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QUASSIIN AS A CONTACT INSECTICIDE.

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INTRODUCTION.

Quassia chips, the active principle of which is quassiin, have been employed for many years in the preparation of spray solutions for the control of the hop aphis (*Phorodon humuli* Schr.). Several formulas have been followed, and there are several methods of preparation according to these formulas. Several factors have brought about the variations in the formulas, (1) instability in the percentage of quassiin in the chips, (2) the total amount of available quassiin in the chips probably not extracted, due to the method of preparation, and (3) the fact that there appeared to be no fundamental data accumulated on this subject. The writer accordingly commenced the investigation, which has been taken up from an insecticidal standpoint, and any chemistry that is mentioned other than very simple matters is taken from the various sources. Acknowledgments are due to Prof. George P. Grey, of Berkeley, Cal., and Mr. G. H. P. Leichthardt, of Sacramento, Cal., for valuable suggestions, and to Mr. R. E. Campbell, of the Bureau of Entomology, who ably assisted the writer in determining the efficiency of the several formulas.

During the investigation of the life history and control of the hop aphis[2] it was observed that there were several formulas for the use of quassia chips. These all appeared to give satisfactory results when carefully prepared and applied, but it will be observed from the following formulas that if the weaker one killed the aphides, the use of the stronger one resulted in a waste of material and extra expense.

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[1] Resigned August 31, 1914.

[2] Parker, Wm. B., The Hop Aphis in the Pacific Region. U. S. Dept. Agr., Bur. Ent. Bul. 111, 39 p., 8 fig., 10 pl., May 6, 1913.

Note.—The results of an investigation to determine the most suitable solution of quassiin for use as a spray for the control of the hop aphis are discussed in this bulletin.

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The following formulas are typical examples of the variation in the amount of ingredients and the cost per 100 gallons:

	No. 1.	No. 2.	No. 3.
Quassia chips .... pounds..	2.8	8	9
Whale-oil soap .... do....	1.6	6	6
Water .... gallons..	100	100	100
Cost per 100 gallons .... cents..	31	69	74.2

These formulas are concocted differently by different growers. Some soak the chips 24 hours in a barrel of water and then boil them for 2 hours. Some boil them for 2 hours without previous soaking, and others boil them with the whale-oil soap. The several formulas and methods of preparation all have their advocates among the hop growers.

CHEMICAL LITERATURE ON QUASSIIN.

The quassia chips commonly used in preparing spray solutions are the wood of the Jamaica quassia (*Picrasma excelsa* Swz.). The literature on the chemical nature of quassiin, the active principle of quassia wood, was found to be very limited, but the few important references that the writer was able to obtain are discussed below.

The wood of *Picrasma excelsa* (Swz.) Planch. (*Quassia e* Swz.; *Q. polygama* Lindsay; *Piceaena e* Lindl.; *Simaruba e* D. C.) or of *Quassia amara* L. (Fam. Simarubaceæ).

Description.—Jamaica quassia. Occurring in various forms, usually chips, raspings, or billets, yellowish white or pale yellow, and of rather coarse texture; odor slight; taste intensely bitter; medullary rays containing tetragonal prisms or small, arrow-shaped crystals of calcium oxylate. Billets of Jamaica quassia are usually 12.5 cm. or more in diameter; in tangential section the medullary rays are mostly 3 to 5 rows of cells in width.

Surinam quassia. Occurring usually in billets not exceeding 7.5 cm. in diameter; the wood is heavier, harder, and more deeply colored than that of Jamaica quassia, and the medullary rays in tangential section are mostly 1 or 2 rows of cells in width.

Constituents.—Although Jamaica quassia is said to contain traces of a yellowish alkaloid, giving a fine blue fluorescence with acidulated alcohol, the important bitter principle is a neutral, crystalline substance, commonly known as quassiin, but determined by Massute to be a mixture of two crystalline bodies, which he denominated α- and β- picrasmin.

Quassiin is extracted by neutralizing the aqueous infusion with soda, precipitating with tannin and decomposing the precipitate with lead oxide or lime. It is commonly said to exist to the extent of only 0.05 to 0.15 per cent, but really exists in much larger amount, Wiggers says 0.75 per cent. This discrepancy is probably due to the fact that it is difficult to procure in the pure state, and that the purification processes involve considerable loss. Quassiin crystallizes in needles or prisms, and is soluble in alcohol and in chloroform and in 1,200 parts of cold water. Its bitterness is most intense. The α-picrasmin ($C_{35}H_{46}O_{10}$) melts at 204° C. The β-picrasmin ($C_{36}H_{48}O_{10}$) at 209° to 212° C. (408.2°–413.6° F.). The bitter principle of Surinam quassia is closely related and of similar action, but not identical.[1] To it the name *quassin* is commonly applied.

[1] Hare, H. A., Caspari, C., and Rusby, H. H. National Standard Dispensatory, ed. 2, revised and enlarged, p. 1334, Philadelphia, 1909.

Quassine, the active principle of *Quassia amara*, is amorphous or crystalline. It has been isolated by Winkler. It is colorless, inodorous, opaque, and inalterable in the air, slightly soluble in water, much more soluble in water charged with salt or organic acids, and in alcohol.

Action on plants: Plants are not injured by spraying with aqueous extracts of quassia.[1]

Quassia.—Constit.: Wood: Picrasmin, $C_{35}H_{46}O_{10}$: quassin, $C_{10}H_{12}O_3$ (or, $C_{32}H_{42}O_{10}$ [?]); quassol, $C_{40}H_{70}O—H_2O$; alkaloid; resin; mucilage; pectin.—Bark: Quassin; alkaloid; resin; pectin. (*Quassia amara* contains 4 bitter principles; *Picræna excelsa* contains only 2): quassol,—[2]

"Quassiin ($C_{32}H_{42}O_{10}$) may be obtained in a fairly pure state by exhausting quassia-wood with hot water, precipitating the solution with neutral lead acetate, removing the excess of lead from the filtrate by sulphuretted hydrogen and shaking the filtered liquid with chloroform. On evaporation, the quassiin is obtained nearly colorless, and, with some difficulty, in a distinctly crystalline condition. Quassiin has an intensely and very persistent bitter taste. It is sparingly soluble in cold water, more readily in hot water, and is easily soluble in alcohol. Its best solvent is chloroform, which extracts quassiin readily from acidulated solutions.

An aqueous solution of quassiin does not reduce Fehling's solution cr an ammonio-nitrate of silver. The solid substance gives no coloration (or merely yellow) when treated with strong sulphuric acid, or with nitric acid 1–25 sp. gr.; nor is any color produced on warming. * * *

A solution of quassiin gives a white precipitate with tannin. The reaction is used by Christensen, Oliveri, and others, to isolate quassiin from its solutions, and by Enders to separate it from picrotoxin. In the author's hands the reaction has not proved satisfactory. The liquid is very difficult to filter, and the filtrate still retains an intensely bitter taste, showing that the precipitation is very incomplete. As an analytical method the reaction is useless, but it is of some value as a qualitative test. The test must be made in cold solution. Possibly a more complete precipitation of quassiin by tannic acid might be effected in an alcoholic solution.

Quassiin gives a brown coloration with ferric chloride. The reaction is best observed by moistening a quassiin residue in porcelain with a few drops of a weak alcoholic solution of ferric chloride, and applying a gentle heat. A fine mahogany-brown coloration is produced." [3]

The quassiin used in the following experiments was extracted according to directions given by Allen.[4] It was further found that when boiled in alcohol a precipitate formed. This was filtered off, the filtrate evaporated to dryness over a water bath, and the resulting dark resinous material extracted with boiling water. When extraction was complete a dark brown crusty material remained. The resulting extract was light yellow and perfectly clear. It was found to be intensely bitter.

When cool this aqueous solution was extracted with chloroform, evaporated over a water bath, and weighed and made into a percentage solution.

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[1] Bourcart, E., Insecticides, Fungicides and Weedkillers, p. 376. London, 1913.

[2] Merkes 1907 Index, ed. 3, p. 366. New York, 1907.

[3] Allen, A. H., Commercial Organic Analysis, ed. 2 revised and enlarged, v. 3, pt. 3, p. 187–188, Philadelphia, 1896.

[4] Except the solution was not acidulated before extraction with acid.

In studying the use of quassiin as a contact insecticide it became desirable to determine in what solvents and solutions this compound was soluble. Table I gives the results of the experiments which were carried out with this purpose in view.

TABLE I.—*Results of solubility tests for quassiin.*

No.	Material.	Action.
1	Chloroform	Readily soluble.
2	Ether	Not soluble.
3	Methyl alcohol	Readily soluble.
4	Ethyl alcohol	Do.
5	Hot water	Do.
6	Cold water	Sparingly soluble 1-1,200.
7	Kerosene	Not soluble.
8	Gasoline	Do.
9	Carbon tetrachlorid	Do.
10	Benzine	Do.
11	Turpentine	Possibly soluble.
	RESULTS OF TESTS WITH SOLUTIONS.	
12	Potassium hydroxid	Readily soluble, solution yellow.
13	Sodium hydroxid	Do.
14	Calcium hydroxid	Do.
15	Potassium cyanid	Do.
16	Sodium carbonate	Do.
17	Hydrocyanic acid	Do.
18	Ammonium hydrate	Do.
19	Whale-oil soap (alkaline)	Do.
20	Sodium chlorid	Apparently insoluble.
21	Hydrochloric acid	Do.
22	Sulphuric acid	Do.
23	Nitric acid	Do.
24	Acetic acid	Do.

The foregoing table represents the results of experiments which were conducted with quassiin in an attempt to determine some cheap solvent or solution, other than hot water, by which it could be extracted from the wood.

EXTRACTION OF QUASSIIN FROM SOLUTIONS.

It was found that when the solutions of potassium hydroxid, sodium hydroxid, sodium carbonate, etc., with quassiin, were acidulated with sulphuric acid, the quassiin could be readily removed in chloroform. This process would apply when testing the percentage of quassiin in such solutions.

DETERMINATION OF PURITY OF QUASSIIN USED.

Since the purity of the quassiin used in spraying experiments is an important factor in figuring proportions, an attempt was made to determine the amounts of material other than quassiin which might be present in the stock solution.

Following a suggestion in Allen, tannin was added to an aqueous solution of quassiin taken from the stock solution. A fine precipitate appeared, but unfortunately it passed through an ordinary filter paper.

It being observed that tannin is not extracted from an aqueous solution by chloroform, an attempt was made to collect the chloroform-soluble material which was not precipitated by the tannin. The solution was accordingly shaken with chloroform, and the chloroform separated in a separating funnel. When replaced in aqueous solu-

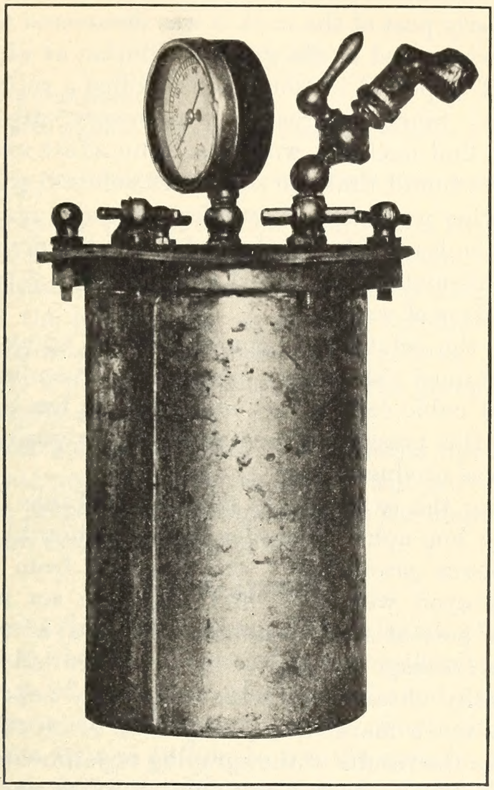

FIG. 1.—Compressed-air spray machine used in applying quassiin solution. (Original.)

tion, the extracted material was found to be intensely bitter and gave all the appearance of being quassiin. It is evident that all of the quassiin is not precipitated by tannin.

Because the material used proved effective as an insecticide at dilutions of 0.4 grams to 1,500, 1,800, and 2,000 cubic centimeters, the writer believes that it was comparatively pure quassiin.

INSECTICIDAL VALUE OF QUASSIIN.

The determination of the insecticidal value of quassiin is the main object of this investigation. In accomplishing this object an attempt is made to compare the action of quassiin to the action of a standard contact insecticide. Nicotine sulphate is taken as the standard, and in these experiments is used at the rate of 1–2,000. The nicotine sulphate used was standardized to 40 per cent and the solution of quassiin was used so that it would correspond with the 40 per cent solution of nicotine sulphate. For instance, instead of using 1 gram of quassiin to 2,000 cubic centimeters of water, 0.4 gram was used to 2,000 cubic centimeters of water.

During the early part of the work it was discovered that the whale-oil soap, even when used at the greatest dilution at which it had any spreading effect (1 pound to 100 gallons), killed a certain percentage of the aphides. Since a spreader is necessary, experiments were inaugurated to find one that would have no effect upon the insects treated. It was found that the soap bark solution which was being used in some other work was an excellent spreader and did not affect the insects in the least. In all of the following experiments a water decoction of this material was used at the rate of 2 pounds of soap bark to 100 gallons of water.

In applying the solutions, a compressed-air spray machine (fig. 1) which maintained 50 pounds pressure and handled as small an amount as 200 cubic centimeters was used. A fine mist nozzle was so adjusted to this pressure of 50 pounds that a washing rather than a mist spray was produced.

In conducting the experiments detailed in Table II prune twigs infested by the hop aphis (*Phorodon humuli* Schrank) and the prune aphis (*Hyalopterus pruni* Fab.) were brought from the field and, after being sprayed with the solutions, were set in moist sand. By placing the pots of sand containing the sprayed twigs on sheets of paper the percentage of the insects that were killed by the solutions were readily obtained. Check twigs were kept to make sure that there was not a marked mortality from some other cause.

Table II gives the results of the spraying experiments with quassiin in aqueous solution and also in solutions of certain alkaline substances.

TABLE II.—*Results of experiments with quassiin as a contact insecticide.*

SERIES NO. 1. WITH SOAP BARK IN LABORATORY.

Formula.	Number of aphides sprayed.	Per cent of aphides killed.
0.4 grams to 3,000 cc	904	85.1
0.4 grams to 2,000 cc	8,060	93.02
0.4 grams to 1,800 cc	1,119	94.6
0.4 grams to 1,500 cc	1,310	93.9
0.4 grams to 1,000 cc	1,831	99.7

SERIES NO. 2. WITH WHALE-OIL SOAP IN FIELD.

Formula.	Number of aphides sprayed.	Per cent of aphides killed.
0.4 grams to 2,000 cc	1,776	99.4
0.4 grams to 1,800 cc	3,197	99.8
0.4 grams to 1,500 cc	3,546	99.8

TABLE II.—*Results of experiments with quassiin as a contact insecticide*—Continued.

SERIES NO. 3. WITH SOAP BARK ON PRUNE APHIS IN FIELD.

Formula.	Number of aphides sprayed.	Per cent of aphides killed.
0.4 grams to 2,000 cc	1,923	97.5
0.4 grams to 1,800 cc	721	99.2
CHECK SERIES.		
Whale-oil soap, 3 pounds to 100 gallons	1,030	[1 2] 84.6
Soap bark, 2 pounds to 100 gallons	1,202	[1] 21
Nicotine sulphate, 0.4 grams to 2,000 cc., with soap bark, 2 pounds to 100 gallons	930	96.9

[1] These were the largest percentages obtained for the check materials.
[2] In field.

From the foregoing table it will be readily seen that quassiin used at the rate of 0.4 grams to 2,000 cubic centimeters, or 6½ ounces of 40 per cent solution to 100 gallons, was almost as effective against the hop aphis and the prune aphis as nicotine sulphate, 0.4 grams to 2,000 cubic centimeters, or 6½ ounces to 100 gallons. The difference is approximately 3 per cent, while quassiin, 0.4 grams to 1,000 cubic centimeters, is fully as effective.

The writer has not so far tested this material upon insects other than those mentioned, but believes that it will prove effective elsewhere if used in proportions corresponding to the amounts of nicotine sulphate that are known to be effective.

CONCLUSION.

Picrasma excelsa Swz. (quassia wood) is a native of Jamaica, and, according to data obtained, is available in considerable quantities.

The percentage of quassiin in the quassia wood varies somewhat, and does not appear to be definitely known. Supposing it to be 0.75 per cent, as given by one author, to use the quassiin at an effective rate of 0.4 grams to 2,000 cubic centimeters, it would take only 1½ pounds of the chips to 100 gallons of spray. To be on the safe side, double the amount of chips calculated to be necessary, and we have the following formula [1] and cost per 100 gallons of spray:

Quassia chips, 0.75 per cent quassiin, 3 pounds, at $0.04	$0.12
Whale-oil soap, 3 pounds, at $0.04	.12
Total cost of materials per 100 gallons	.24

Quassiin can be readily extracted from quassia wood, *Picrasma excelsa* Swz., in a comparatively pure form. (See p. 3.) It probably could be more cheaply extracted in an impure water-soluble form by using sodium carbonate solution. The percentage of quassiin could be determined and the material evaporated until a standardized solution was made. Such a material could be diluted and used with

[1] This formula corresponds very closely to formula No. 1, page 2.

whale-oil soap, or some other spreader, as in the case of nicotine sulphate. The writer believes that quassiin has possibilities as a commercial insecticide and that it could be cheaply prepared and possibly sold at a lower price than some of the materials that are now on the market.

The foregoing data were obtained under conditions existing at Sacramento, Cal., and may not hold for a more humid climate. The efficiency of the quassiin should be determined for some other locality before a commercial recommendation is made.

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