Chemistry. — "*On the estimation of the geraniol content of citronella oil*". By Dr. A. W. K. DE JONG. (Communicated by Prof. VAN ROMBURGH).

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The chemists of the firm of SCHIMMEL & Co. have a method for the estimation of geraniol in citronella oil which in the "Bericht" of this firm of October 1899, 20 and also in that of October 1912, 39, is described as follows: "Etwa 2 g Phthalsäureanhydrid und 2 g des zu untersuchenden Oels werden mit 2 ccm Benzol zwei Stunden in einem Kolben, wie er zu Acetylierungen benutzt wird, auf dem Wasserbad erwärmt, dann erkalten gelassen und mit 60 ccm wassriger Halbnormal-Kalilauge 10 Minuten geschüttelt. Der Kolben ist hierbei mit einem eingeschliffenen Glasstopfen verschlossen. Nach dieser Zeit ist alles Anhydrid in neutrales phthalsaures Kali und der saure Geraniolester in sein Kalisalz ubergeführt worden. Nun wird das überschussige Alkali mit Halbnormal-Schwefelsaure zurucktitriert. Zieht man dann von der Menge Alkali, die der eingewogenen Phthalsäure entspricht, die fur den Versuch verbrauchte Menge ab, so erfahrt man, wieviel Alkali dem an Phthalsaure gegangenen Geraniol aquivalent ist, woraus der Prozentgehalt an Geraniol zu berechnen ist".

This method is at the outset subject to suspicion, since it is based on the assumption that geraniol is quantitatively esterified by phthalic anhydride, whereas this is not even the case with acetic anhydride (98.5 p.c. was found to be esterified).

For the following experiments a very pure phthalic anhydride was prepared; 1 grm. was neutralised by 135 c.c. $^1/_{10}$ n KOH, whereas 135.1 c.c. was calculated for the pure substance.

The citronellal used was isolated from citronella oil by means of the bisulphite compound. The sp. gr. at 26° was 0.8526; $[\alpha]_D = +10°21'$. It was faintly acidic; 1 grm. was neutralized by 0.2. c.c. $^1/_{10}$ n KOH.

The geraniol was isolated from Palmarosa oil by means of the calcium chloride method. The sp. gr. at 26° was 0.8752.

To the mixture of anhydride, citronellal or geraniol 4 c.c. of benzene was added. After heating, the flask was cooled rapidly, so

that the crystals which separated remained small and dissolved readily in $\frac{1}{2}$ n KOH. The phenolphtalein was added as powder.

Duration of heating: 2 hours.

Temperature of the water bath in degrees C.	Quantity of phthalic anhydride used	Quantity of citronellal used	cc. N/10 KOH		Difference
			found	calculated	
85	1.2600 grm.	0.4450 grm.	169.9	170.1	0.2
85	0.9480 „	0.5120 „	127.6	127.95	0.35

At this temperature citronellal is not attacked by the anhydride, or scarcely so.

Temperature of the water bath in degrees C.	Duration of heating	Quantity of phthalic anhydride grm.	Quantity of geraniol used grm	Quantity of geraniol found	
				grm.	%
99	2 hours	2.1740	0.4645	0.4158	89.5
88	2 „	2.1810	0.4960	0.4575	92.2
84	2 „	2.1300	0.4860	0.4481	92.2
77	2 „	2.1160	0.4950	0.4527	91.5
88	2 „	1.0550	0.4490	0.4073	90.7
82	3 „	1 6930	0.4515	0.4173	91.4

This showed clearly that the esterification of the geraniol had not been complete. The mixture does not boil, however, and I thought that this might possibly be the cause of the shortage. Hence a few further estimations were made in which the heating was done with a small flame.

Duration of heating: 2 hours.

Quantity of phthalic anhydride used in grm.	Quantity of geraniol used in grm.	Quantity of geraniol found	
		grm.	%
2.0540	0.8890	0.8193	92.2
2.0495	0.4970	0.4497	90.5

Nor did an increase in the benzene from 4 c.c. to 8 c.c. change the result. Found: 90.6 %.

With this way of heating the citronellal is also attacked more extensively.

Quantity of phthalic anhydride used in grm.	Quantity of citronellal used in grm.	Number of c.c N/10 KOH		
		found	calculated	difference
0.9490	0.5950	126.5	128.1	1.6
1.2850	0.5050	171.15	173.45	2.3

Evidently the scientific investigators of the firm of SCHIMMEL & Co only worked with mixtures of geraniol, citronellal and limonene. As the following estimations show, results are obtained with mixtures of geraniol and citronellal which differ but little from the true values.

Temperature of the water bath in degrees C.	Quantity of phthalic anhydride used in grm.	Quantity of geraniol used in grm.	Quantity of citronellal used in grm.	Quantity of geraniol found	
				grm.	%
88	2.4883	0.5610	1.3602	0.5480	97.7
82	2.1090	1.0115	0.8120	1.0255	101.4
86	2.3600	1.3745	0.7560	1.3883	101.0

That the presence of the citronellal should lead to better esterification of the geraniol is very improbable; since in the previous experiments about 92 % of the geraniol was esterified, the amount of citronellal esterified in the last three estimations would be 0.032 grm., 0.095 grm. and 0.123 grm. respectively.

It would appear from this that the amount of citronellal esterified increases with that of the geraniol. The cause for the esterification of citronellal in the presence of geraniol must be sought in the formation of the acid phthalic ester of geraniol. Phthalic acid itself has little effect because it is only slightly soluble in benzene. It is well known that citronellal is very sensitive to acids, being converted by them into isopulegol.

In acetylating citronellal without sodium acetate the same phenomenon is observable when working with mixtures of acetic acid and acetic anhydride.

An indirect method was employed corresponding to the way in which the geraniol was estimated by phthalic anhydride. The apparatus consisted of a small flask with long neck to which a ground in U-tube was attached. Into the flask there was always weighed 2 c.c. of citronellal and 2 c.c. of the acetic anhydride mixture. 5 c.c. of $^1/_2$ n KOH were placed in the U-tube, which was fitted with a soda-lime tube.

Acetic anhydride content of the mixture %	Quantity of citronellal esterified in %		Mean
	A	B	
95.0	28.3	32.0	30 2
75.9	51.9	55.8	53.9
53.6	70.0	68.8	69.4
31.2.	59.4	—	59.4
15.25	43.7	41.8	42.5
Acetic acid of 97.2 %	30.9	30.9	30 9

When the duration of heating was increased from 2 hours to 3 hours, the amount of citronellal esterified was also increased. On using 95 % acetic anhydride, 40.1 % and with 52.9 % anhydride, 76.7 % of the citronellal was esterified.

Clearly the presence of acetic acid in the mixture favours the esterification of the citronellal. It might be concluded, that the citronellal which is not esterified, is nevertheless transformed in some other way, for instance into a terpene or similar body. In order to investigate this point larger quantities of the various products were prepared in the manner in which the estimation of the so called total geraniol content is carried out (Bericht of SCHIMMEL & Co April 1910, 155).

A portion of each product was examined by means of phthalic anhydride for the presence of alcohols, of another portion the saponification number was determined in the ordinary way and a third portion was acetylated by the indirect method, by heating 2 c.c. of the product with 2 c.c. of acetic anhydride of 95 % and 0.2 grm. of sodium acetate for 3 hours.

Acetic anhydride content of the mixture %	Number of c.c. of N/10 phthalic acid esterified	Saponification number	% acetylated according to indirect method
95.0	1.6	124.3 [1])	67.7
53.6	—	219.0	13.4
31.2	1.0	180.3	19.8
15.25	—	129.0	28.4
Acetic acid of 97.2 %	1.3	98.0	38.6

Altogether the following amounts of citronellal were therefore acetylated.

95.0 %	37.7 + 74.6 = 112.3
53.6	72.0 + 16.0 = 88.0
31.2	57.3 + 22.9 = 80.2
15.25	39.2 + 31.6 = 70.8
Acetic acid of 97.2 %	29.1 + 41.6 = 70.7

The original use of 95 % anhydride therefore leads to partial formation of a diacetate, while the other acetic anhydride mixtures do not yield 100 %, which would indicate that these cause, in addition, the formation of hydrocarbons terpenes.

The presence of geraniol, like that of acetic acid, leads to a better esterification of the citronellal, as was the case in the estimations with phthalic anhydride.

While according to the indirect method with acetic anhydride of 95 % in two hours only 30.2 % of citronnellal was esterified, mixtures with geraniol gave the following result:

Quantity of geraniol grm.	Quantity of citronellal grm.	Quantity esterified grm.
0.4940	1.1365	0.9478
0.8275	0.9465	1.3195
1.3390	0.8260	1.8740

Assuming that in the mixture 98.5 % of the geraniol is esterified,

[1]) This higher figure is most probably due to increased absorption of water, when working on a large scale.

as was found in the experiment with the pure substance, we can calculate that the following quantities of citronellal were esterified: 40.6, 53.3 and 67.2.

It further follows that no complete esterification is possible without the use of sodium acetate. Even by increasing the duration of heating to 10 hours only 93.3 % of the geraniol-citronellal mixture (1 c.c. to 4 c.c.) was esterified

Finally some estimations were made in which for every 2 c.c. of citronellal 0.2 grm. of sodium acetate (previously melted) was employed.

Acetic anhydride content of the mixture %	Citronellal esterified in %		Mean
	A	B	
95.0	95.0	95.3	95.1
88.3	93.5	—	93.5
75.9	90.0	92.4	91.2
52.9	84.4	—	84.4
31.2	54.5	—	54.5
15.25	40.2	—	40.2
Acetic acid of 97.2 %	30.3	31.4	30.8

Hence the presence of sodium acetate increased the quantity of acetylated citronellal in those mixtures which contained 53—95 % of anhydride, and did not affect the others. The rise of temperature due to the addition of the sodium acetate is not the cause of the improved acetylation in the former mixtures, since heating the mixture in a sealed tube without sodium acetate to the same temperature (about 149°) did not result in better esterification. The curve shows, however, that when sodium acetate is used, the presence of acetic acid is harmful, whereas, in the absence of sodium acetate, the acid has a favourable effect up to a certain concentration. It follows therefore that in using sodium acetate we induce a different reaction from that which occurs in the absence of this salt.

Buitenzorg, 27 May 1918.