession of the civet glands. These are two perineal glands, forming a deep pouch in the posterior part of the abdomen, which pouch is divided into two sacs, each about the size of a marble, in which the civet, secreted by the

FIG. 11.
CIVET CAT

surrounding glandular follicles, is stored. The civet in the pouches is at first semi-fluid, but later is of a stiffer consistency and darker in colour. The function of the civet bag is not exactly known, but it is presumed to be of use in sexual attraction and also as a means of defence. Hunters tell us that hounds when close to a civet cat are almost overpowered by the odour it emits. Nevertheless, a hound will leave off hunting any other animal when once it has crossed the trail of a civet cat. The animals producing civet are—

Viverra civetta—the African civet cat,

V. zibetta—the Indian civet of Bengal, China and Malayan regions.

V. civettina—on the Malabar coast.

V. megaspila—the Burmese civet of Burma, Cochin China, the Malay Peninsular and Sumatra.

V. tangalunga—the Java civet of Java, Sumatra and Borneo.

V. malaccensis—the Rasse of India, Ceylon, Assam, China, Java, and Sumatra.

Almost all the civet imported to Europe comes from the African civet, and since we find a comparatively large number of true civets inhabiting India and Malaysia, while one only species of the genus is found in Africa, it seems strange that practically no civet is imported into Europe from those regions.

We learn from travellers that in parts of India, and especially in Java and Sumatra, civet is in great request by the natives as a perfume, and possibly the demand there is so large that export to Europe is not worth while. The civets seem always to have been more numerous in India than in Africa, several remains of extinct species having been found in Pliocene rocks of India. It is interesting to note that in earlier periods of the earth's history, the lower Miocene and upper Eocene, civets inhabited England and parts of Western Europe.

The African Civet. The African Civet is one of the largest civet cats, the length of the body being about $2\frac{1}{2}$ to 3 ft., while the height is from 10 ins. to a foot. The stout tail, about 18 ins. long, is of a darker colour than the body, almost black towards the tip, but marked in the anterior portion with transverse ridges of a paler colour. The brownish grey fur is coarse and rough-looking, marked over the whole body with dark streaks and patches; while the legs, two patches round the eyes, and a broad patch on the chest, are black. The chin and the sides of the neck are white. The erectile crest running down the back is exceedingly noticeable, the hairs being longer, stouter, and darker than the rest of the fur. Not much is definitely known of its habits in a wild state; indeed, considering the hundreds of years in which civet has been an article of commerce, it is surprising how little we really know of the animal. Like the majority of carnivores the civet is nocturnal, hiding in thick grass and undergrowth during the day, and only issuing forth at night to hunt its prey, which consists of small birds and mammals, snakes, frogs, large insects, and possibly some fruits. Both ancient and modern writers agree that it is often found in holes and small caves; but whether the holes are dug by the animal itself is doubtful. The civets are quite at home in the water, and are said by the natives to prey on the wild fowl which are so abundant on some of the reed-covered lakes, and to rob the eggs from their nests. The animals are captured in various ways, and kept in cages, where they are carefully fed and tended for the sake of their secretion. While young they are fed on a pap, composed of meal, with a little fish and flesh added, but when adult the diet consists entirely of raw meat. Though in captivity they become partially tamed, they are never entirely domesticated, and are always dangerous to handle, flying into rages without the least warning, and attacking fiercely anyone who comes within reach of their teeth. When the civet is to be collected, which operation takes place about every four days, the animal is placed in a small cage only just big enough to contain it, and the legs are secured. It is then teased and irritated, as the secretion is formed in larger quantities when the animal is angered. The civet is extracted from the pouch with a horn or iron spatula, and if the animal is in good condition, well grown and a male, about a dram to a dram and a half is obtained. The female yields less than the male. When fresh it is almost liquid and of a pale yellow colour, but with time and exposure to the air it darkens slightly, and becomes of the consistency of pomade. After having been freed from hairs it is packed in ox-horns, which are covered over with hide and bound round with grass fibre. The average horn contains 30 ozs., though occasionally horns are received holding as much as 70 ozs. The Indian and other civet cats mentioned above all closely resemble the African variety in appearance and habits, and the civet obtained from them is of identical quality and odour. The Rasse alone differs, being a much smaller animal and lacking the erectile crest. It is carried about in cages by the natives of Java who keep it for the sake of its perfume. It is a fierce little animal, absolutely untamable, and never breeds in captivity. The Javanese are extremely fond of civet and anoint their hair, bodies and clothing with the raw article, and also with mixtures of civet with various extracts of flowers. The houses and everything in them are strongly scented with it, and at public ceremonies and functions the perfume is so strong as to be quite nauseating to Europeans.

Civet is very frequently adulterated, the principal adulterants being butter or other fats, banana pulp, and sometimes vaseline. A gummy matter which has not been identified is also sometimes used for adulterating purposes. J. O. Braithwate has examined a sample of known authenticity and compared three commercial samples with it. His results were as shown in the table on the following page.

The markedly lower percentage of volatile acids in the commercial samples, as compared with the authentic specimen, indicate the presence of foreign fatty matter.

	Sample from Zoological Gardens (Freed from Sawdust).	Commercial Sample A.	Commercial Sample B.	Commercial Sample C.
Loss at 100°	+	30·1	12·5	23·4
Ash	+	2·1	4.4	3·9
Pet. Ether Ext.	Almost wholly soluble	62·9	70·07	50·
Total Acid, No. of Petrol. Ether Ext.	140	108	166	175
Volatile Acid, No. Pet. Ether Ext.	32·3	11	11·5	9
Nature of Residue in Petrol. Ether	Hairs, etc.; almost odourless.	Dry, slight odour, stercoraceous.	Dry, slight odour, stercoraceous.	Moist, sticky, strong stercoraceous odour.
Sugar in Residue Insol. in Petrol Ether	None.	None.	None.	Present in quantity.

Sample A is noteworthy for the large amount lost on drying, and evidently contains added water. The characters of the residues differed considerably. In the case of the sample from the Zoological Gardens there was practically nothing but hair, and this residue was almost odourless. Samples A and B gave dry residues with more or less faecal odour, while C was particularly unpleasant in this respect; the sticky nature of the residue in the latter (C) was shown to be due to an adulteration of the drug with saccharine matter.

The following method is a certain and easy one for the detection of vaseline in civet. Five grams are mixed with 50 cubic centimetres of acetone and well disintegrated. The mixture is allowed to settle and the clear liquid is poured off. The residue is well mixed with another 50 cc. of acetone, and then poured on to a filter and the insoluble matter washed with a little more acetone. The residue is dried at a low temperature. If the civet is free from vaseline it will be greyish-white and powdery, but if vaseline be present it will be oily or pasty. If this be the case, shake the oily residue with 50 cc. of petroleum ether, and filter, and well wash the residue with more petroleum ether. If vaseline is present the petroleum ether will be highly fluorescent, and on evaporation will leave the vaseline which can be weighed. As little as 5 per cent. can be detected by this method. Sack has quite recently investigated the composition of civet and has isolated from it a body which is a ketone, and which he terms zibethone. This was separated from the civet in the following manner. The civet is boiled for several hours with a strong solution of caustic potash in alcohol. The alcohol is removed by evaporation, and the residue treated with water and extracted with ether. The ether is evaporated, and the residue so obtained is steam distilled until all the skatole (another constituent of the civet) is removed. It is then again shaken with ether and the ether removed by distillation. This leaves an oily residue, which is treated with a little alcohol, and the alcoholic solution filtered. The alcohol is removed by distillation in vacuo, and leaves a yellow syrup amounting to 10 to 15 per cent. of the civet used. This substance possesses a pleasant musk-like odour, together with the peculiar animal aroma of the civet. It can be coverted into a crystalline compound from which the zibethone can be recovered in a state of absolute purity.

A genuine civet should have the following characters—

Moisture	15 to 30%
Mineral matter	0 to 2%
Soluble in petroleum ether	almost entirely
Acid value of petroleum extract	130 to 150
Sugar	none

Castor. Castor or Castoreum is a valued material in the manufacture of high-class perfumes, and is used as an odorous fixative in the form of an alcoholic tincture.

It consists of the dried membranous follicles of the Beaver, *Castor fiber*, which are situated between the anus and the genital organs of both sexes of the animal. There are two pairs attached to each animal, the lower ones being pear shaped and somewhat larger than the upper pair. They contain an oily, viscid, highly odorous substance which is a glandular secretion. The follicles are removed after the death of the animal and dried either by smoke or in the sun. When quite fresh, castor is a white liquid of the consistence of very thick cream. In commerce two varieties are met with, namely, the Canadian and the Russian. Canadian castor, however, is the one variety met with in this country, Russian castor very rarely reaching the London market. Castor is sold in the form of more or less soft, unctuous masses, which gradually harden, and which is contained in sacs from 2 to 3 ins. long, very flattened and wrinkled, and of a deep brown colour. A good quality sample should be very powerful in odour and very bitter and nauseous in taste. So far as the English market is concerned, castor comes on offer only once a year. The Canadian castor is, to all intents and purposes, a monopoly of the Hudson's Bay Company, and the year's collection is offered by public sale annually, towards the end of the year, the amount offered being now about 1,000 lbs.

Castor varies considerably in composition, the principal constituent being a resin which is present to the extent of from 40 to 70 per cent. The characteristic odour is due to a small amount of an essential oil. A peculiar crystalline principle, which has been named castorin is also present to the extent of from 4 to 5 per cent. Mingand gives the following analysis of castor—

Ether extract	88.4%
Alcohol ,,	0·8
Aquean ,,	0·1
Acetic ,,	0·6
Residue	2·2%
Volatile matter	7·9%
Mineral matter	0·75%

It is strange that about 150 years ago, when it was well known that castor was the product above described, a writer in so important a scientific journal as the *Philosophical Transcactins* erroneously describes it as the product of the testicles of the Beaver. He wrote the following interesting remarks—"To prepare the matter of Beaver's stones, boil a proper quantity of water with half a shovelful of woodashes, tie the bags in couples and put them in the boiling water for half a quarter of an hour. Lay birch bark on the fire and smoke the bags well over it for an hour till they be well dried ; lay them up for a week or more till perfectly dry and hard ; they may then be packed up for use or exportation." Castor is still used to a small extent as a drug, but its employment is almost entirely confined to perfumery as an odorous fixative material.

Ambergris. Ambergris is an exceedingly valuable animal product for which perfumers pay very high prices. Its name is derived from its supposed resemblance to amber, and signifies "grey amber" or as many people think "amber grease."

It is an opaque grey to blackish solid material, containing a certain amount of fatty material, of very low specific purity, and yielding only a small amount to alcohol. Its odour is not attractive, but in exceedingly small amounts it gives a character to perfumes not obtainable in any other way, and also acts as a most valuable fixative, a character in common with that of other animal perfumes. It is found on the sea coast, or floating on the sea near the coasts of India, Africa, and Brazil; it is also sought for by the whale fishers, who always look for ambergris in the intestines of the sperm whale when they catch one. They are most successful in finding it in those which appear torpid, sick and lean.

It is now well known that ambergris is a pathological product, the result of some particular disease in the sperm whale, *Physeter macrocephalus*. Sometimes the whale manages to reject the secreted ambergris and recovers from his disease, sometimes he does not, and dies. His body is eaten by other fish, who will not touch the ambergris, which is thus left floating on the sea. A sick whale may be caught alive, and the whalers will then rejoice over their luck as the ambergris they find in the whale's intestines may be worth far more than the rest of the whale.

Ambergris occur in small pieces varying from a few ounces to a few pounds, but occasionally huge lumps are found, and it is recorded that a piece weighing 182 pounds was sold by the Dutch India Company for 116,400 florins.

Although it is now well established that ambergris is a pathological secretion of the sperm whale, many fanciful stories have been told of its alleged origin.

A writer named Klobius quotes no less than eighteen current opinions as to its origin and production. The principal views held were the following—(1) It was believed to be the excrement of a bird, common in Madagascar, melted by the sun's heat, washed out to sea, swallowed by a whale, and passed through it unaltered. (2) Others believed it to be part of the excrement of certain cetaceous fish. (3) It was also surmised to be the wax or gum exuding from certain trees growing on the sea shore, which dropped into the sea, congealed and became ambergris. (4) A common Oriental idea was that it sprang from the bed of the sea as naphtha does from the earth, or that it was a kind of bitumen gradually working up from the ocean and hardening in the sun. (5) By some it was held to be a kind of marine fungus torn up from the bottom of the sea by violent tempests. (6) The origin of ambergris was also ascribed to honeycomb which had fallen into the sea from rocks where bees had built their nests. (7) Dr. Boylston and Mr. Dudley (Phil. Trans., 385-387) asserted that ambergris was an animal concretion found in balls in the body of the male sperm whale. (8) A certain Herr Neumann, chemist to the King of Prussia (Phil. Trans., 433, 434, 435), denied that ambergris was an animal product at all, and that if it were found in whales it must have first been swallowed by them. His own opinion was that it was a species of bitumen exuding from the earth into the sea. Quoting from an old scientific work of the eighteenth century we find the following. " The pieces are frequently seen composed of divers strata . . . . . with stones and other bodies endorsed therein, and the strata are sometimes full of little shells . . . . . whence it may be conjectured that the ambergris had originally been in a fluid state . . . . . and enveloped such bodies as happened to be in its way."

Musk. The veneration in which musk has been held for centuries by the Chinese, and the exceedingly high value placed upon it by the perfumer, are reasons why a somewhat full account of this perfume material is now given. The old name of musk in China is Shay hïang, signifying " the perfume of the deer." Tavernier is probably the first traveller who makes mention of this substance, describing in his diary that he purchased over 7,000 pods during one of his voyages.

In common with all the animal perfume materials, musk is an intense fixative agent, but in contra-distinction to other animal perfumes, it possesses an odour which is so intense and so sought after, that it does not, in many cases, become merely subordinated to other odours, but is, in the finished perfume, one of the predominating notes of the whole composition.

Musk was probably introduced into Europe by the Arabs: at all events it figures in the list of presents sent to the Emperor of Greece by Saladin in 1189. In the tenth century Avicenna mentions it in his pharmacology as a remedy for various diseases, and, of course, Marco Polo in his travels found musk to be a common commodity amongst the Orientals. Musk is the highly odorous secretion of the Musk deer, *Moschus moschiferus*, formed by a special gland situated in the skin of the abdomen. The deer live in a wild state, very seldom gregarious in their habits, rarely being found except singly or in pairs. They usually conceal themselves during the day and come out to feed at night, and again in the very early morning. They are found principally on the mountains of the North of India and in Central Asia, their habitat being within 70° to 170° longitude E, and 65 to 15 latitude N. They are found to a smaller extent in Northern Siberia, and they are also hunted in the north-east of Cochin China. But it is principally in Mongolia, Thibet, Nepaul, Cashmire, Assam and Surkutan in China that the animal is hunted—and to some extent in the neighbourhood of Lake Baikal. The secreting gland is peculiar to the male animal, and the secretion appears to be in relation to the sexual organs, since it is more abundant and more odorous at the time when the female deer is in season.

It is only found in the adult animal and ceases when he has passed a certain age. The gland is about the size of a tangerine orange, buried under the skin of the abdomen immediately above the preputial orifice, but not having any direct communication with the genital organs. It possesses a small orifice, through which the secretion exudes on the contraction of a powerful muscle by the deer.

Fig. 12.
MUSK DEER

The whole animal is permeated by the powerful odour of the secretion, and even the excrement on drying causes the surrounding atmosphere to be permeated with the odour of musk, a fact which the hunter turns to very useful account in following the trail of the deer.

Hunting the musk deer is very difficult, and is sometimes undertaken as a sport by Anglo-Indians. The natives, however, find it very difficult and sometimes very hazardous. The use of dogs is scarcely practicable, since the deer is so agile, as to easily outdistance any dog in mountain country. The deer are, to a large extent, caught by building hedges or barriers across places where they are known to be, with openings at fixed distances in which traps are inserted. The traps must be visited regularly, as otherwise leopards or other animals will devour any deer that have been caught. The deer are killed—unfortunately even young ones whose musk pouches are only in a very early stage of development, and the pouches carefully laid out to dry before they are packed for transmission to the merchants.

FIG. 13.
MUSK POD

There seems reason to believe that, in spite of the interruption of hunting during the whole of the winter, the feeble breeding power of the musk deer, coupled with the senseless killing of everything the hunter catches, the extermination of the animal will only be a matter of a comparatively short time.

The principal varieties of musk are the following—(1) Tonquin musk, (2) Cabardine musk, (3) Nepaul musk, and (5) Assam musk.

Tonquin musk comes from Thibet, and is certainly the most prized commercially. It arrives, in the pod, in small boxes covered with silk and lined with lead, which are known as catties, because they contain one catty ($22\frac{2}{3}$ oz.) of musk. The pod of tonquin musk. is round, slightly flattened, but never pear-shaped A lappet of skin is left round the edge of the pod, and when this is cut down, so that it is only about $\frac{1}{8}$th of an inch broad, the pod is said, to be trimmed. The so-called " Blueskin " musk is merely the old-fashioned Tonquin pod prepared in a special manner. The two or three layers of skin covering the opposite side of the pod to that on which the orifice lies are removed, leaving exposed the thin membranous skin which lies immediately next to the musk grains. This membrane is of a bright metallic blue colour, somewhat resembling steel—hence the name " Blueskin." The preparation of blueskin musk is an operation of a very delicate nature, and is performed by specially trained natives, principally in Shanghai.

According to C. Court Treatt, the advantages to be claimed for blueskin musk are the following—

(*a*) The character of the contained grain can be more readily ascertained.

(*b*) There is less chance of adulteration, since the delicate blueskin will stand no rough handling.

(*c*) It is easier to grain than the old-fashioned—one has only to break the blueskin with the fingers instead of cutting through a leathery jacket with a knife.

(*d*) There is less skin to go bad ; a pod whose skin has begun to putrefy may affect the odour of a whole parcel of musk.

(*e*) Many buyers like the interesting appearance of blueskin ; a blueskin pod with its bright iridescent covering is quite a beautiful object in itself.

Tonquin musk constitutes from 80 to 85 per cent. of the musk of commerce, and is, of course, the most esteemed variety. In common with other musk, except Nepaul musk, it usually possesses a more or less ammoniacal odour, due to its not having been completely dried, and having therefore undergone a small amount of fermentation.

Cabardine musk is not of so fine an odour as Tonquin musk. A distinction is made between Russian and Chinese cabardine musk. The pods are more oval and flatter in shape, and they usually have wide margins of adherent skin. They are more hairy than Tonquin pods, and are frequently much more moist, and, so, more fermented. In this condition they are sometimes half full of a yellow liquid,—are then known commercially as " squeakers." The Russian cabardine musk trade is carried on from Siberia *via* Petrograd, the Chinese variety coming over through the same sources as Tonquin musk, which it more nearly resembles in general characters than does the Russian variety.

Nepaul musk only arrives in London at irregular intervals, much of it being used in India and in the Arabian districts. The pods are very small, being only about one-third of the size of the Tonquin pod. They are in the form of hard, round balls covered with hair about an inch long. The grain is quite dry and, on account of this careful preparation, never has any odour of ammonia.

Assam musk is only obtainable in very small quantities, the supply, other than any which may be used by the natives, being sent entirely to England. The pods resemble the Nepaul pods, but the skin is considerably darker. The grain is almost black, and has an odour differing somewhat from that of all other varieties of musk.

Grain musk, which is the form in which many perfumers prefer to buy it, is made by splitting open the pod and scooping out the grain, great care being taken not to scrape away any of the blue skin with it, as this is liable to putrefy, and would thus spoil the whole of the bulk of the grain. The grain is soft and unctuous to the touch, and is in the form of small deep reddish-brown particles somewhat resembling clotted blood, with a bitter and somewhat astringent taste. The odour is so powerful that one part of musk can impart a strong musk odour to 3,000 parts of an odourless powder. According to some, the odour of musk is not only due to the compounds which it contains—amongst which the ketone, muskone, is the principal—but also to the development of some substance during a slow process of fermentation. Any specimen of musk which has been kept in a closed space for any length of time gives off a distinct odour of ammonia.

The adulteration of musk is very common, and it requires an expert to recognize pure samples. Dried blood, albumen, earthy matter, etc., etc., are used for this purpose, and the adulteration commences with the journey with the caravan which has collected the pods from the hunters, to the headquarters of the exporting merchant. In the leisurely journey, the pods are carefully opened and the adulterant inserted in so skilful a manner, that only an expert could detect what had been done.

There used to be a tax on all musk so brought in to Shanghai, and it was generally paid in kind. If the merchant tendered adulterated musk pods in payment of the tax, the collectors did not argue with him—but promptly cut his head off. Hence the fact that musk used for payment of the tax was severely left alone, and was always pure.

Musk owes its odour, in the main, to about 0·5 up to 2 per cent. of a ketone apparently allied to the ketone of civet which has been referred to above. It is a thick, colourless, oil, only very slightly soluble in water, but easily soluble in alcohol. It forms crystalline derivatives from which it is easily recovered in a chemically pure condition.

It may be as well to mention here that, as will be seen when we deal with synthetic perfumes, artificial musk has no connection, from a chemical point of view, with natural musk, the artificial substance being an entirely different body from muskone, only resembling it in that it possesses a powerful musk-like odour.

Musk is used in perfumery in the form of an alcoholic tincture, and finds employment in a large number of the most esteemed liquid perfumes.

CHAPTER V

ARTIFICIAL PERFUMES

The development of the synthetic perfume, although of considerably less commercial importance than that of the coal tar dye, is of at least as great scientific interest and value as the results which followed the epoch making discovery of our own countryman, W. H. Perkin, who discovered the first of the coal tar colours. There is one clear and definite reason why the evolution of the synthetic perfume is of much later date than that of the coal tar dye. The intense colour of the dye is at once visible, and practically unmistakably visible, to the eye of any person with the exception of the very few really colour blind persons. Now with odours the matter is entirely different. Nearly every substance which is recognized as having a pleasing odour, or what is commonly regarded as a "perfume," is appreciated as such in a state of considerable dilution, and very few persons, who, for example, highly appreciate the perfume of a bottle of essence of white rose, or of eau de Cologne, would consider the concentrated materials to which the finished article owes its fragrance as being agreeable perfumes. As a solitary example, we may mention methyl anthranilate, one of the chief constituents of oil of neroli, which in itself is one of the principal ingredients of eau de Cologne, would be regarded with aversion by the admirers of the eau de Cologne. Hence, when a body is discovered, it often requires a chemist who has been specially trained to the valuation of odours, to recognize what its odour is likely to be when the substance is used in a diluted or compounded condition.

Prior to the last twenty or thirty years, this simple fact had not received sufficient attention, and the skilled chemist did not always realize the odour value of substances he was handling. As an extreme example of this, we may mention that when the coal tar body diphenyl-oxide was discovered thirty years or so ago, its discoverer recorded its physical characters, and described it as having a " slight odour of oranges." Ten years or so ago diphenyl-oxide was " rediscovered " by a chemist who had a due perception of odour value. He recognized its immense possibility as a perfume material, and to-day diphenyl-oxide is made on a commercial scale and sold as " artificial geranium," the substance, when in dilute solution, having an intense odour closely resembling that of the geranium leaf. The first thing we have to do is to understand what a synthetic perfume is. Synthesis is the " putting together," the building up, as distinguished from analysis, or breaking down, in chemical operations.

If by starting from one substance we succeed in effecting chemical combinations and changes, so that from the original body we eventually build up an entirely different, and, usually, more complicated compound, we have synthesized that compound. And when we use the term synthetic in its true sense as applied to a perfume, it is a substance built up in this manner. The wider term " artificial perfume " embraces something more than this. For example, if we are able to extract from some natural source one given constituent of, for example, oil of neroli, and from some other natural source another constituent occurring in oil of neroli, and so, eventually extract all the constituents of natural oil of neroli from quite varied sources, so that by mixing them together we obtain an oil which closely resembles the natural oil of neroli, we should not have synthesized any single ingredient, but should merely have separated them from other substances in which they existed ready-formed, and mixed them so as to make, not a *synthetic*, but an *artificial* oil of neroli.

As a matter of fact the artificial oil of neroli of commerce is so made in regard to nearly the whole of its ingredients. But one very important constituent, methyl anthranilate, is in fact prepared by synthesis from coal tar derivatives, so that the artificial oil does contain some synthetic perfume material.

The distinction between the words artificial and synthetic above mentioned, is not a very important one from the point of view of the practical perfumer, but to the chemist it is highly important, as in general the methods used for extracting ready-formed ingredients, and for synthesizing new substances, are of very different characters.

The early development of the synthetic perfume was, in the main, in the hands of the Germans, who exploited them strongly against the natural flower perfumer. The French, being naturally the leaders of the flower perfume industry of the world, opposed the newly-introduced synthetic perfume very strongly on the grounds of the general coarseness of their odours. To-day the antagonistic schools have come together, and perfumers universally recognize the value of blending the synthetic perfume with the natural, whilst the most bigoted exponent of the synthetic will not deny that as *delicate* perfumes they are of little use without the assistance of the natural substances. As an illustration of this position we may quote the following interesting remarks by the well-known French perfume chemist Dr. Eugène Charabot.

"I still have a vivid remembrance of the uneasiness which, on the morrow of the discovery of ionone, tended to cloud the hopes founded by the industrious agricultural populations of the Grasse district on the cultivation of the violet.

"After seeing the profits, which were afforded them in former times by abundant olive harvests, disappear, these cultivators had sunk their labour and their modest resources in planting violet plants under the shade of the olive trees which had broken their promises. And it was feared that there would happen the same thing which had come about in the dyestuff industry, where chemistry, by its marvellous methods of synthesis, had succeeded in realizing the same groupings of atoms as the vegetable organism, thus gaining over Nature a victory, the consequence of which was the ruin of agricultural industries and the upsetting of the economic position of several districts. But events soon showed that all fears in this respect were devoid of foundation.

"The industry of natural perfumes was destined to evade these disturbing influences; and we have seen the artificial perfume industry born and develop, not merely without inflicting the least injury on the industry of Grasse, but even assisting its progressive evolution. Nature maintained the monopoly of the fine perfumes, whilst the art of the chemist created odorous products of low price, which enabled compositions to be prepared within the means of humbler customers.

"New needs are created by the possibility of satisfying them, so that the use of perfumes has extended to all classes of society. Since the employment of artificial perfumes necessitates that of a certain proportion of the natural products, the immediate result was that the latter found new outlets in cheap perfumery, whilst still retaining the basis of the better class of scents.

"If I confined myself to the statement that the artificial perfumes have been the making of cheap perfumery, I should be doing these products an injustice, which I wish to avoid by pointing out another circumstance which has contributed to the union of the destinies of the two industries with which we are dealing. The chemical products do not serve exclusively for the preparation of strong and coarse perfumes ; they also have their place in fine perfumery. Properly applied they are capable of increasing the power of the sweetest scents, to which they impart originality, strictly on condition that they are accompanied by a large proportion of natural products, of which they, in this way, again favour the continued consumption. Thus it is difficult at the present day to conceive the employment of the one class to the exclusion of the other. These facts are more than sufficient to justify my opinion regarding the influence exerted by the chemical perfumes on the development of the natural perfume industry. They are expressed in the ever growing importance of the floriculture of the South of France and the ever increasing demand for flower products.

" And my conclusion is emphatic, that the industry of natural perfumes and that of the artificial perfumes, rivals in appearance, lend each other mutual support in the path of progress on which they both are travelling. Thus there is one more instance of the truth, with the fruitful instruction which it bears with it, that real, continuous progress, universally beneficial, is invariably manifested when Science and Industry are bound together in close union, strong and fertile."

With these preliminary remarks, we may now pass on to the detailed examination of a number of the more important of the synthetic and artificial perfumes, commencing with Ionone.

Ionone. The perfume of the violet has always been an exceedingly popular one. The odorous constituents of the violet flower are so delicate and exist in such minute quantity, that it is a practical impossibility to isolate them for the perfumer's use. Natural violet perfume, therefore, is prepared for manufacturers in the form of pomade, or sometimes concrete. The well-known resemblance of the odour of the root of several species of Iris, led to the general employment of powdered orris root in the preparation of the "violet powder" of the Victorian era, a powder in which violet perfume was usually conspicuous by its absence. The chemists, Tiemann and Krüger, determined to attempt to prepare a violet perfume by synthetic methods. But, owing to the practical impossibility of obtaining sufficient of the natural violet perfume for proper investigation, they commenced their work by an exhaustive research into the chemistry of the odorous constituents of the closely allied perfume of orris root. From orris root they succeeded in isolating a body, known chemically as a ketone, which they named irone, which had an intense odour resembling that of violets, although not absolutely identical with it. Having succeeded in establishing the identity of the substance they wished to synthesize, they then started out to attempt to prepare an identical body by synthetic methods. As a matter of fact they did not succeed in preparing irone in this manner, but eventually they did succeed in preparing an allied body, which they termed Ionone, and which had an odour even more like that of violets than irone itself. They produced this new ketone, ionone, by first separating the body known as citral, which forms the principal constituent of oil of lemon, oil of verbena, and oil of lemon-grass. On a commercial scale, citral is always obtained from oil of lemon-grass. Citral, thus separated, was heated with acetone (the highly volatile liquid which is used as a solvent for cordite, etc.) in the presence of a small amount of caustic alkali. In this manner they obtained a condensation product, which they termed pseudo-ionone. The odour of this is neither particularly pleasant, nor characteristic of violets. But, by heating this pseudo-ionone with dilute sulphuric acid in the presence of a little glycerine, they converted it into an isomeric body, which they termed ionone. This body was found to possess an intense odour of violets, and was put on to the market in the form of a 10 per cent. solution in alcohol, and was sold at a very high price, being protected by a patent. To-day, the patent having expired, it is sold in a pure 100 per cent. condition, and the price is quite reasonable.

Ionone is a pale yellow, or almost colourless oil, of specific gravity from 0·935 to 0·940, having an intense violet odour, but also slightly recalling that of the vine blossom.

It was for many years believed that ionone was an absolute chemical individual. Later researches, however, have shown that it is a mixture of two closely allied isomeric ketones, which have been named *alpha*-ionone and *beta*-ionone. So that by separating ionone into its two isomeric constituents, two bodies are obtained each having an intense violet perfume, but each having a distinctly different " note," or " timbre " as the French prefer to call it. *Alpha*-ionone has the sweeter and more penetrating odour of the two, rather resembling orris root than violets in perfume, whilst *beta*-ionone more closely resembles the violet flower.

In addition to these bodies, other very closely allied ketones can be prepared by substituting for acetone, a closely allied substance, and so producing very closely allied condensation products. The result is that we have a number of bodies, all of which have intense violet odours, but which differ slightly between themselves. So that by judiciously blending them a number of artificial violet perfumes can be prepared, each with a slightly different "shade." So that the artificial violet perfume sold by the manufacturers to the perfumers under various proprietary names may, and do, actually vary in character, on account of the different proportions in which these violet ketones are blended.

The discovery of ionone has helped to popularize violet perfume amongst the masses to an enormous extent. Much of the violet perfume as sold to the public contains no trace of true violet perfume, but is made entirely with the artificial ionone. Such mixtures are always rather coarse and have a "chemical" odour, especially if, as is often the case, there is too much ionone in the perfume. This very common fault is not due to any error of judgment on the part of the perfumer. He knows—sorrowfully, perhaps, from an artistic point of view—that there is a large class of user who will be content with nothing but a strong perfume.

The better class of violet perfume offered to the public, however, is, in most cases, a natural extract of the violet flower, fortified with a little artificial ionone. Such perfumes, properly prepared, leave little to be desired.

In reference to the practical use of ionone, Messrs. Schimmel & Co. have made the following useful comments.

"This beautiful article maintains its position in the front rank of preparations for perfumery, and will probably remain without a rival among artificial perfumes for some time to come. Although the violet scent has long been a favourite perfume, its popularity has doubled through the invention of ionone, and it is not too much to say that the introduction of that body alone has made it possible to produce a perfect extract. Some of the leading European perfumers produce violet extracts which may be recommended as examples of excellence, and which have deservedly become commercial articles of the first importance. The inventors of ionone have earned the gratitude of the entire perfumery industry, and may be congratulated in turn upon the remarkable success of their invention. As we have already pointed out on a previous occasion, the preparation of a violet extract in which ionone is made to occupy its due position is not such an easy task as is often assumed ; on the contrary it requires a long and thoughtful application. To obtain a perfect result with ionone is an art in the true meaning of the word, and on that account no inexperienced hand should attempt it. We again and again lay stress upon this fact, because in our business we are constantly brought face to face with people who think that they can make a suitable violet extract by simply mixing alcohol with ionone solution. This view is quite wrong. The employment of ionone presupposes above everything else that the user is acquainted with the peculiarities of the article, and knows how to deal with them. Again and again the uninitiated come to us with the complaint that ionone has no odour at all, or that it smells disagreeably, although, as a matter of fact, these objections are usually withdrawn upon closer acquaintance with the article. The assumptions in question are only due to a blunting of the olfactory nerves, or, more correctly, to a nasal delusion, which also occurs sometimes in the case of other flower odours, and to which people are known to be particularly liable when smelling freshly gathered violets. The principal thing in connection with the employment of ionone is to discover its proper degree of dilution. In its natural state the body is so highly concentrated as scarcely to remind one of violets. This is the reason why it was placed in trade in the form of a 10 per cent solution, and not in its pure state. This form has proved an exceedingly useful one. In using it for extracts, powders, sachets, etc., the solution must be further diluted and fixed with some orris oil, civet and musk."

Vanillin. When describing the characters of the vanilla bean, we pointed out that the valuable perfume material owed its odour, in the main to a crystalline substance which was termed vanillin. These crystals were separated and examined, and attempts were made to prepare it artificially. The first method by which it was prepared is of historical interest only: this was by the oxidation of the glucoside coniferin, by means of chromic acid. The researches of Tiemann and Haarmann eventually led to a most interesting synthesis of vanillin, and one which, to-day, is the principal method by which it is manufactured commercially. The starting point for this synthesis is the essential oil of cloves. This oil, so largely used in the preparation of flavouring essences, contains from 75 to 90 per cent. of a substance called eugenol, to which the cloves owe their characteristic odour and flavour. The eugenol is quite easily extracted from the oil, in a state of absolute purity. If eugenol be heated for a short time with a little caustic alkali, it undergoes a slight alteration—a molecular rearrangement—and is converted into iso-eugenol. By treating this body with acetic anbydride, it is converted into acetiso-eugenol. This body is then treated with an oxidizing agent, and is converted into acetyl-vanillin, from which pure vanillin is obtained by decomposition by means of an alkali.

The vanillin so obtained is absolutely identical with, and indistinguishable from, the natural vanillin occuring in the vanilla bean. So that, in this case, the synthetic product is not one which merely *resembles* that which it purports to imitate, but is absolutely identical with it. It is, of course, true that the odour of synthetic vanillin, is not *quite* identical with that of the vanilla bean, because the bean contains traces of other substances than vanillin, which all contribute to the odour of the bean. Vanillin can be made by a number of other processes, including several which start from substances found in coal tar. For example, Tiemann and Reimer have succeeded in preparing it from guaiacol, a phenolic body existing in, or manufactured from, coal tar.

The process is carried out in the following manner—About 100 parts of caustic soda are dissolved in 100 parts of water, and to the solution thirty-five parts of guaiacol are added, whilst hot. After the mixing, the solution is cooled to 60 to 65°, and then sixty parts of chloroform are gradually added through the usual type of side tube, or through the condenser, which should be long and kept cold with water nearly at ice temperature. About one-third of the chloroform should be added at first, and the liquid in the heating apparatus should be well stirred. A thermometer must be kept in the heating flask, so that the temperature may be completely under control. Directly a temperature of 70° is indicated the flask must be immersed in cold water until it is reduced again to 65°. The temperature is thus kept between 65° and 70° during the whole course of the reaction, and if it should fall below 60° the flask must be immersed in warm water again. In about 15 minutes, a second third of the chloroform is added, the precautions as to temperature being still observed. After another quarter of an hour the balance of the chloroform is added. Towards the end of the reaction the temperature will fall, as reaction is now much slower, and it will be found necessary to immerse the flask in warm water from time to time to maintain the temperature limits above mentioned. The reaction takes about two hours to complete. The reaction mixture should be repeatedly shaken, especially towards the completion of the reaction. When the reaction has entirely ceased, excess of chloroform should be recovered by distillation, and the contents of the flask allowed to cool and then rendered acid by careful addition of dilute sulphuric acid. The vanillin can be separated and purified by means of its acid sulphite compound and recrystallized ; but unless the greatest care and skill are exercised, traces of unaltered guaiacol will be found to be adherent to the crystals of vanillin, which will entirely spoil the odour or flavour of anything in connection with which it may be used.

Vanillin is a white crystalline body melting at 82°. It is sometimes adulterated, principally with antifebrin, but adulterations are easy to detect on analysis, so that to-day, the commercial article is generally found to be quite pure. It is used in the form of an alcoholic solution in perfumery, and imparts a very sweet odour to combinations with which it is used. It also has a useful fixative value.

Artificial Musk. For many years attempts have been made to prepare the musk perfume artificially. Although there efforts were eventually crowned with well-deserved success, we may say at the outset, that every substance known as artificial musk is an entirely different compound from that which is the actual odour bearer in natural musk, with which they have no chemical relationship. Natural musk, as has been pointed out previously, owes its odour to a ketone known as muskone. No attempt has been made to synthesize this body, every chemical research on the musk odour having taken an entirely different direction. The first attempt to prepare an artificial musk that we can trace is that of Margraff and Elsner. They ground amber to powder, mixed it with sand, and then distilled it from an iron retort. The resulting oil was washed to free it from foetid matter resulting from the decomposition, and then digested with fuming nitric acid, the temperature being kept low all the time. A resinous matter results, which when washed and dried has a distinct, although not very pronounced, musk odour. The first serious attempt, however, to prepare a definite chemical compound with a musk-like odour was covered by an English patent, taken out on behalf of German chemists. In this process they started from meta-xylene, a coal tar hydrocarbon, and isobutyl alcohol, which were together heated with zinc chloride, and the resulting hydrocarbon was nitrated, and so converted into a nitro-hydrocarbon having a fairly powerful musk odour. The first artificial musk, however, to achieve commercial success was that patented by Albert Baur, and known during the duration of the patent as Musk-Baur. This artificial musk is prepared by heating toluene, a coal tar hydrocarbon, with butyl bromide and aluminium chloride, and nitrating the resulting hydrocarbon. The full chemical name of the substance is trinitro-tertiary butyl-xylene, and it is this body which is known in commerce as musk-xylol, or xylene musk. It is a crystalline compound of slight yellowish colour, melting at 110° to 113° C., and having a very powerful odour of musk. It is only soluble to a very slight extent in alcohol or the usual organic solvents, but sufficient can be dissolved to impart a powerful odour to the solution. The best solvent for it is benzyl benzoate, in which it is fairly soluble. It is used as an adjunct to numerous types of perfumes, and also acts as a very powerful fixative.

There is another closely allied musk-like substance, also discovered by Baur, who showed that if acetyl chloride were condensed with hydrocarbons an acetyl group was introduced into the molecule and so-called ketone musk resulted. By using various closely allied hydrocarbons and other bodies, quite similar artificial musks can be obtained, which have odours which differ but slightly between themselves. Musk-ambrette which is generally considered the finest of all the artificial musks, is an entirely different compound, and is the dinitro compound of butyl-meta-cresol methyl ether. It is a crystalline compound, with a sweet musk odour, melting at 85°.

Heliotropine. The basis of nearly every perfume of the "cherry-pie" type is heliotropine, a substance which is present in small quantity in a few natural flower oils. It is, however, now manufactured on a very large scale by a synthetic process, and this type of perfume is based almost entirely on the artificial product. In Japan there is almost a monopoly of the world's supply of camphor, the solid substance which separates from the essential oil distilled from the camphor tree. As a bye product in the manufacture of camphor there is obtained a large quantity of the liquid essential oil from which almost the whole of the camphor has been removed. Now this essential oil of camphor is very rich in a body termed safrol, which is identical with the principal odorous constituent of oil of sassafras—whence its name. The safrol must first be rectified to obtain it in a perfectly pure condition, when it is suitable for the manufacture of heliotropine. This is effected by a careful fractionation of the oil, when the fraction distilling between 220° and 240° is reserved, and again carefully refractionated until the pure safrol is obtained. This boils at 231° to 233° C. From a chemical point of view safrol is the methylene ether of allyl-dioxybenzene. This is converted into an isomeric body, isosafrol, by heating the safrol with 5 per cent. of its weight of a saturated solution of caustic soda at 100° to 110° C., in exactly the same manner as eugenol is converted into isoeugenol for vanillin manufacture. The crude isosafrol so obtained is carefully rectified, and the pure compound boiling at 253° to 254° C., is collected. Five parts of isosafrol are then treated with a solution of 25 parts of potassium bichromate, 35 parts of sulphuric acid, and 80 parts of water, and the mixture is boiled under a reflux condenser. When the reaction is complete the product is washed with water to remove chromium compounds and excess of acid, and the washed oil steam-distilled, and the distillate dissolved in ether. The ethereal solution is then well shaken with a solution of sodium bisulphite, which extracts the heliotropine from the ether and forms a chemical combination with it. The aqueous solution containing this compound is treated with alkalies, when heliotropine is set free and can be dissolved out by ether, and the resulting heliotropine purified by recrystallization.

Heliotropine is a sweet, powerful perfume, closely resembling that of the plant from which it takes its name, and is used to a very large extent in the preparation of liquid perfumes, and for soap perfumery.

Coumarine. Coumarine is a synthetic perfume of considerable importance. It is a white crystalline substance melting at 67° to 68° C., and is the active odorous substance found in the Tonquin or Tonka Bean, the seeds of two or more species of Dipteryx, in which it is present to the extent of about 3 per cent.

It also occurs abundantly in the dried leaves of Liatris odoratissima, an herbaceous plant growing freely in North Carolina, where it is known as Deer's tongue or Hound's tongue. From 1 lb. of dried leaves, as much as 100 to 150 grains of coumarine can be obtained. Coumarine has also been identified in a very large number of plants, but generally speaking, only in small amount.

It was first obtained synthetically by our countryman Perkin, who obtained it by heating salicylic aldehyde with acetic anhydride and sodium acetate. The mixture solidifies to a mass from which, by treatment with water, an oil separates containing coumarine and aceto-coumaric acid. On heating, the latter is decomposed into acetic acid and coumarine. Hence, on distillation, the principal product obtained is coumarine.

Coumarine is a white crystalline body having a powerful odour of the Tonquin bean, and is used in perfumery as a substitute for the natural beans. Perfumes of the New Mown Hay type are usually based on coumarine. Coumarine is sometimes adulterated with acetanilide, which, however, is very easily detected by the analyst. Coumarine is soluble in alcohol, and is used in the form of an alcoholic solution in the preparation of liquid perfumes. It is also used to a fair extent in the perfuming of snuff, when it is mixed in with the powdered tobacco in the dry form, and not in solution.

A New Series of Alcohols and Aldehydes. During the past few years a series of bodies which were never suspected to have any odour value, have been introduced to the perfumery industry, and have proved themselves to have the most extraordinary value in modifying the odour of numerous flower combinations, thus enabling perfumers, by a judicious use of a selection of these bodies, to prepare new " bouquets " which their rivals find very difficult to match. The bodies in question are the higher alcohols and aldehydes of the so-called fatty or aliphatic series. They have odours which can scarcely be described, except by the words fruity and flowery, more or less of the same general character, but each differing from the other. The one great secret of their successful employment is that they must be used in very minute quantities, or the composition is spoiled. Only a few of them have, so far, been detected as natural constituents of essential oils, but no doubt many of them exist naturally, but have not yet been isolated. The lowest member of the alcohol series which is of any interest to perfumers is octyl alcohol. This has a very sweet, rose-like odour, and it is especially suitable for imparting the natural perfume of the rose flower to essence of rose which usually lacks something of the smell of the flower itself. This feature is also present in the next higher alcohol, nonyl alcohol, but diminishes as we ascend the series. The alcohols in question are liquids, only solidifying at very low temperatures as the following table indicates—

	Melting point.	Boiling point.
Octyl alcohol	–22° to –21°	95°
Nonyl ,,	–11° to –10°	102°
Decyl ,,	–10° to – 8°	110°
Duodecyl ,,	+13° to +15°	142°
Undecylenic alcohol	–12° to –11°	128°

The above series of synthetic perfume materials are very difficult to manufacture, and consequently very costly.

Similar to the alcohols, are the corresponding aldehydes. For example, octyl aldehyde, which occurs naturally in neroli and rose oils has a deep honey-like odour, and is very useful for rounding off perfumes which possess a heavy odour. Nonyl aldehyde has an odour which belongs to the rose and orange types of odour, and can be used to great advantage in any perfume based on rose, geranium or neroli oils. Decyl aldehyde has been found in rose and orange oils, and is probably the most useful body of the whole series of this group of aldehydes. There are several other aldehydes of this series, all very powerful in odour, and all very difficult to manufacture in a state of purity, and consequently very expensive. They are easily oxidized, and therefore are difficult to keep in a pure condition. They are best preserved in a 10 per cent. alcoholic solution, in which form they do not undergo oxidation for a considerable time.

Terpineol. This very important body is the basis of nearly all the perfumes of the lilac and lily of the valley type. The terpineol of commerce is a mixture of at least three isomeric alcohols, in which the modification known as *alpha*-terpineol largely predominates. It possesses the great virtue of being quite unaffected by alkalies, so that it can be used safely in soap perfumery. It blends exceedingly well with quite a large number of other perfumes, so that it is one of the most useful artificial perfumes that the manufacturer can possibly have. For example, the compound perfumes known under the names muguet, syringol, lilacine, and artificial gardenia are all based on terpineol. Geranium oil and heliotropine, ylang-ylang, and sandal wood oil all blend well with terpineol. Terpineol was first prepared by Tilden by the action of dilute mineral acids on terpin hydrate, and it is to-day produced entirely by the action of acids on turpentine, from which terpin hydrate is prepared. It is a thick, viscous oil, having an intense odour, recalling that of hyacinth, lilac, and hawthorn. It is comparatively cheap, hence its very extensive employment in cheap perfumery, although it is also used in high-grade work as well.

Aubepine. Hawthorn and May blossom perfumes almost owe their existence to the discovery of the body known to chemists as anisic aldehyde, or in commerce as aubepine. It is the methyl ether of para-oxy-benz-aldehyde. It is prepared commercially by the careful oxidation of anethol, the characteristic constituent of aniseed oil. This is treated with nitric acid at a very gentle heat, when anisic aldehyde results. This is a heavy oil of specific gravity 1·1275, boiling at 245° to 246° C. It possesses a well marked odour of hawthorn blossoms, especially when diluted.

Other Alcohols. There are quite a number of bodies of an alcoholic nature which to-day are absolutely essential constituents of many perfumes, in addition to those above described as the higher alcohols of the fatty series. Of these we can only select a few of the more important for a short description. One of the most largely employed is geraniol. This body is a natural constituent of geranium, rose, citronella and other oils, and is not produced by synthetic methods, but is separated from the cheaper of the oils in which it exists naturally. Geraniol is one of the chief ingredients used in the manufacture of artificial otto of rose, for which a large demand exists, on account of the high price of the natural article. The geraniol of commerce is made from either palma-rosa oil (the so-called Indian Geranium oil) or citronella oil. The oil, or the distilled fraction consisting mainly of geraniol, is rubbed down with an equal quantity of dry powdered calcium chloride, and the mixture kept in a desiccator at a temperature of -4° C. for sixteen hours. The soft mass is then rubbed down with dry petroleum ether, and the liquid portion removed by means of a suction filter. This leaves a solid compound of geraniol and calcium chloride on the filter. This is treated with warm water, which decomposes the compound and liberates the geraniol which can then be purified by fractional distillation. It is a colourless oil of specific gravity 0·881, possessing a sweet rose odour, but wanting strength, which, in the manufacture of artificial otto of rose, has to be supplied by other ingredients. Citronellol is an alcohol closely allied to geraniol, which is also a constituent of otto of rose. This has a sweet rose odour, but of a different character from that of geraniol. It can be prepared by a chemical process, and is a commercial article used to a considerable extent in perfumery, especially where rose odours are concerned.

Phenyl-ethyl alcohol is one of the triumphs of synthetic perfume chemistry. It has long been recognized that the rose flower has a perfume which differs in some definite way from that of the otto of rose distilled from the flowers. This has been found to be due to the fact that phenyl-ethyl alcohol is a constituent of the rose perfume, but is very soluble in water, so that it dissolves in the distillation waters, and does not appear in the separated otto of rose. So that the complete perfume of the rose has to be sought for in both the otto and the rose water. The phenyl-ethyl alcohol cannot, however, be easily recovered from the rose water, so that it has to be made synthetically. The method of its preparation is very complicated, and need not be described here. It is a colourless, heavy oil of specific gravity 1·024, having a peculiar rose and honey odour. It is soluble in 60 times its volume of water, hence the ease with which it is lost in the distillation of rose flowers. It is an absolutely essential ingredient in all well-made artificial otto of rose.

Cinnamic alcohol, a natural constituent of storax and balsam of Peru, is now made synthetically by reducing cinnamic aldehyde diacetate, and saponifying the resulting mixture of cinnamic esters. Cinnamic alcohol is an oil when it contains traces of impurities, but when absolutely pure melts at 33° C. It has a weak but delicate odour, recalling that of roses and hyacinths, and is most useful in compounding perfumes of the hyacinth or narcissus type.

Artificial Esters. By the condensation of bodies known as alcohols, with acids, compounds are produced known as esters. Esters are amongst the most important of the natural constituents of essential oils, and in many cases are the principal odour bearers of the oil. It was, therefore, to be expected that chemists should devote a considerable amount of attention to the possibilities of preparing esters as perfume materials by synthetic methods. This has been done on a very large scale, and to-day a very large number of synthetic esters are commercially manufactured as synthetic perfumes. Here, again, only a few can be described, as a description of all the perfume esters would occupy far too much space.

Methyl anthranilate is one of the most important constituents of oil of neroli. It is prepared synthetically, and used to manufacture artificial oil of neroli, an important article of commerce. The starting point of this ester is the coal tar derivative, benzoic acid, which is nitrated, and then reduced to anthranilic acid, which can then be condensed with methyl alcohol, with the formation of the ester methyl anthranilate. It is a yellowish oil of specific gravity 1·168, having an intense blue fluorescence, and possessing an odour of neroli and similar flower oils.

Methyl benzoate, prepared by condensing methyl alcohol and benzoic acid is a well-known product, sold commercially under the name of Niobe oil. It is a colourless oil of specific gravity 1·102, and has a fragrant odour somewhat suggesting ylang-ylang. It is a favourite ingredient of artificial ylang-ylang oil, and of the perfume known as Peau d'Espagne. It blends well with sandal-wood oil, musk, geranium oil, and otto of rose.

Methyl salicylate is the product of condensing methyl alcohol and salicylic acid. It is practically identical with oil of wintergreen, and has practically replaced that well-known American perfume in such products as tooth paste, etc.

Amyl salicylate, prepared in a similar manner by the condensation of amyl alcohol and salicylic acid is a regular commercial product, sold under various names, such as Orchidée, trèfle, or artificial orchid essence ; it is the basic constituent of all artificial orchid perfumes, and most of those known as Trèfle or trefoil. It is a colourless oil of specific gravity 1·052.

The alcohol geraniol, which has been already described is readily converted into a number of esters, by condensing it with the respective acids. The principal of these are geranyl formate, geranyl acetate, geranyl propionate, geranyl butyrate, and geranyl isovalerianate. These esters have rose-like odours, and are exceedingly useful in rounding off the odour of artificial otto of rose and similar products.

Of the esters of the alcohol linalol, the acetate is the most widely employed. It is prepared on a fairly large scale, and so closely resembles bergamot oil in odour, that it can well be used as a substitute for that oil.

Benzyl acetate, prepared by the interaction of benzyl alcohol and acetic acid is a natural constituent of the oils of jasmin, ylang-ylang and other similar flower oils. It is an oil of powerful jasmin odour, and is the basic constituent of the artificial essential oils of both jasmin and ylang-ylang.

Bornyl acetate, the acetic ester of the alcohol borneol, is a commercial article used as an artificial substitute for pine needle oil. This oil contains a considerable quantity of bornyl acetate, so that the synthetic ester has a quite similar, but much more powerful odour. Cinnamic alcohol forms the basis of several esters which are prepared artificially and which are of use in perfumery. Of these, cinnanyl propionate has a pleasant grape-like odour, and is of considerable use in the modification of fruit or flower odours. Cinnamyl butyrate is very similar, and, if used in very small amount, is of great value in imparting a fruity bouquet to a flower perfume. Cinnamyl cinnamate is a heavy ester differing from the last mentioned very considerably. It exists naturally in storax and, probably, in oil of hyacinth. It is useful in perfumes where a heavy odour is wanted, and has also very powerful fixative properties. The esters of plenyl-ethyl alcohol, which has been described above, are of a highly aromatic nature, the acetate gives what is known to perfumers as a fine "leaf" effect to a flower bouquet. The propionate has a rather fine rose odour, and is useful in producing a characteristic odour in blends of the rose type.

Artificial Aldehydes. The higher aldehydes of the fatty, or aliphatic, series have, for the sake of convenience, been referred to under their corresponding alcohols. There are, however, a number of aldehydes belonging to entirely different groups, which are prepared synthetically, and which are of considerable value in perfumery. Foremost of these, perhaps, is the so-called artificial oil of almonds. The natural essential oil of almonds consists, when freed from a little prussic acid, etc., which is present, almost entirely of benzaldehyde. Since this body can be prepared in a state of absolute purity, the artificial benzaldehyde is so nearly identical with the natural essential oil, that they are practically indistinguishable. It must be borne in mind, however, that in the preparation of artificial benzaldehyde, hydrochloric acid is usually used as a condensing reagent, with the result that traces of chlorine are very frequently present in the product. This is very objectionable, since substances perfumed with such benzaldehyde, white soap for example, gradually darken in colour and lose their attractiveness. Where benzaldehyde is required for high-class perfumery work, it is absolutely necessary that it should be free from any traces of chlorine.

Benzaldehyde is manufactured in various ways, amongst which is the following. Benzal chloride is treated with milk of lime at an elevated temperature, by which process the lime combines with the chlorine, which is replaced by an hydroxyl group, benzaldehyde resulting. The benzal chloride has to be prepared from toluene, a hydrocarbon of coal tar, which must be carefully purified by fractional distillation, and is then treated with chlorine, which results in the formation of benzal chloride.

Another important synthetic aldehyde is salicylic aldehyde. This is an almost colourless oil having the characteristic odour of oil of meadowsweet. It is made in the following manner. Caustic soda is dissolved in water, and phenol (carbolic acid) in the calculated quantity is added. The mixture is warmed to a temperature of about 65°, and then the flask containing the mixture is attached to a reflux condenser. The calculated amount of chloroform is then slowly run in, the temperature being very carefully regulated. When the reaction is complete the excess of chloroform is driven off by a gentle heat, and the residue is subjected to steam distillation. The distillate consists of a mixture of salicylic aldehyde and unaltered phenol. The aldehyde is purified by being converted into a crystalline compound with sodium bisulphite, from which salicylic aldehyde is liberated in a pure condition by treating the compound with caustic alkali. Salicylic aldehyde is exceedingly useful in the production of odours in which that of meadowsweet is desired. Cinnamic aldehyde is the principal odorous constituent of cinnamon and cassia bark oils, which possess perfumes which are of extreme value to manufacturers. A considerable quantity of cinnamic aldehyde is, however, now prepared by synthetic methods, and a good deal of the so-called cinnamon oil of commerce is really an artificial mixture based on the synthetic aldehyde. This can be prepared in the following manner. A mixture of 10 parts of benzaldehyde—the synthetic oil of almonds recently described—15 parts of acetaldehyde, 900 parts of water, and 10 parts of a 10 per cent. solution of caustic soda are allowed to stand for ten days at a temperature of 30° C., with regular intervals of stirring. The cinnamic aldehyde formed is extracted with ether and purified by fractional distillation. Cinnamic aldehyde is a sweet, odorous liquid, boiling at 252° to 254°, and closely resembling cinnamon oil in odour, but without its delicacy.

We now come to one of the most interesting of the synthetic aldehydes, and one which has only come to the front during the past few years. This is phenylacetic aldehyde, which may be regarded as one of the modern triumphs of synthetic perfumery. It is prepared in the following manner. Methyl cinnamate (16 parts) is dissolved in methyl alcohol (20 parts) and treated with bromine (20 parts). The mixture solidifies in the cold. It is then shaken with a solution of caustic soda (12 parts) in water (24 parts). The temperature should be kept down to 40° C. After two hours the mixture is neutralized with dilute sulphuric acid, and an oily layer separates, and is mixed with water (to 250 parts) and sodium carbonate (55 parts). The aldehyde is then distilled in a current of steam, and extracted with ether, and the ether evaporated. The aldehyde has a strong tendency to alteration, and it is difficult to either make it or keep it in an absolutely pure condition. It keeps better, however, in an alcoholic solution. Phenyl-acetic aldehyde is an oil of specific gravity 1·085, and boiling at 205° to 207°. It has a very intense odour of hyacinth and narcissus—so intense as to be, to most persons, sickly and objectionable. Its value as a perfume appears best in very dilute solutions. It is one of the indispensable constituents in artificial imitations of flower perfumes of the hyacinth, narcissus and jonquil type.

We may conclude the section dealing with synthetic perfume materials with the description of a few important compounds not coming within the above classes. Acetophenone is a ketone which is found naturally in the essential oil of labdanum resin. It is a fragrant, crystalline substance, melting at 20° and boiling at about 200° C. As found in commerce it usually contains traces of impurities which prevent it from crystallizing, so that it is usually found in the liquid condition. It can be prepared synthetically by distilling a mixture of calcium benzoate and calcium acetate, or in the following manner, which is that by which most of the commercial synthetic is prepared. Dry aluminium chloride in powder is placed in a capacious flask attached to a reflux condenser, and covered with benzene. The flask is kept in ice cold water, and acetyl chloride is allowed to drop slowly into the liquid. A vigorous reaction ensues, and much hydrochloric acid gas is evolved. After about one hour the reaction is finished, and the mass is transferred to ice cold water, when a brown oil separates. The mixture is extracted with benzene, the benzene extract washed with dilute caustic soda, then with water, and dried over calcium chloride. The anhydrous liquid is then decanted and distilled, and when the benzene has been recovered, the fraction, boiling at 195° to 202° C., is almost pure acetophenone. This substance has a very lasting and powerful sweet odour, and is very useful in soap perfumery. It is a good auxiliary to such odours as those of new mown hay, syringa, and the like.

Paracresol and naphthol, both coal tar derivatives, form ethers which are of the highest value in perfumery. Paracresol yields a methyl and an ethyl ether, the former occurring naturally in ylang-ylang oil. Both ethers are prepared synthetically, and both have sweet flower odours, resembling that of ylang-ylang oil.

The synthetic perfume sold under the name yara-yara or nerolin (old) is the synthetic methyl ether of *beta*-naphthol. Bromelia or nerolin (new) is the corresponding ethyl ether. Both are crystalline compounds with an orange flower odour. They are prepared by heating five parts of beta-naphthol with five parts of methyl or ethyl alcohol, and two parts of concentrated sulphuric acid for several hours at 125° under a low pressure.

There are two substances which have recently been introduced into synthetic perfumery, having a powerful odour of geranium leaves, and which form the basis of the artificial geranium perfume of commerce. These are diphenyl-methane and diphenyl oxide. Of these, the former is a crystalline body melting at 26° to 27° C. It can be prepared by treating benzyl chloride and benzene with zinc dust, or by condensing benzene with methylene chloride in the presence of aluminium chloride. Diphenyl oxide, or phenyl ether is also a crystalline compound, which can be prepared by digesting diazo-benzene sulphate with phenol, or by distilling copper benzoate. It is to-day manufactured on a comparatively large scale as an artificial geranium perfume. Indole is a nitrogenous compound, related chemically to the indigo group of dye substances. It exists in minute amounts in several flower oils and probably in most animal perfumes. In a concentrated form it has a faecal odour, and is very objectionable, but on dilution, minute quantities are found to be very useful as slightly modifying and fixing other odours. It is prepared synthetically, and is very expensive.

The above survey of the principal perfume materials manufactured by synthetic methods is sufficient to indicate the enormous scope of this comparatively new branch of the industry. There are enormous numbers of such bodies, and fresh ones are continually being discovered. Frequently where, for example, the acetic ester of a given alcohol is found to have a useful odour, the whole series of the esters is prepared with different acids, all of which have similar but not identical odours, which are of considerable use in preparing bouquets have the same predominating perfume, but which can be modified to an almost infinite extent by a judicious mixing of the subsidiary odours.

In conclusion, the two guiding rules in the use of synthetic perfume materials are these: be sure they are chemically pure, and do not use too much of them. Neglect either of these precautions, and an indifferent or valueless product will be the result.

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