small portions, 10 Gm. (0.04 mole) of I-hydrochloride. The mixture was refluxed for 2 hours, allowed to stand at 26° for 6 hours, decomposed with water and worked up as usual. The oily yellow material (6.5 Gm., 82%) had a strong OH peak in its infrared spectrum. It was benzoylated directly with 20 ml. of benzoyl chloride and 150 ml. of 10% sodium hydroxide solution for 15 minutes, the mixture was decomposed with ice, extracted with dilute hydrochloric acid, the acid solutions were made alkaline and re-extracted with ether. The oily product from the dried ether extract weighed 5 Gm. (50%) and exhibited an ester band in its infrared spectrum. Its hydrobromide crystallized from ethyl formate-isopropyl ether, m.p. 194–197°.

Anal.—Calcd. for $C_{20}H_{23}NO_2 \cdot HBr$: C, 61.54; H, 5.94. Found: C, 61.00; H, 6.10.

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Analysis of the Volatile Components of Ylang-Ylang Oil by Gas Chromatography

By DAVID B. KATAGUE and ERNST R. KIRCH

Five samples of commercially available ylang-ylang oil were analyzed by gas chromatography. Of the various stationary liquid phases used, a 20% Ucon on Chromosorb P(w/w) gave consistently the best separation. The composition of extra, first, second, and third quality fractions and pure oil No. 123 was determined on the basis of relative retention times.

Most essential oils are complex mixtures of individual organic compounds that contain varied functional groups which make complete and detailed analysis relatively difficult or at times impossible using conventional procedures.

Thus, prior to the advent of gas chromatography, the analyses of essential oils were tedious and time consuming. Furthermore, in certain instances in which other methods were used, the analyses were not considered complete (1). The availability and development of gas chromatography as an analytical tool has not only greatly facilitated the separation, and at times the identification, of the constituents of a number of essential oils, but also reduced the time required for analyses (2, 3).

One of the important ingredients in a number of perfumes and other cosmetic products is ylang-ylang oil. This is obtained from the flowers of the ylang-ylang tree (*Cananga odorata*, Hook *f et* Thomson), which is probably a native of the Philippines (1). The important commercial sources of this oil for use in the United States today are the Nossi-Be and Comoro Islands. The oil is available in four different quality fractions, based on the respective boiling points, and is classified commercially as extra, first, second, and third quality fractions. The extra fraction exhibited the highest specific gravity and the lowest refractive index when compared to the other fractions. The samples labeled extra and first quality possess the strongest and finest odors.

That the chemical composition of the oil may be related to the manner in which the oil is extracted from the flowers has been shown by Glitchitch and Naves (4). They found that when the flowers were initially extracted with petroleum ether and the extract concentrated and distilled, the product was almost free of sesquiterpenes (5). On the other hand, if the flowers were steam distilled, a relatively high concentration of sesquiterpenes was found. This was interpreted by some authors to mean that the sesquiterpenes are formed during distillation from compounds insoluble in petroleum ether and should not be considered true natural products in the strict sense (1).

The chemical composition of ylang-ylang oil was cursorily investigated as early as 1873 working with samples obtained in the Philippines (6–8). In 1932, Glitchitch and Naves (4) using a classical separation identified certain constituents of the extra oil and reported a semiquantita-

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tive estimate of some of the group components.

A more detailed composition of an absolute ylang-ylang oil was reported by Naves in 1959 (9). This particular oil which was prepared by solvent extraction consisted of the following: *p*-cresylmethylether, 5.7–6.6%; linalool, 6.5–8.1%; methylbenzoate, 6.9–7.4%; benzyl acetate, 19.6–26.5%; and benzyl benzoate, 6.2–9.9%.

Because of the interest in this oil, it was thought advisable to undertake a more detailed analysis of the various commercial samples commonly available in this country. This report deals with the analyses of five samples of ylang-ylang oil by gas chromatography.

EXPERIMENTAL

Apparatus.—The apparatus used in this investigation was the Beckman GC-2 gas chromatograph equipped with a thermal conductivity cell and connected to a Sargent SR recorder with a K-4 disk integrator. The carrier gas was helium. The column used consisted of 6 ft. of copper tubing with a diameter of 1/4 inch.

Column Preparation.—The following stationary liquid phases were used: (*a*) Tide detergent extract (alkyl aryl sulfonates); a commercial sample (20 Gm.) of Tide detergent was extracted in a soxhlet with methanol (200 ml.) and the extract concentrated to a semisolid consistency; (*b*) Apiezon L;[1] diethyleneglycol succinate (DEGS); LAC-R-446 (the adipate polyester of diethyleneglycol partially cross-linked with pentaerythritol); Carbowax 4000;[2] and Ucon 50.[3]

As a solid support, acid-washed Johns-Manville Chromosorb P, 30/60 mesh size, was used. Approximately 20 Gm. of Chromosorb P was required to fill the 6-ft. column employed. In general, a certain weight of a particular liquid phase was dissolved in a minimum amount of an appropriate solvent. To this solution, the proper amount of solid support was added gradually with constant stirring to insure uniform mixing. The mixture was then spread on a large evaporating dish, air-dried at first, and then oven-dried until all the solvent was evaporated. The packing thus prepared was poured slowly into the copper tubing at a uniform rate with persistent tapping to insure uniform packing. Pyrex glass wool was used to plug both ends of the column.

It was determined that 30 ml. of methylene chloride was sufficient to dissolve and deposit 2.0 Gm. of Ucon and 1.0 Gm. of Carbowax on the 20 Gm. of Chromosorb P, while 40 ml. was needed when 2.5 Gm. of Carbowax was used. Thirty milliliters of benzene was used to deposit 1.8 Gm. of DEGS and 1.5 Gm. of LAC-R-446. The same amount of benzene was sufficient to deposit 2.1 Gm. of Apiezon L and 3.0 Gm. of Tide detergent "extract." All solvents employed were of AR grade.

[1] Marketed by James G. Biddle Co., Philadelphia, Pa.

[2] Trade name for polyethylene glycol, marketed by Carbide and Carbon Chemicals Co., a Div. of Union Carbide and Carbon Corp.

[3] Trade name for polyalkylene glycol, marketed by Carbide and Carbon Chemicals Co., a Div. of Union Carbide and Carbon Corp.

TABLE I.—RETENTION TIMES AND RELATIVE RETENTION TIMES OF STANDARD COMPOUNDS ON 20% UCON AT 190°[a]

Compounds[b]	B. p., °C.	Retention Times, Min.	Relative R.T., Min.
α-Pinene	154	2.4	0.296
Furfural	161	4.5	0.555
p-Cresyl methyl ether	176	6.0	0.740
β-Pinene	170	6.8	0.840
Eucalyptol	176	7.0	0.864
Linalool	198	8.1	1.00
p-Cresol	202	9.6	1.18
m-Cresyl acetate	217	9.9	1.22
Linalyl acetate	220	10.0	1.23
Citronellal	208	10.1	1.25
Benzaldehyde	179	10.3	1.27
Methyl benzoate	199	11.0	1.36
Citral	214	12.1	1.49
Bornyl acetate	225	13.4	1.66
Terpineol	220	15.5	1.92
Methyl phenylacetate	220	16.5	2.04
Benzyl alcohol	205	18.0	2.23
Safrole	234	18.8	2.34
Caryophyllene	285	19.0	2.35
Isosafrole	242	19.2	2.37
Phenyl propyl alcohol	219	19.3	2.39
Methyl salicylate	223	19.8	2.44
Ethyl phenyl acetate	226	19.9	2.46
Geraniol	230	20.5	2.54
Benzyl acetate[c]	214	24.0	2.96
Geranyl acetate	248	25.0	3.08
Eugenol methyl ether	249	32.0	3.95
Eugenol	252	34.0	4.20
Isoeugenol	267	38.0	4.81

[a] Flow rate, 40 ml./min.; filament current, 200 ma.; maximum attenuation; linalool, 1.00. [b] Nerol, nerolidol, farnesol, terpenyl acetate, and benzyl benzoate were not eluted even after 70 minutes at the conditions of the experiment. [c] At 756 mm.

Procedure.—The carrier gas flow rate was maintained at 40 ml./min. The temperature ranged from 160 to 190°. The chart speed used was one inch per minute and a filament current of 200 ma. was maintained.

Unless otherwise specified, 0.01 ml. of oil samples were used at maximum sensitivity under the ideal conditions stated above.

For purposes of identification, the comparison of retention times and relative retention times[4] of an unknown with known pure standards were employed. Twenty-nine known compounds were analyzed under conditions identical to that at which the unknown was analyzed. Each peak was then confirmed by the enrichment method. In some cases, infrared spectra were run for confirmation.

The quantitative amount of each peak was measured based on the integrated area under each peak. Computation was based on the integrator. All the percentages as calculated were based on the total eluted.

Samples[5] and Standard Compounds.—The following quality fractions of ylang-ylang oil were analyzed. Their respective refractive indexes at 28° and specific gravities at 24° as determined are listed

[4] The relative retention time is the ratio of the retention time of an unknown constituent to that of a standard constituent.

[5] The authors wish to express their thanks to Fritzsche Brothers Inc., New York, for supplying the five samples of ylang-ylang oil.

Samples	$n_D^{28°}$	Sp. Gr.$^{24°}$
Extra	1.5008	0.963
First quality	1.5041	0.946
Second quality	1.5063	0.936
Third quality	1.5091	0.933
Pure oil No. 123	1.5089	0.915

In addition to the above oils, a number of known pure compounds were analyzed under exactly the same operating conditions as those used for the oils. Table I lists both retention times and relative retention times based on linalool. The corresponding boiling points at 760 mm., unless otherwise stated, are also listed. The compounds are arranged according to their increasing retention and relative retention times. A number of compounds not eluted after 50 to 70 minutes at experimental conditions mentioned are also listed.

RESULTS AND DISCUSSION

Five samples of ylang-ylang oil were analyzed, using various liquid phases in different concentrations with respect to the solid support. The samples analyzed were the extra, first, second, and third quality fraction and pure oil No. 123.

With the extra fraction oil and a 25% w/w Apiezon L on Chromosorb P at 190°, four peaks were obtained, the first two of which only showed good resolution. A change in the column temperature to below or above 190° or a reduction in the amount of Apiezon L to as low as 10% w/w did not improve the resolution. Four peaks at best could be observed at 190° with either a 10% or 25% LAC-R-446, while with DEGS only two broad peaks were obtained. An extract of a detergent (Tide) as the liquid phase was found to decompose at the same temperature and gave incomplete separations.

Carbowax or Ucon gave better resolutions. Both of these liquid phases were investigated in various proportions and at different operating temperatures.

It should be noted that with the extra and first fraction oils at least nine distinct peaks were obtained at 160° and eight peaks at 190° with Carbowax in 10% proportions. Figures 1 and 2 show the typical chromatogram of the extra oil at two temperatures.

Only four, or at best five, peaks (Figs. 3–5) were obtained with the second and third quality fractions and pure oil No. 123, either at 160° or 190°. The results may be due to the absence of the same components as found in the extra and first quality oils, or they may be different components that could not be separated using Carbowax as the liquid phase. It was thought desirable to use another liquid phase.

One of these liquid phases is Ucon (a polyalkylene glycol and its aliphatic diesters). It is reported (10, 11) to be an efficient liquid phase for the separation of components of some volatile oils. With this material in a 20% w/w on Chromosorb P, we were successful in obtaining consistent and better separation of all the oil samples investigated. Figures 6 and 7 represent typical chromatograms obtained with the extra and first quality oils at 190°.

Comparing the results obtained for all the oil samples investigated, it should be noted that the second and third quality as well as the pure oil

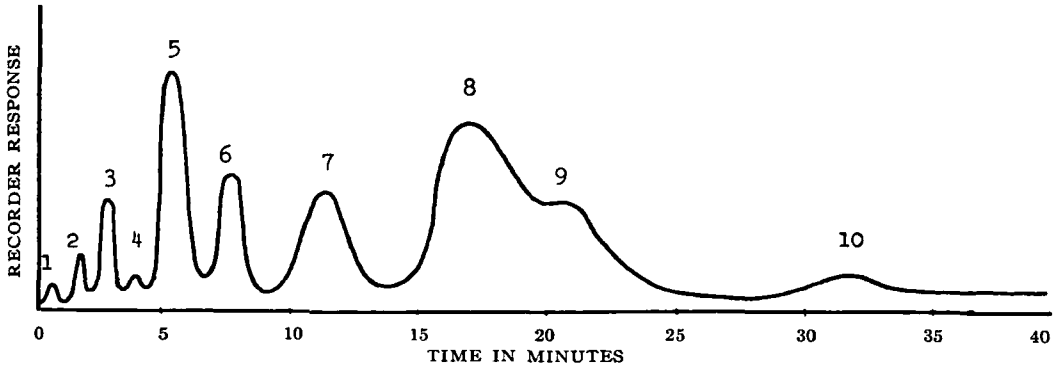

Fig. 1.—Typical chromatogram of extra fraction on 10% Carbowax at 160°.

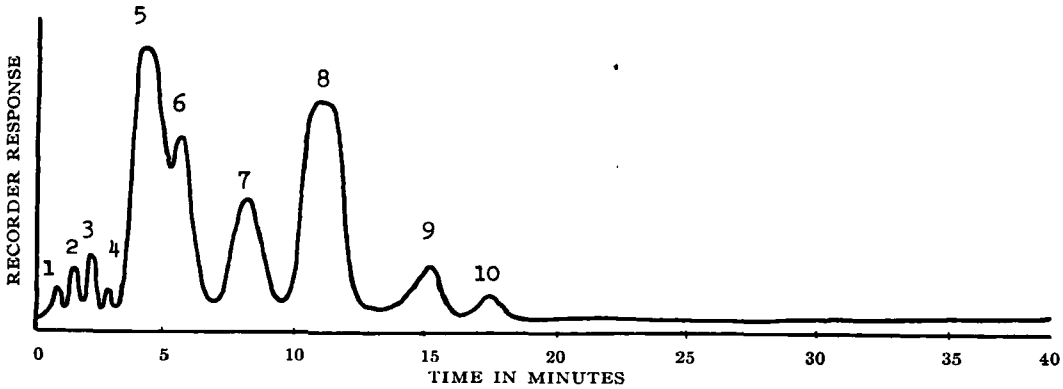

Fig. 2.—Typical chromatogram of extra fraction on 10% Carbowax at 190°.

No. 123 (Figs. 8–10) gave fewer number of peaks. Similar results were obtained at 160° with every one of these oils with the exception that the time required for complete elution was about twice as long.

The primary volatile components of all the oils investigated are listed in Tables II and III giving relative retention times of the peaks and the per cent composition. A particular peak number in a table corresponds to the same number in the various figures. The identity of peaks 2, 4, 5, 6, and 7 was confirmed by the enrichment method using one standard at a time. Peaks 3, 8, and 9 were collected and infrared spectra were run. Peaks 1 and 10, corresponding to low and high boiling components, respectively, were too small

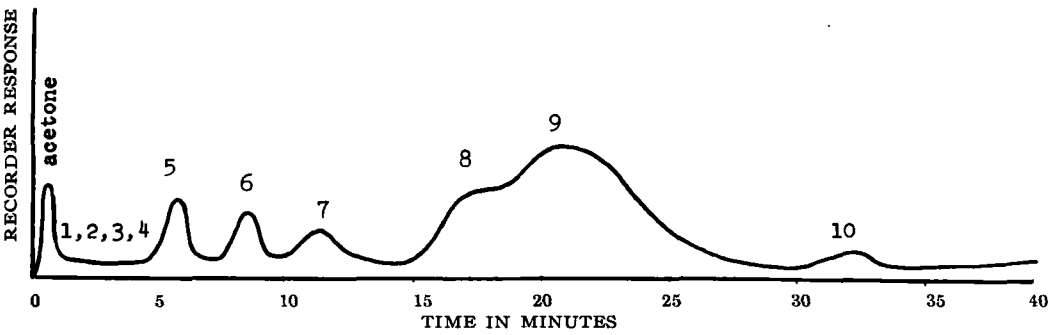

Fig. 3.—Typical chromatogram of second fraction on 10% Carbowax at 160°.

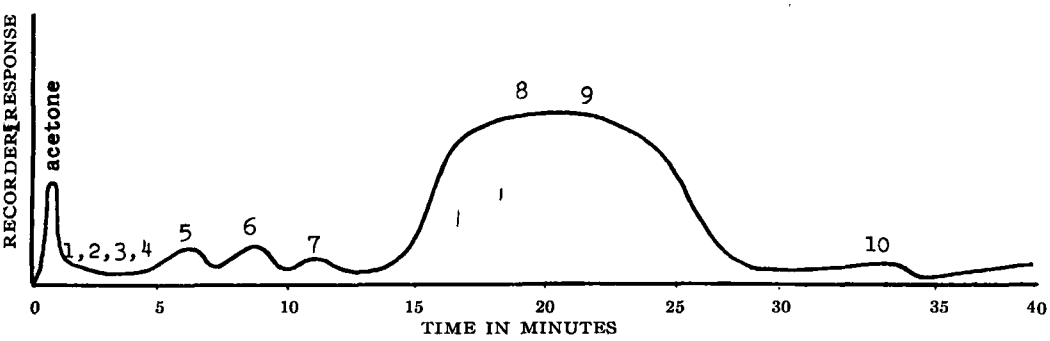

Fig. 4.—Typical chromatogram of third fraction on 10% Carbowax at 160°.

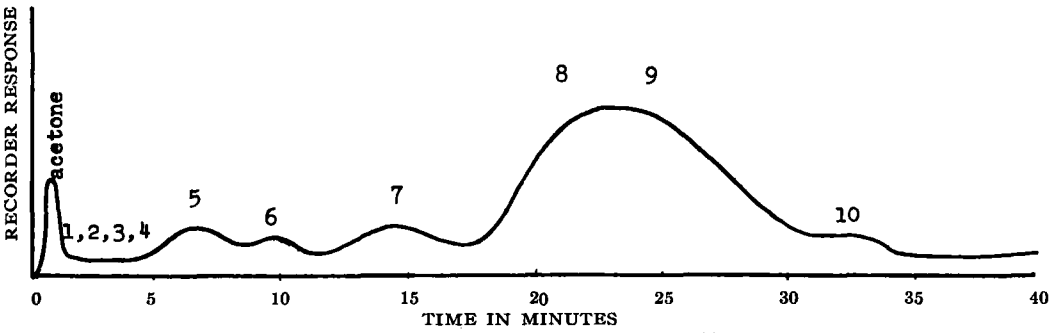

Fig. 5.—Typical chromatogram of pure oil No. 123 on 10% Carbowax at 160°.

TABLE II.—PER CENT COMPOSITION OF YLANG-YLANG OIL, EXTRA AND FIRST FRACTION WITH THEIR RESPECTIVE RELATIVE RETENTION TIMES COMPARED TO STANDARDS[a]

Peak No.	Component	Relative Retention Times Unknown	Relative Retention Times Known	Per Cent Composition Extra	Per Cent Composition First
1	Low boiling components	0.124	...	0.7	0.6
2	α-Pinene	0.296	0.296	1.3	1.2
3	A phenol	0.370	...	1.9	1.6
4	Furfural(?)	0.508	0.555	1.7	2.4
5	*p*-Cresyl methyl ether	0.746	0.740	18.5	13.0
6	Linalool	1.00	1.00	10.8	9.5
7	Methyl benzoate	1.35	1.36	13.2	11.1
8	An aromatic ester	1.82	...	26.7	33.0
9	Geranyl acetate	2.99	3.08	25.1	27.5
10	High boiling components	4.70	...	From 0.5 to 1.0	

[a] Liquid phase Ucon; temperature, 190°; helium flow rate, 40 ml./min.; linalool, 1.00 (8.1 min.).

TABLE III.—PER CENT COMPOSITION OF YLANG-YLANG OIL, SECOND AND THIRD QUALITY FRACTIONS, AND PURE OIL NO. 123 WITH THEIR RELATIVE RETENTION TIMES COMPARED TO STANDARDS[a]

	Peak No. Component	Relative Retention Times Unknown	Relative Retention Times Known	Per Cent Composition Second	Per Cent Composition Third	Per Cent Composition Pure
1	Low boiling components	0.124	...	Traces	No peak	Traces
2	α-Pinene	0.296	...	Traces	No peak	Traces
3	A phenol	0.370	...	Traces	No peak	Traces
4	Furfural(?)	0.508	...	Traces	No peak	Traces
5	*p*-Cresyl methyl ether	0.746	0.740	2.6	0.7	2.4
6	Linalool	1.00	1.00	2.4	0.5	1.9
7	Methyl benzoate	1.35	1.36	2.9	Traces	1.5
8	An aromatic ester	1.82	...	11.8	2.5	7.7
9	Caryophyllene	2.39	2.35	11.5	9.2	12.5
10	Geranyl acetate	2.99	3.08	68.8	86.9	73.9

[a] Liquid phase Ucon; temperature 190°; flow rate, 40 ml./min.; linalool, 1.00 (8.1 min.).

and indistinct for practical confirmation. The retention times for peaks 5, 9, and 10 are within the allowable range as described by James and Bernhard (12, 13).

Alpha-pinene (peak 2) was found to be present both in the extra and first fraction oil. A phenol (peak 3) as indicated by the frequencies of the infrared spectrum as shown in Table IV was also observed in the same two oils. Peak 4 was increased when furfural was added to either one of these oils. *p*-Cresyl methyl ether (peak 5) was present in a higher concentration in the extra as compared to the first fraction, while the amount of linalool (peak 6) was about the same in the two oils. Methyl benzoate as shown by peak 7 is present in slightly higher amounts in the extra fraction.

Terpineol has been reported present in the oil (1). When chromatographed individually under identical conditions used for the oils, a retention time of 15.5 minutes was observed. Peak 8, with a retention time of 14.7 minutes, was not completely enriched. An overlapping, however, was evident. Infrared spectra of peak 8 and standard terpineol were not identical, but indicate an aromatic ester grouping. Infrared spectrum of benzyl acetate compared to peak 8 was similar (Table V).

The constituent represented by peak 9 has a retention time of 24.5 minutes. Two reported components were found to have retention times close to this peak. Geranyl acetate and benzyl acetate were observed to elute after 25 and 24 minutes, respectively. Only geranyl acetate showed

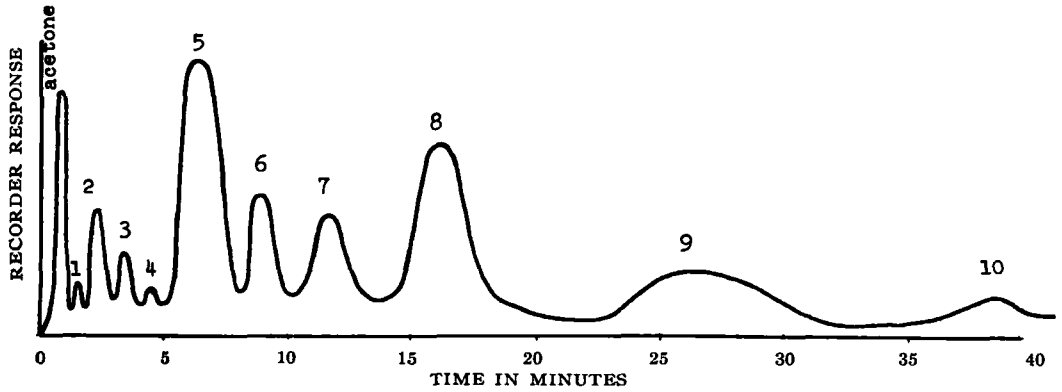

Fig. 6.—Typical chromatogram of extra fraction on 20% Ucon at 190°.

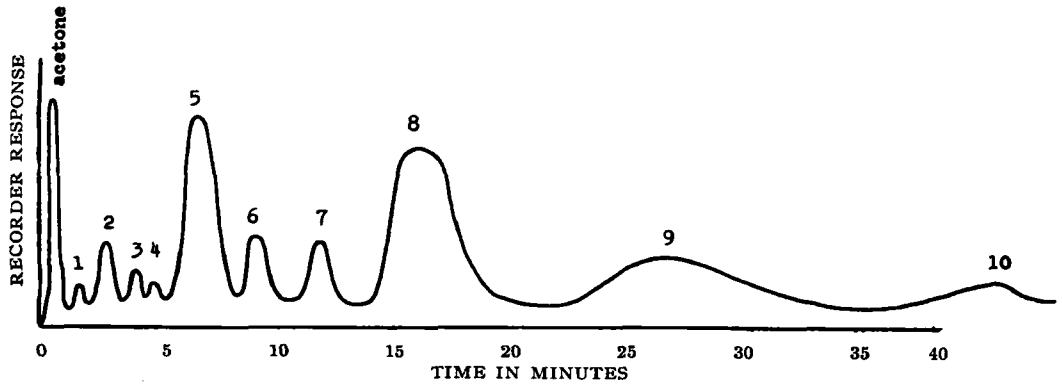

Fig. 7.—Typical chromatogram of first fraction on 20% Ucon at 190°.

an increase in the peak when added to the oil. The infrared spectra of peak 9 and standard geranyl acetate were identical. Table VI shows the infrared frequencies and intensities of peak 9.

Comparing the components of the extra and first fraction oils with the other oils, it should be mentioned that the first four peaks were not observed in the second, third, and pure oil No. 123. The first peak observed (peak 5) was *p*-cresyl methyl ether which was present to the extent of about 2.5% in both the second fraction and pure oil No. 123 samples, but was present only in a concentra-

TABLE IV.—INFRARED FREQUENCIES AND INTENSITIES OF PEAK 3, YLANG-YLANG OIL EXTRA[a]

Frequency, cm.$^{-1}$	Intensity	Frequency, cm.$^{-1}$	Intensity,	Frequency, cm.$^{-1}$	Intensity
3550	Strong	1450	Strong	1100	Strong
3110	Medium	1300	Medium	1030	Strong
1850	Weak	1280	Strong	830	Strong
1630	Weak	1250	Strong	810	Weak
1520	Strong	1180	Medium	750	Strong

[a] A phenol.

TABLE V.—INFRARED FREQUENCIES AND INTENSITIES OF PEAK 8, YLANG-YLANG OIL EXTRA[a]

Frequency, cm.$^{-1}$	Intensity	Frequency, cm.$^{-1}$	Intensity	Frequency, cm.$^{-1}$	Intensity
3100	Medium	1360	Medium	970	Medium
1750	Strong	1250	Strong	930	Weak
1510	Medium	1095	Weak	850	Medium
1450	Medium	1050	Strong	750	Strong
1380	Medium	1000	Medium	700	Strong

[a] An aromatic ester similar to benzyl acetate.

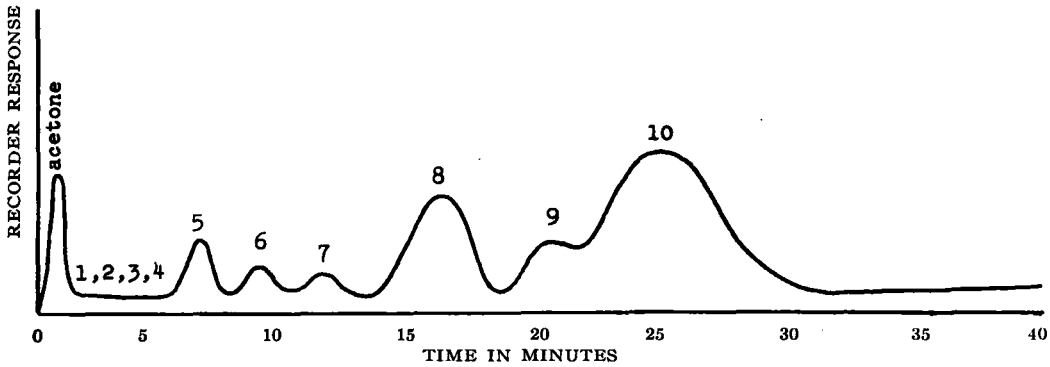

Fig. 8.—Typical chromatogram of second fraction on 20% Ucon at 190°.

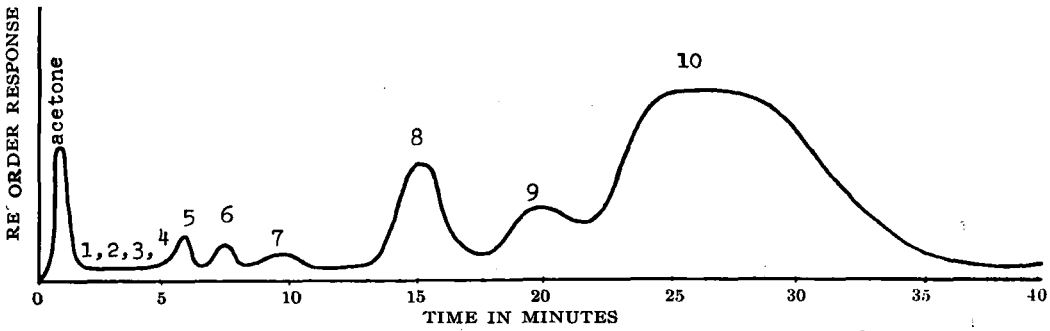

Fig. 9.—Typical chromatogram of third fraction on 20% Ucon at 190°.

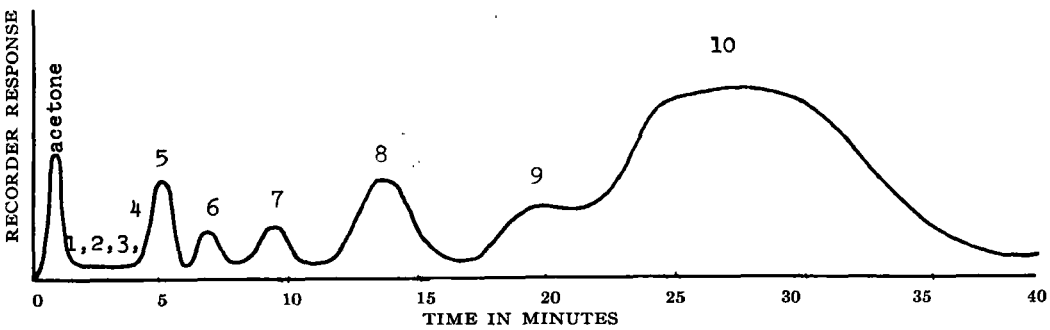

Fig. 10.—Typical chromatogram of pure oil No. 123 on 20% Ucon at 190°.

TABLE VI.—INFRARED FREQUENCIES AND INTENSITIES OF PEAK 9, YLANG-YLANG OIL EXTRA[a]

Frequency, cm.$^{-1}$	Intensity	Frequency, cm.$^{-1}$	Intensity	Frequency, cm.$^{-1}$	Intensity
2950	Strong	1375	Medium	1030	Medium
1720	Strong	1355	Medium	970	Weak
1630	Weak	1310	Weak	890	Weak
1590	Weak	1250	Strong	780	Weak
1450	Medium	1100	Weak	710	Weak

[a] Identical to standard geranyl acetate.

tion of 0.7% in the third fraction. Linalool (peak 6) was slightly higher in concentration in the second fraction than in the pure oil. Again, the amount of this alcohol in the third fraction was almost negligible. Methyl benzoate (peak 7) represents about 2.9% of the second fraction and 1.5% of the pure oil, while only a trace of it was found in the third fraction. An aromatic ester (benzyl acetate), as represented by peak 8, was found to be present in greater amounts in both pure oil No. 123 and the second fraction, as compared to the third fraction.

Caryophyllene has been reported to be one of the sesquiterpenes present in the oil (1). The addition of caryophyllene to the above fraction oils increased peak 9 which eluted at 19.3 minutes. It should be noted that this was not observed in the first or extra oils.

The last peak (peak 10) obtained with second and third quality and pure oil No. 123 represents geranyl acetate and was found to be present in these oils in a relatively high percentage, 68.8 to 86.9%. This amount is about three times as high as was found in the extra or first fraction oils.

It had been mentioned earlier that the literature reports a whole series of compounds present in ylang-ylang oil (1). In practically all cases, the analytical work was carried out on the extra fraction only. The percentages reported by these authors represent several classes of compounds rather than individual compounds. For example, Glitchitch and Naves (4) reported the presence of 0.1 to 0.2% of aldehydes and ketones including benzaldehyde. The latter compound was not found in any of the oils investigated by us. The terpene content reported by the same authors ranged from 0.3 to 0.6%, while we found that the alpha-pinene content of the extra fraction oil as analyzed was in the neighborhood of 1.3%. Some of the samples analyzed in our laboratory showed a concentration of *p*-cresyl methyl ether as high as 18% and a concentration of a phenol as high as 1.9%, while Glitchitch, *et al.*, reported only 3% of phenols and phenol ethers including *p*-cresyl methyl ether. A range of 52 to 64% of alcohols and esters were reported to be present in the extra fraction by the same authors. It was established in this investigation that 10.8% linalool, 13.3% methyl benzoate, 25.1% geranyl acetate, and 26.7% of an aromatic ester (benzyl acetate) were present in the same quality fraction analyzed. Furthermore, Glitchitch, *et al.*, reported about 35% sesquiterpenes to be present in the extra fraction oil. No sesquiterpenes were detected in the extra oil analyzed by us, but caryophyllene was definitely found in the second, third, and pure oil No. 123 in concentration of about 10% (Table III).

SUMMARY

Ylang-ylang oil obtained commercially by distillation of the flowers of *Cananga odorata*, Hook *f et* Thomson, *forma genuina* was analyzed by gas chromatography, using 20% Ucon on Chromosorb P (w/w). The composition of the extra, first, second, and third quality fractions and the pure oil No. 123 was determined on the basis of relative retention times.

The following natural components were identified in ylang-ylang oil: *d*-alpha-pinene, *p*-cresyl methyl ether, linalool, methyl benzoate, geranyl acetate, caryophyllene, and a phenol and an aromatic ester (benzyl acetate). Identification was confirmed by the enrichment method and in certain instances by use of infrared spectra.

On a qualitative basis, the extra and first fractions were similar in that all the components listed above were present except caryophyllene. The second, third, and pure oil 123 oils were similar in that all components listed above were present in significant quantities except *d*-alpha-pinene and a phenol. These two compounds were present in trace amounts in the second and pure oil fractions and were absent in the third fraction.

On a quantitative basis, all five fraction oils analyzed differed in the relative concentration of the components present.

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