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## RELATION BETWEEN THE PHYSICAL PROPERTIES AND CHEMICAL COMPONENTS OF VARIOUS GRADES OF GERANIOL AND THEIR ATTRACTIVENESS TO THE JAPANESE BEETLE

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## INTRODUCTION

Geraniol, one of the higher alcohols ( $C_{10}H_{17}OH$ ), was first reported to be attractive to the Japanese beetle (*Popillia japonica* Newm.) by Richmond (8)<sup>1</sup>, who with Metzger (9) used this material in a bait trap designed to capture this insect. Subsequently Van Leeuwen (10) and Metzger (4, 5, 6) improved the bait and the trap, and at the present time at least 100,000 such devices are in use by governmental and private agencies. The baiting of these traps involves the consumption of several thousand pounds of geraniol annually.

This substance is used chiefly as a perfume for soap and in various perfumery formulas, and it is purchased according to standards established by consumers who use it for this purpose. Its use as an insect attractant, therefore, afforded a new outlet for the material.

The geraniol first employed in Japanese beetle traps was found to vary considerably in quality according to its source, and it was evident that the terms "pure", "absolute", "extra", etc., did not define the purity of the material obtained from more than one producer. There are no c. p. or U. S. P. standards for geraniol. In

<sup>1</sup> Italic numbers in parentheses refer to Literature Cited, p. 14.

order to obtain a satisfactory material, therefore, the following specifications were prepared:

Specific gravity at 20° C.....	0. 879-0. 882.
Solubility in 60-percent ethyl alcohol.....	1 part in 4 parts of the alcohol.
Optical rotation, 10 mm.....	±0°30'
Aldehydes.....	Absent.
Total alcohols as geraniol.....	87 percent or more.

These specifications described a geraniol of good quality and a material known to attract the Japanese beetle. It was, moreover, readily available commercially.

No difficulty was experienced in purchasing geraniol on this basis until 1933, when the quantity required by governmental agencies became so large as to induce considerable competition among manufacturers. At this time several lots were offered at a price much below any previous quotation, but they failed to meet the specifications in one or more respects. Although these called for a highly refined grade of geraniol, there was no information available to indicate that such material was more attractive to the beetles than a material of a lower grade. Consequently, a study was undertaken to determine the relative attractiveness of different grades of geraniol to Japanese beetles.

#### TESTS CONDUCTED IN 1933

The first tests were conducted in 1933 with 10 lots of geraniol purchased from various manufacturers and ranging from the best grade of each producer to the poorest. These tests included a determination, in the laboratory, of the physical properties of each lot and a comparison, in the field, of its attractiveness to the beetle with that of the check geraniol meeting the specifications heretofore mentioned.

#### PROCEDURE

The specific gravity was determined by means of a Westphal balance. The boiling range was obtained by distillation in a Ladenburg flask, and the figures were corrected to an atmospheric pressure of 760 mm. The quantitative test for aldehydes was made by the fuchsin method. In 1933 a complete analysis of each lot was not made, because at that time it was not realized that this would be necessary.

Field tests of attractiveness to the Japanese beetle were conducted according to a procedure developed by the senior author (3, 6), by placing a trap baited with the material to be tested at a distance of 2½ feet from a trap of the same type containing the check material as bait (fig. 1). Data obtained over a period of several years indicate that, when two similar traps baited with the same material are placed in such a manner, each captures approximately the same number of beetles. When different baits are used, therefore, any appreciable variation in the number of insects taken is due to the difference in the attractiveness of the baits. Five pairs of traps were used in each test with a distance of 10 feet between pairs. The materials being tested were vaporized by means of a wick from a bottle inserted in the bait container of the trap (4).

The difference between the number of beetles captured in the trap containing the experimental bait and in the check trap was computed in terms of a percentage for each collection. The mean percentage

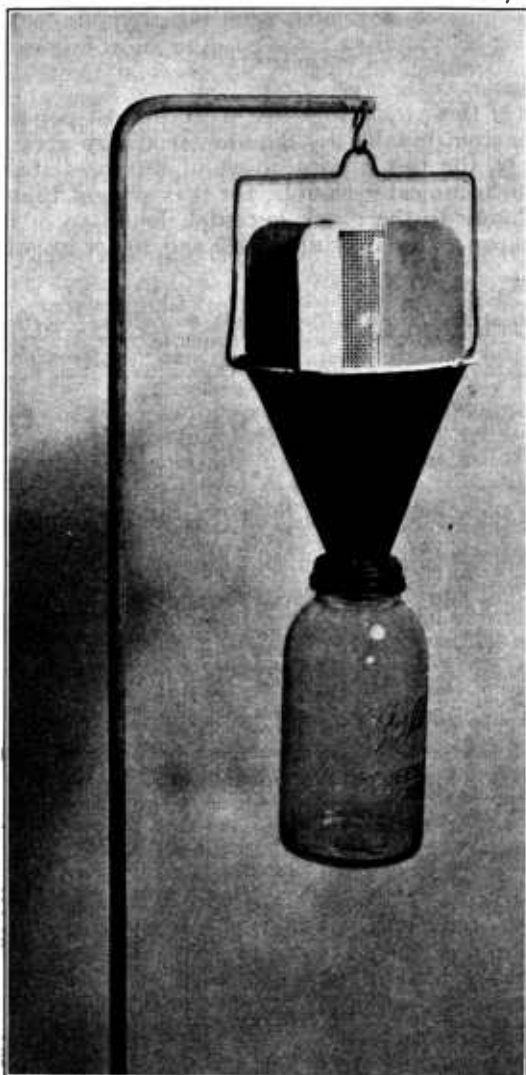


FIGURE 1.—Trap employed in testing the attractiveness of various lots of geraniol to the Japanese beetle.

difference was then determined and the standard deviation obtained by the following formula (2, p. 174):

$$S. D. = \sqrt{\frac{\text{sum of } d^2}{N}}$$

where  $d$  represents the deviations from the mean and  $N$  is the number of collections. The probable error of the mean was determined by the following formula (2, p. 174):

$$P. E. \text{ of mean} = 0.6745 \times \frac{S. D.}{\sqrt{N}}$$

## RESULTS

The results of these tests, together with the cost per pound of each lot, are summarized in table 1. The materials are arranged in three groups, namely, the best grades, those of intermediate quality, and the cheapest or technical geraniols, for it is evident that lots 1 and 2 correspond closely to the check geraniol, lots 3 to 8, inclusive, are obviously cheaper material, while lots 9 and 10 are greatly inferior in quality.

TABLE 1.—Physical properties, attractiveness to Japanese beetles, and cost of the lots of geraniol tested in 1933

Grade and lot no.	Optical rotation at 20° C. <sup>1</sup>	Solubility in 60-per-cent ethyl alcohol	Specific gravity at 20°/15° C.	Aldehydes	Total alcohols as geraniol	Odor
Check.....	+0° 42'	Parts 1 in 2.5	0.879	Absent.....	Percent 89.7	Characteristic of best grades.
Best:						
1.....	0° 0'	1 in 2.5	.874	...do....	88.0	Do.
2.....	+0° 22'	1 in 2.7	.876	...do....	87.8	Do.
Intermediate:						
3.....	+0° 30'	1 in 3.5	.888	Present.....	82.7	Do.
4.....	-0° 22'	1 in 5.5	.873	...do....	82.3	Strong citronellal tone.
5.....	+0° 57'	1 in 2.8	.884	Absent.....	85.0	Strong geranyl acetate tone.
6.....	0° 0'	1 in 3.1	.876	Present.....	81.2	Characteristic of best grades.
7.....	+2° 7'	1 in 2.9	.878	Absent.....	84.6	Weak.
8.....	+2° 5'	1 in 2.5	.878	...do....	84.3	Characteristic of best grades.
Technical:						
9.....	-1° 43'	1 in 7.5	.898	Present.....	70.35	Strong citronellal tone.
10.....	0° 0'	(?)	.899	...do....	75.03	Do.

Grade and lot no.	Boiling range					Mean increase in attractiveness over check	Cost per pound
	Under 225° C.	225.1°-230° C.	230.1°-235° C.	235.1°-245° C.	Over 245° C.		
	Percent	Percent	Percent	Percent	Percent		
Check.....	0	58	35	7	0	Percent	Dollars
Best:							
1.....	3	86	9	2	0	2.9 ± 2.76	1.70
2.....	0	60	35	2	3	10.5 ± 4.1	2.00
Intermediate:							
3.....	27	61	9	3	0	8.3 ± 2.49	1.13
4.....	21	47	27	5	0	20.0 ± 2.74	1.13
5.....	0	9	72	14	5	24.87 ± 2.91	1.30
6.....	0	69	27	7	0	6.1 ± 2.9	1.40
7.....	2	30	63	3	2	22.0 ± 3.11	1.80
8.....	0	40	52	5	3	7.0 ± 3.51	1.00
Technical:							
9.....	37	13	3	9	38	45.0 ± 4.06	.93
10.....	0	0	45	20	35	45.0 ± 5.9	1.25

<sup>1</sup> Determined with sodium light and a tube length of 100 mm, and checked with white light through various liquid filters.

<sup>2</sup> Insoluble 1 in 10.0.

## BEST GRADES OF GERANIOL

Commercial geraniol is essentially a mixture of geraniol and citronellol. As citronellol may have an optical rotation ranging from  $-1^{\circ}40'$  to about  $+4^{\circ}$ , depending on its source, the best grades of commercial geraniol usually have an optical rotation of from  $+45'$  to  $-45'$ . Geraniol in its purest form has an optical rotation of  $0^{\circ}0'$ . Such material is not, however, an article of commerce and, while commercial geraniol may sometimes have an optical rotation of  $0^{\circ}0'$ , as in the case of lot 1, manufacturers will not agree to furnish commercial material that meets this specification. The check and lots 1 and 2 have optical rotations that are within the limit established for the best grades.

The specific gravities of these three lots at  $20^{\circ}$  C. are in the narrow range of 0.005, both the test materials being slightly below the check in this respect.

The three lots are soluble in small proportions of 60-percent ethyl alcohol, indicating the absence of appreciable quantities of citronellal and geranyl acetate, which are insoluble in alcohol of that concentration.

The total alcohol as geraniol is high. The importance of this specification has been overemphasized, however, as the term "total alcohols as geraniol" sometimes includes citronellal, if the aldehyde is present, because this material is converted quantitatively into isopulegol acetate along with geraniol and citronellol in the process of total-alcohol determination (1). Since no aldehyde is present in these lots, this factor is of no importance. Some manufacturers state this factor as "alcohol in the original oil", which includes ester geraniol in the saponification number and gives the impression of a very high alcohol content. Where the presence of esters is suspected, it is necessary to make a separate test for them after removing any aldehydes that may be present.

The odor of geraniol of good quality is characteristic and can easily be recognized by one familiar with it. The check and lots 1 and 2 appear to be free from any impurities that can be detected by their odor.

Examination of the boiling ranges of these samples shows that practically no material boiled below  $225^{\circ}$  C. or above  $245^{\circ}$ , while the greater portion of each lot distilled over between  $225^{\circ}$  and  $235^{\circ}$ , the accepted range for geraniol of good quality. Excessive quantities of citronellol and citronellal tend to lower the range appreciably, while geranyl acetate and sesquiterpenes have the opposite effect.

In attractiveness to Japanese beetles samples 1 and 2 show no significant difference from the check, since the probable error of the mean is so high as to show the fallacy of the slight apparent increase given in the table.

The range in price indicates the wide variation encountered in purchasing material of this nature.

## GERANIOL OF INTERMEDIATE QUALITY

The variation in the optical rotation from  $-0^{\circ}22'$  (lot 4) to  $+2^{\circ}7'$  (lot 7) shows that this specification is of little value in materials of this grade.

In specific gravity there is also a much wider variation than in the first group, there being a difference of 0.015 between lot 4 and lot 3. When attractiveness to the beetles is considered, however, the variation from the standard specification of 0.879-0.882 does not appear to be significant.

There is also a wide range in the solubility of these materials in 60-percent alcohol, from 1 part in 2.5 parts of alcohol, corresponding in this respect to two materials in the first group, to 1 part in 5.5 parts of alcohol. The attractiveness of this group to the beetles indicates that a wider range in solubility than is given in the specifications could be tolerated.

The qualitative test for aldehydes revealed their presence in lots 3, 4, and 6. The odor of lot 4 indicates that it contains an appreciable quantity of citronellal.

In all cases total alcohols as geraniol are lower by several percent than in the check and lots 1 and 2. As the odor of the latter is characterized by a strong geranyl acetate "tone", no doubt a test for the ester would reveal the fact that the alcohol figure is increased by the presence of ester in the original oil. The materials comprising this group have no general characteristic odor.

In lot 5 the presence of geranyl acetate is again indicated by the larger percentage boiling between 235° and 245°. None of the materials appears to contain an appreciable quantity of sesquiterpenes, etc., as evidenced by the small percentages boiling above 245°.

In attractiveness to beetles lots 3, 6, and 8 show no significant increase over the check, while lots 4, 5, and 7 give increases of more than 20 percent. Since no detailed analysis was made, the cause of this increase cannot be determined.

None of the materials in this group is inferior to the check in attractiveness, and it appears that any of them could be substituted for the check or the materials of the first group without the loss of effectiveness.

#### TECHNICAL GRADES OF GERANIOL

Lots 9 and 10 are obviously inferior to the others. This fact is not shown in the optical rotation, since that of lot 10 is 0°0', a figure not generally found in the better grades. The specific gravity, however, is higher than that of any of the other materials, an indication of the presence of impurities.

Lot 10 was found to be insoluble in 10 parts of 60-percent ethyl alcohol, while lot 9 is soluble in the ratio of 1 part to 7.5 parts of the alcohol. This test is important, since the solubility is much less than in the best or intermediate grades.

The qualitative test showed aldehydes to be present. The odor of both samples also indicates the presence of citronellal in an appreciable quantity. Total alcohols as geraniol are comparatively low in this group.

These two materials have a wide difference in distillation range, with 37 percent of lot 9 boiling below 225° C., and none of lot 10. The percentage of each distilling between 225° and 235° is comparatively small, but a large percentage boils above 245°, showing that the sesquiterpene content is high. The difference in distillation

range and cost illustrates the fluctuation that may be expected when material is not purchased on definite specifications.

Both these lots are considerably more attractive to the beetle than is the check geraniol.

#### TESTS CONDUCTED IN 1934

From the foregoing tests it is evident that the limits of the properties of the various lots are so far apart that almost any product sold as geraniol would conform to specifications drawn from the data. Although lots 9 and 10 appeared to be satisfactory for use as an attractant, it seemed possible that all geraniol coming within the wide limits of these two lots might not be so attractive as the two samples tested. The work was continued the following year in an attempt to develop more definite specifications for a cheap grade of geraniol.

The tests in 1934 were made on 11 lots of technical or soap geraniol purchased from as many manufacturers. The physical properties of each lot were determined as in 1933, and each was analyzed for its geraniol, citronellol, citronellal, and ester content.

#### PROCEDURE

The methods of analysis for geraniol are still unsatisfactory in several respects, and there is a difference of opinion regarding the most accurate procedure. The methods used by the writers were adopted after consultation of the literature and with several leading manufacturers of geraniol. The procedures are based upon those given by Gildemeister and Hoffman (*1, v. 1, pp. 575-589*) and Parry (*7, v. 1, p. 174*).

Each lot was tested in the field for attractiveness to the Japanese beetle by the procedure followed in 1933, except that in all cases, including the check, eugenol was added at the rate of 1 part to 10 parts of the geraniol.

#### RESULTS

The results of both the laboratory and the field tests are summarized in table 2.

TABLE 2.—*Physical properties, attractiveness to Japanese beetles, and cost of lots of geraniol tested in 1934*

Grade and lot no.	Solubility in ethyl alcohol <sup>1</sup>		Specific gravity at 20°/15° C.	Color	Odor
	60 percent	70 percent			
Check .....	<i>Parts</i> 1 in 3.5.....	<i>Parts</i> 1 in 1.5.....	0.8784	Colorless.....	Characteristic of best grades.
Similar to check:					
11.....	1 in 3.3.....	1 in 1.6.....	.8798	do.....	Do.
12.....	1 in 3.5.....	1 in 1.6.....	.8823	do.....	Do.
13.....	1 in 4.6.....	1 in 1.6.....	.8811	do.....	Do.
14.....	1 in 3.0.....	1 in 1.5.....	.8770	do.....	Do.
Slightly inferior in quality, superior in attractiveness:					
15.....	1 in 4.2.....	1 in 1.6.....	.8881	Very light yellow.	Do.
16.....	1 in 5.0.....	1 in 1.6.....	.8777	do.....	Do.

<sup>1</sup> Solubility in both 60- and 70-percent alcohol is given, because none of the cheaper grades of geraniol was soluble in small quantities of 60-percent alcohol.

TABLE 2.—Physical properties, attractiveness to Japanese beetles, and cost of lots of geraniol tested in 1934—Continued

Grade and lot no.	Solubility in ethyl alcohol		Specific gravity at 20°/15° C.	Color	Odor
	60 percent	70 percent			
Much inferior in quality, superior in attractiveness: 17-----	Parts (3)	1 in 2.0	0.8922	Amber-----	Strong citronellal tone, underlying tone of unknown character. Strong citronellal tone, odor of organic acid prominent.
18-----	(3)	1 in 1.75	.8854	Light yellow-----	
Much inferior in quality, equal in attractiveness: 19-----	(3)	1 in 2.0	.8904	Yellow-----	Strong geranyl acetate tone. Strong citronellal tone. No outstanding character.
20-----	(3)	1 in 2.0	.8859	do-----	
21-----	(3)	1 in 2.3	.8970	Amber-----	

Grade and lot no.	Boiling range					Analyses					Mean increase in attractiveness over check <sup>1</sup>	Cost per pound
	Under 225° C.	225.1 to 230° C.	230.1 to 235° C.	235.1 to 245° C.	Over 245° C.	Citronellol	Geraniol	Total free alcohols	Citronellal	Esters		
	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent		
Check-----	0.0	87.0	2.0	6.0	5.0	29.70	57.42	87.12	0.0	0.35	-----	Dollars
Similar to check:											Percent	
11-----	.0	60.0	25.5	9.5	5.0	35.35	48.96	84.31	1.15	1.26	6.67±2.21	1.40
12-----	.0	50.0	31.0	10.0	9.0	31.26	52.39	83.65	1.16	1.21	2.67±1.74	1.50
13-----	.0	40.0	50.0	5.0	5.0	34.30	48.25	82.55	.0	1.23	1.03±2.01	3.00
14-----	.0	.0	92.0	5.0	3.0	34.95	51.20	86.15	.83	.86	3.28±1.99	1.85
Slightly inferior in quality, superior in attractiveness: 15-----	.0	.0	70.0	18.0	12.0	28.85	40.77	69.62	.87	11.51	15.54±1.85	.99
16-----	.0	65.0	16.0	9.0	10.0	37.31	36.50	73.81	2.77	8.64	10.59±2.23	1.09
Much inferior in quality, superior in attractiveness: 17-----	6.0	39.0	25.0	13.5	16.5	23.55	44.97	68.52	3.55	8.34	24.99±2.07	.93
18-----	.0	5.0	60.0	15.0	20.0	30.85	44.60	75.45	3.49	2.36	10.03±1.93	1.25
Much inferior in quality, equal in attractiveness: 19-----	.0	15.0	47.0	25.5	12.5	34.15	27.80	61.95	2.46	20.31	6.17±2.04	1.25
20-----	13.0	51.0	26.0	5.0	5.0	31.05	28.82	59.87	9.87	20.21	1.21±1.98	.95
21-----	.0	6.5	37.5	31.5	24.5	29.10	24.12	53.22	6.23	15.25	.17±1.94	1.25

<sup>1</sup> For these tests 1 part of eugenol was added to 10 parts of the geraniol.<sup>2</sup> Insoluble 1 part in 10.0.

A preliminary examination of the data reveals that the various lots of geraniol, although purchased as a cheap material, differ appreciably in many respects and can be placed in the following groups: (1) Lots corresponding closely to the check in attractiveness to the beetle, in analysis, and in physical properties; (2) lots slightly inferior to the check in quality, but superior in attractiveness; (3) lots much inferior to the check in quality but superior in attractiveness; and (4) lots much inferior to the check in quality and equal to it in attractiveness. Each of these groups will be discussed separately



and the reasons pointed out for the relationship which exists between attractive value and the various other factors under consideration.

LOTS CORRESPONDING CLOSELY TO THE CHECK IN ATTRACTIVENESS, IN ANALYSIS,  
AND IN PHYSICAL PROPERTIES

This group includes four materials, lots 11, 12, 13, and 14. Although all were purchased as soap or technical geraniol, it is evident that they approach the better grades of geraniol in quality.

In attractiveness to the beetle there is no significant difference from the check in any case. The results correspond closely to those obtained with lots 1 and 2 in 1933.

These data indicate that several purveyors of geraniol apparently have only a vague conception of the exact composition of their materials.

LOTS SLIGHTLY INFERIOR TO THE CHECK IN QUALITY BUT SUPERIOR IN  
ATTRACTIVENESS

This group includes lots 15 and 16. Both are less soluble in 60-percent ethyl alcohol than most of the materials in the first group. The odor is characteristic of a good grade, with less of the roseline "tone", however, which is pronounced in the best material.

Lot 15 is characterized by a very high boiling range, as none of the substance distilled under  $230.1^{\circ}$  C. while 70 percent came over under  $235^{\circ}$ . On the other hand, 65 percent of lot 16 distilled between  $225.1^{\circ}$  and  $230^{\circ}$ .

Free alcohols as geraniol and citronellol are lower than in the first group. Lot 15 contains a very small quantity of citronellal, while lot 16 contains 2.77 percent. There is an appreciable quantity of ester in both lots.

In attractiveness to the Japanese beetle there is an appreciable increase over the check in both lots.

These two materials have a total alcohol content below that of the lots in the first group, but above that of the materials in the subsequent groups. The relatively high percentage of esters seems to be the factor which causes the increased attractiveness over the check.

LOTS MUCH INFERIOR TO THE CHECK IN QUALITY BUT SUPERIOR IN ATTRACTIVENESS

Lots 17 and 18 are included in this group. The specific gravity of both materials is higher than that of the check and of all the lots included in the first group. Both are insoluble in 60-percent alcohol, a definite indication of geraniol of inferior quality. The odor of each is characterized by a strong citronellal "tone", and that of lot 17 by an underlying "tone" of an unknown character. Lot 18 has an underlying odor of an organic acid, possibly valeric.

The low quality of these materials is further indicated by the wide boiling range. Only 64 percent of lot 17 and 65 percent of lot 18 boiled between  $225.1^{\circ}$  and  $235^{\circ}$  C., and 30 percent of lot 17 and 35 percent of lot 18 boiled above  $235^{\circ}$ .

There is a difference of nearly 7 percent in the total free alcohol content of these materials. In lot 18 it is higher than in either of the

materials in the second group. This lot cannot be classed with lots 15 and 16, however, because of its insolubility in 10 parts of 60-percent ethyl alcohol, its color, odor, and high-boiling fractions. Lots 17 and 18 contain citronellal in approximately the same quantities. The ester content of lot 17 is comparable with that of the materials in the second group, while that of lot 18 is low.

Lot 17 proved to be considerably more attractive than the check, showing the largest increase of any of the materials tested in 1934. Lot 18 gave a much smaller increase.

It is evident that the two lots in this group are as unlike in several respects as they are similar in others. The significant point, however, is that both are cheap grades of geraniol which proved to be more attractive than the check. In respect to lot 18, it is believed that the organic acid, which was detected from the odor and also by fractional distillation, may be a significant factor. No obvious reason can be given for the presence of such a material in geraniol.

#### LOTS MUCH INFERIOR TO THE CHECK IN QUALITY BUT EQUAL TO IT IN ATTRACTIVENESS

The specific gravities of all three materials in this group (lots 19, 20, and 21) are considerably higher than that of the check geraniol. All are insoluble in 10 parts of 60-percent ethyl alcohol. The odor of these materials varies considerably. The high ester content of lot 19 is reflected in the large percentage boiling between 235.1° and 245° C. The large quantity of citronellal in lot 20 is indicated by the fact that 13 percent boils below 225°. Lot 21 has a high boiling range, 56 percent coming over above 235°.

Analyses show that the total free alcohols as geraniol and citronellol are considerably lower than in any of the materials discussed previously. There are appreciable quantities of citronellal in all three lots. The ester content of all three is much greater than that of the materials in the other groups.

In attractiveness to the beetles none of these materials showed any significant increase or decrease over the check.

The data of these materials show that a geraniol containing high percentages of ester and aldehyde and a comparatively low percentage of free alcohol is less attractive to the beetle than a geraniol containing a higher percentage of free alcohol with a large quantity of ester. The data also indicate that the materials in this group are fully as attractive as the best grades included in the first group. To obtain the best results in the field, however, it is believed advisable to limit the ester, aldehyde, total alcohols, etc., to approximately the range of the materials in the second and third groups, since there is no appreciable difference in cost between these lots and those in the last group.

#### PHYSICAL PROPERTIES AND ATTRACTIVENESS OF SOME OF THE COMPONENTS OF GERANIOL

To correlate the analyses of the various lots of geraniol with their attractiveness to the beetle, it was necessary to obtain information regarding the attractiveness of several of the components of geraniol. The substances considered were as follows: Citronellol, citronellal,

geranyl acetate, and geraniol sesquiterpenes. These data are given in table 3.

TABLE 3.—Physical properties, attractiveness to the Japanese beetle as compared with the check geraniol, and cost of several components of geraniol with and without the addition of eugenol

Material	Specific gravity at 20° C.	Solubility in 60-percent ethyl alcohol	Boiling range	Mean decrease in attractiveness below that of check geraniol <sup>1</sup>		Cost per pound
				Without eugenol	With 1 part of eugenol to 10 parts of material	
		Parts	° C.	Percent	Percent	Dollars
Citronellol.....	0.8619	1 in 4	225-226	46.3±1.33	10.4±2.10	2.20
Citronellal.....	.8671	(?)	205-208	68.8±1.89	54.7±1.89	.80
Geranyl acetate.....	.9091	(?)	242-245	57.4±1.74	17.9±2.02	2.30
Geraniol sesquiterpenes.....	.8673	(?)	-----	39.5±2.63	31.4±4.27	.45

<sup>1</sup> The check geraniol was that described in table 2, and in these tests contained 1 part of eugenol to 10 parts of geraniol.

<sup>2</sup> Insoluble.

It is evident that citronellal and geraniol sesquiterpenes are much cheaper than even the most inexpensive grades of geraniol and can, consequently, be employed as adulterants to greater advantage than can citronellol or geranyl acetate, although the ester is probably present in an impure state in geraniol whereas the price quoted is for the best-quality ester.

Appreciable quantities of the ester would tend to raise the specific gravity. The sesquiterpenes may have the same effect, as they are extremely variable in composition even though the lot examined has a low specific gravity.

Citronellol is the only substance tested that is soluble in 60-percent ethyl alcohol. It is obvious, therefore, that any lot of geraniol containing an appreciable quantity of any of the other materials would not be soluble in alcohol of that strength.

Citronellol and citronellal boil below the boiling range of geraniol and therefore tend to lower its boiling range when they are present in excessive quantities. Geranyl acetate boils above the range for geraniol, as do the sesquiterpenes, and both would therefore raise the boiling range of geraniol.

The attractiveness of these materials was compared with that of the check geraniol and eugenol mixture, the geraniol being the material described under the check in table 2. The data given in table 3 show that both with and without eugenol none of the components was so attractive as the check. The addition of eugenol increased the attractiveness of all these materials, but this increase was considerable (about 30 and 40 percent, respectively) only in the case of citronellol and geranyl acetate.

These results shed further light on the data obtained in 1933, which showed certain technical grades of geraniol to be much more attractive than the purer grades when tested alone, but of approximately equal attractiveness when eugenol was added to both. They indicate that citronellol and geranyl acetate are the principal attractants among the components of geraniol, and that citronellal and terpenes are of negligible importance. It is impossible to obtain

cheap grades of geraniol free from aldehyde and terpenes, but it is believed that their presence in geraniol in restricted quantities does not lower its attractive power. Geranyl acetate appears to increase the attractiveness of geraniol when present in appreciable quantities, although the ester itself is less attractive than geraniol. This may be due to the fact that the ester and geraniol form a blend that is more attractive than the geraniol it has displaced. The citronellol content is not believed to be of appreciable importance, since this material is usually found in quantities somewhat proportional to the geraniol present.

#### REVISED SPECIFICATIONS FOR GERANIOL

As a result of the tests and analyses discussed in this bulletin, it appears possible to propose specifications for a grade of geraniol which will be more attractive to the Japanese beetle than the material formerly employed and which can be obtained at a lower cost. These specifications are as follows:

Specific gravity at 20° C.....	0.875-0.895.
Solubility in 70-percent ethyl alcohol.....	1 part in not more than 2 parts of alcohol.
Aldehydes as citronellal.....	Not more than 3.5 percent.
Esters as geranyl acetate.....	Not more than 15 percent.
Total free alcohols as citronellol and geraniol....	More than 70 percent.
Odor.....	Absence of any significant indication of added materials.
Boiling range.....	Not more than 5 percent boiling under 225° C. or more than 18 percent boil-over 245° (760 mm pressure).

These specifications have been sent to several manufacturers of geraniol, who quoted on a commercial grade meeting the standards at an average of approximately \$0.60 per pound as of April 1, 1935, which is \$0.90 per pound less than the price formerly paid.

#### SUMMARY

The specifications that have been used in purchasing geraniol for Japanese beetle traps call for a material of good quality with a minimum of impurities.

Tests conducted during 1933 and 1934 on a total of 21 lots of geraniol indicate that a material of high quality is not essential for maximum attractiveness to the beetle.

The cheap grades of geraniol, known as "technical or soap geraniol", vary widely in composition, and none of these grades is entirely satisfactory for use in attracting the beetles.

A certain percentage of esters in geraniol increases the attractiveness over a sample that is free from esters.

Aldehydes and sesquiterpenes in limited quantities do not inhibit attractiveness.

None of the components of geraniol that were tested is so attractive as the recommended mixture of geraniol and eugenol. When used with eugenol, citronellol and geranyl acetate are more attractive

than when used alone. The addition of eugenol has very little influence on the attractiveness of citronellal and geraniol terpenes.

The investigation has made it possible to devise specifications for a cheap grade of geraniol which can be met by all manufacturers of this material. Geraniol meeting these specifications can be obtained for about \$0.60 per pound, and it is more attractive to the Japanese beetle than the more expensive grades, which cost in quantity approximately \$1.50 per pound.

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