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CHROMATOGRAPHIC INVESTIGATION OF JASMIN ABSOLUTES

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SUMMARY

Several Jasmin absolute (oil) samples of different origin were studied by glass capillary gas chromatography (CGC) and by CGC–mass spectrometry. Only quantitative differences were observed. There are only 15 major components. About 100 minor constituents were identified after fractionation by partial evaporation, preparative gas chromatography and chemical group separation. The concentration of important smell contributing compounds is lower in the French oil sample than in the other oils. In the head space or most volatile fraction this situation is reversed. This is ascribed to the enhancing and fixating effects of the less volatile fractions of the oils. A new way to study such effects is proposed.

INTRODUCTION

"Absolue de Jasmin" or the essential oil of jasmin is one of the more important and expensive perfumery materials. It is obtained in various Mediterranean countries —France (since about 1850), Italy (?), Egypt (1912), Marocco (1940), Algeria (1940)— from the flowers of *Jasminium grandiflorum* L, imported from Spain to the Grasse region in France about 250 years ago.

Chemical research on jasmin oil was started in 1899 by Verley[1], followed by Hesse and Müller[2] and Hesse[3–6] who identified half a dozen compounds. Amongst the early authors who published on jasmin oil (refs. 7–24) many famous names are found and by 1970 around 30 compounds had been identified. The most important of these, contributing essentially to the smell of jasmin oil, are claimed to be jasmone (I), methyl jasmonate (II), 5-(*cis*-2-pentenyl)-5-pentanolide or jasmin lactone (III), linalool, benzyl acetate, benzyl benzoate and indole.

In 1973 Polak[25,26] claimed to have identified about 100 compounds in jasmin oil. Only a few were mentioned however and details were not provided. In 1973 Stoffelsma *et al.*[27] claimed to have isolated a number of lactones from jasmin oil. New additions have regularly been made to the growing list of jasmin oil constituents[28–32].

In the present paper we describe some results of our studies on Algerian, Egyptian, Italian and French jasmin oil of 1968 and 1972.

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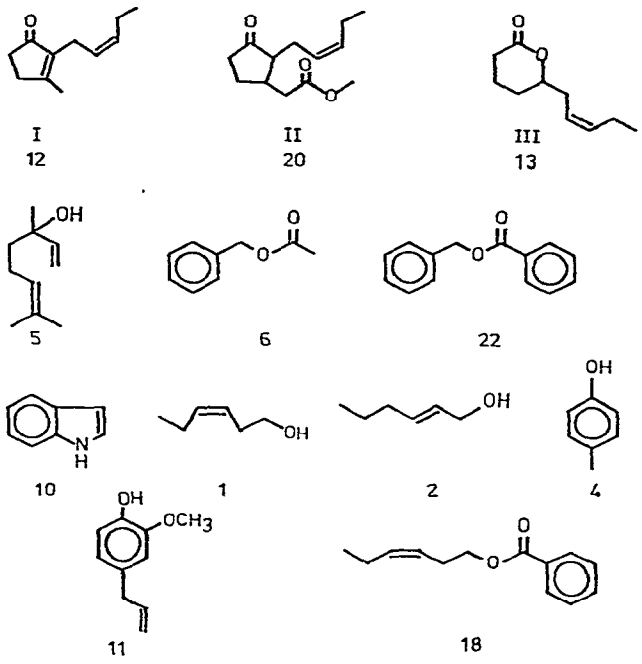

The numbers refer to Table II.

INSTRUMENTAL DETAILS

The total oils were analysed by glass capillary column gas chromatography (CGC)[33] using various stationary phases. The columns were mounted in Varian 1400 and 2100 gas chromatographs. Identification of the compounds was obtained by coupling the chromatographs to a Finnigan 3000 and 3200 quadrupole mass spectrometer fitted with a 6000 Finnigan data system. Both electron impact and chemical ionization were used.

Quantitative gas chromatographic (GC) results were obtained with a Varian CDS 101 integrator.

To obtain the low boiling fraction of relatively small samples, 1 or 2 ml of the oil was placed in a closed and evacuated glass device consisting of two small 3.5-ml flasks, one holding the sample at room temperature or slightly above, the other cooled in liquid nitrogen (Fig. 1A). The vacuum promotes the transfer of volatiles to the cool flask. It is essential that no ground joints or stoppers are used, but that, as shown, the evacuated device is heat sealed and is therefore absolutely airtight. The composition of the low boiling fraction obtained in this way depends on the duration of the experiment, on the temperature of the sample flask and on the efficiency of the device to allow transfer of the volatile fraction. Still, the results of similar experiments were fairly reproducible.

To study the head space composition of the oils as a function of time, the glass device shown in Fig. 1B was used. The stopper A can be moved up and down with an external magnet applied to the iron core (B). Oil is placed in C. When the stopper is raised, space C is in contact with space D and equilibrium between the liquid and gaseous states can be established. Pushing down the stopper closes off space C and

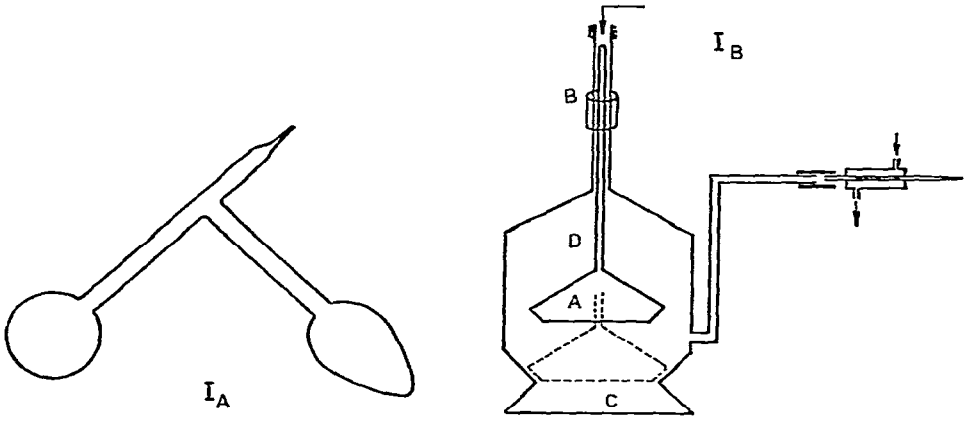

Fig. 1. Collection devices for the volatile fraction (A) and head space (B) of complex mixtures. Details as in text.

the vapour in D can be quantitatively removed by a nitrogen stream. Analysis of the vapour can be carried out in the head space or after collection in a cooled trap. Mostly we trapped the head space on a small packed column cooled with a cold air stream during collection. This collector was subsequently used as a precolumn with a large-bore capillary for analysis. The composition of the head space determined in this way is the true equilibrium composition, provided some simple precautions are taken (sufficient equilibration time and complete transfer of volatiles to precolumn). These were ascertained experimentally (1 h for equilibration and nitrogen purge stream of 10 ml/min for 1 h). The precolumn (20 cm × 2 mm I.D.) was packed over 10 cm with 6% SE-30 on Gas-Chrom Q (80–100 mesh). The precolumn was then mounted in the chromatograph in such a way that the packing does not sense the injection block temperature (between the injector insert and the analytical column).

SAMPLES AND ODOUR EVALUATION

There is a great difference in commercial value between oils of the various producing countries mentioned above. The chemical reasons for this are unknown. The samples we studied were obtained from different reputed perfumery companies and were of French (1968 and 1972 crop), Algerian (1968–1972), Italian (1972) and Egyptian (1978) origin.

A test smell-panel of eight people was selected out of 100 candidates. Most attention was given to the ability to recognise the same sample after an interval of several days or weeks. A surprisingly large difference was observed, particularly for threshold perception, between individuals. Results of repeated smell evaluations, influencing all subsequent research, can be summarized as follows:

all jasmin oils smell differently, even when of the same origin but different crop year;

the difference between French and Italian oils of 1972 was typical and also the greatest;

Algerian and Egyptian oils are closer to Italian than to French oil.

In the present work the accent was therefore placed on the chemical difference between French and Italian oils of 1972.

Individual compounds of the oils were collected by preparative scale CGC. For this, a wide-bore glass capillary (up to 100 m × 0.7–0.9 mm I.D.) was mounted in a 1400 Varian gas chromatograph equipped with a non-destructive micro-katharometer detector, or in a 2100 Varian gas chromatograph with flame ionization detector and a splitter. Up to 2 μl of pure oil were injected and the individual peaks were collected in traps as described[34]. After collection the traps were broken and placed in 10-ml flasks. The collected amounts, often only in the microgram range, were sufficient for several olfactory evaluations, even spread out over several days or weeks.

None of the compounds or fractions collected had a jasmin oil smell. Even compounds I, II and III were distinctly different in odour from the total oil. It is also important to note that the odour of the total oils varies considerably with time when spread out thinly or when allowed to evaporate.

COMPOSITION OF JASMIN OIL

Before and during the present work a number of compounds were mentioned in the literature as constituents of jasmin oil or of jasmin flower extracts; they are presented in Table I. The percentages mentioned by the authors are not strictly comparable, because it is not always clear whether jasmin flower extracts, "concretes" or "absolutes" were studied.

TABLE I

JASMIN OIL COMPOSITION ACCORDING TO THE LITERATURE UP TO 1980

Name	*Mentioned by*	*Year*	*% mentioned*
Benzyl acetate	Hesse	1899	65
Linalool	Hesse	1899	15.5
Linalyl acetate	Hesse	1899	7.5
Benzyl alcohol	Hesse	1899	6.0
Indole	Hesse	1899	2.5
Methyl anthranilate	Hesse	1899	0.5
Benzyl benzoate	Hesse	1899	5
Jasmone	Hesse	1900	3
p-Cresol	Elze	1926	
Geraniol	Elze	1926	10
Farnesol	Elze	1926	
cis-3-Hexenyl benzoate	Ruzicka	1933	—
Eugenol	Sabetay	1939	0.2
Nerol	Naves	1942	
Cresol	Naves	1942	
Benzoic acid	Naves		
Benzaldehyde	Naves		
α-Terpineol	Naves		5
Nerolidol	Naves		
Isophytol	Demole	1956	
Phytol	Lederer	1958	
Geranyllinalool	Lederer	1958	
Phytyl acetate	Lederer	1958	

TABLE I (*continued*)

Name	*Mentioned by*	*Year*	*% mentioned*
Methyl palmitate	Lederer	1958	—
Methyl linoleate	Lederer	1958	—
Methyl jasmonate	Demole	1962	
5-(*cis*-2-Pentenyl)-5-pentanolide	Demole	1962	
Vanilline	Demole	1962	
Methylheptenone	Demole	1962	—
6,10-14-Trimethyl-2-pentadecanone	Demole	1962	—
Methyl N-acetylanthranilate	Demole	1964	
Methyl N-methylanthranilate	Calvarano	1965	
Benzyl cyanide	Polak	1973	
2-Phenylnitroethane	Polak	1973	
2(3)-Vinylpyridine	Polak	1973	
Quinoline	Polak	1973	
2-Methylquinoline	Polak	1973	
4-Hexanolide	Stoffelsma	1973	
4-Heptanolide	Stoffelsma	1973	
4-Octanolide	Stoffelsma	1973	
4-Nonanolide	Stoffelsma	1973	
4-Vinyl-4-pentanolide	Stoffelsma	1973	
cis-/*trans*-Ethyl jasmonate	Mookherjee	1974	
Methyl dehydrojasmonate	Mookherjee	1974	
Jasmonyl acetate	Mookherjee	1974	
Hexen-3-yl acetate	Lemberg	1974	
Hexen-3-yl propionate	Lemberg	1974	
Hexen-3-yl isobutyrate	Lemberg	1974	
Methyl benzoate	Lemberg	1974	
cis-/*trans*-Linalyl oxide	Lemberg	1974	
Ethyl jasmonates	Kaiser	1974	
Bicyclic jasmolactone	Kaiser	1974	
Alkylpyridines (four)	Toyoda	1978	
Alkyl nicotinates (ten)	Toyoda	1978	
α-Farnesene	Garnero	1980	
β-Farnesene	Garnero	1980	
Phytadienes (?)	Garnero	1980	
Isophytyl acetate	Garnero	1980	
Ursolic acid	Garnero	1980	
A series of fatty acids	Garnero	1980	
A series of *n*- and *iso*-C_{21}–C_{36} hydrocarbons	Garnero	1980	

The literature mentions about 100 constituents of jasmin oil.

We were unable to find a large number of these compounds in our jasmin oils. Geraniol (10%) and α-terpineol (5%) are obviously errors. Of the more recent reports we did not find the compounds mentioned by Polak[25,26], but then no details are given by this author on the way they were isolated. We also could not confirm the presence of a series of lactones, although in this case the published procedure was carefully followed[27]. We conclude that the trace components in different oils are very variable.

Hesse, who first isolated jasmone, and also Ruzicka and Pfeiffer[9] and Treff and Werner[10] who established its structure, mention that the jasmone odour is similar to that of jasmin oil. In our opinion this is not so and, moreover, jasmone is not typical for jasmin oil since its presence was later detected in other oils.

THE NON-VOLATILE FRACTION

The "absolute" of jasmin (jasmin oil) is not completely volatile. When a silica gel trap is connected to a preparative size GC column only a fraction of the input can be recovered: *ca.* 75% for the French oils and *ca.* 85% for the Italian oil.

The gel permeation chromatographic (GPC) traces of French and Italian oil of 1972 are shown in Fig. 2. There are more high-molecular-weight constituents in the French oil. This is consistent with the volatility difference mentioned above. The GPC peak M.W. 615 is probably due to steroid waxes and above that M.W. the material can be ascribed to fatty oil. The peak of M.W. 445 belongs to steroidic compounds as explained below.

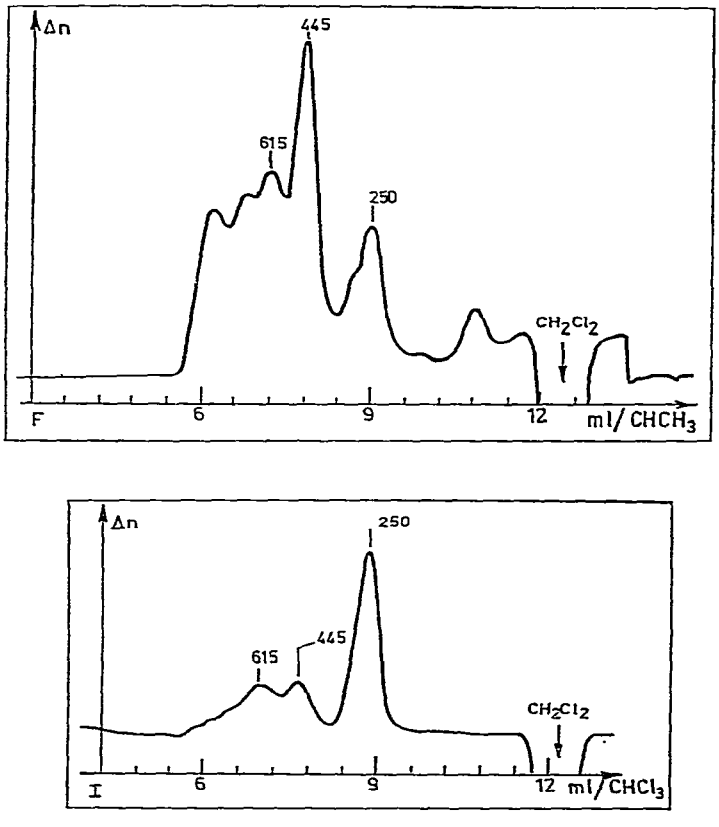

Fig. 2. GPC traces with chloroform at 0.7 ml/min on 10-μm Poragel for French (F) and Italian (I) jasmin oil.

The non-volatile constituents of the oils were further studied by thin-layer chromatography (TLC) on activated silica gel plates with chloroform–ethyl acetate–ethanol (100:7:1) as solvent. For preparative work the bands were made visible under UV light by spraying with Rhodamine 6G solution. The collected bands were extracted on a glass filter with diethyl ether, which removes the compounds but not

the Rhodamine 6G. Spots with the following R_F values were noted: 0.014; 0.06; 0.09; 0.13; 0.19; 0.22; 0.25; 0.37; 0.49; 0.55; 0.66; 0.75. The spot with $R_F = 0.09$ is ursolic acid (M.W. 456) and the spot with $R_F = 0.25$ is β-sitosterol (M.W. 428) as was ascertained by mass spectrometric (MS) analysis and TLC with authentic samples. Two other spots had probable M.W. 442 and 444 and are possibly also steroids. Higher M.W. could not be analysed with our spectrometer facilities. None of the identified or unknown TLC spots had any smell.

THE VOLATILE FRACTION: DIFFERENCE BETWEEN OILS

GC analysis of total samples

An optimized chromatogram for French and Italian jasmin oils of 1972 on a high temperature silylated (HTS) glass capillary column is shown in Fig. 3. The peaks have deliberately been kept in scale and the figure shows that the oils contain only a small number of major constituents. It is well known however that by increasing the sensitivity of registration the number of peaks shown on the chromatograms of essential oils and other complex mixtures increases dramatically, almost at will.

Fig. 4 shows wide-bore CGC traces for French, Italian and Algerian oil obtained with a 1400 Varian gas chromatograph with micro-katharometer detector. The sensitivity was set to allow main peaks going off scale to accentuate minor peaks.

Identification of the peaks in the chromatograms of Figs. 3 and 4 was achieved by GC–MS in electron impact (EI) and chemical ionization (CI) modes, by co-chromatography with authentic material and by comparing the MS data of references and those mentioned in the literature. The following (commercially unavailable) compounds were synthesized: *cis*-3-hexenol; linalyl acetate; jasmin lactone; *cis*-hexenyl benzoate; methyl N-acetylanthranilate and 6,10,14-trimethyl-2-pentadecanone (numbers 1, 9, 13, 18, 19 and 23 of Fig. 4 and Table II). The visual differences in the three chromatograms are negligible; there are about fifteen major and fifteen minor peaks. Integration of the peaks, assuming that the response factor for all substances is the same, leads to the values given in Table II. This table also reveals the chemical nature of each peak. The numbers given to the peaks correspond to those in Fig. 4.

There are many more low boiling constituents in the non-French oils. The first half of the chromatograms (peaks 1–15) represents less than 20% of the total for the French oil while it is about 40% for the other oils. It is also noteworthy that, compared to other essential oils, the hydrocarbon content of jasmin oil is very low, and the number of compounds in the oil is low compared to other similar mixtures. Considering Table II it can be stated that French oil contains relatively more alcohols, and the other oils more esters.

It is always possible that a minor compound is responsible for the characteristic smell of a mixture. Therefore, the peaks of the chromatograms of Fig. 4 were tested by the panel mentioned above. The chromatographic conditions (wide-bore capillary, 2-μl sample, split and collection technique as described[34]) facilitate this. None of the peaks has a typical jasmin smell and in none of the oils was detected a particularly strong smelling peak or fraction. Each peak has its own smell and contributes therefore to the total. In fact only a minority of the peaks have what could be called a strong smell, the others hardly smell at all. In the opinion of our panel only

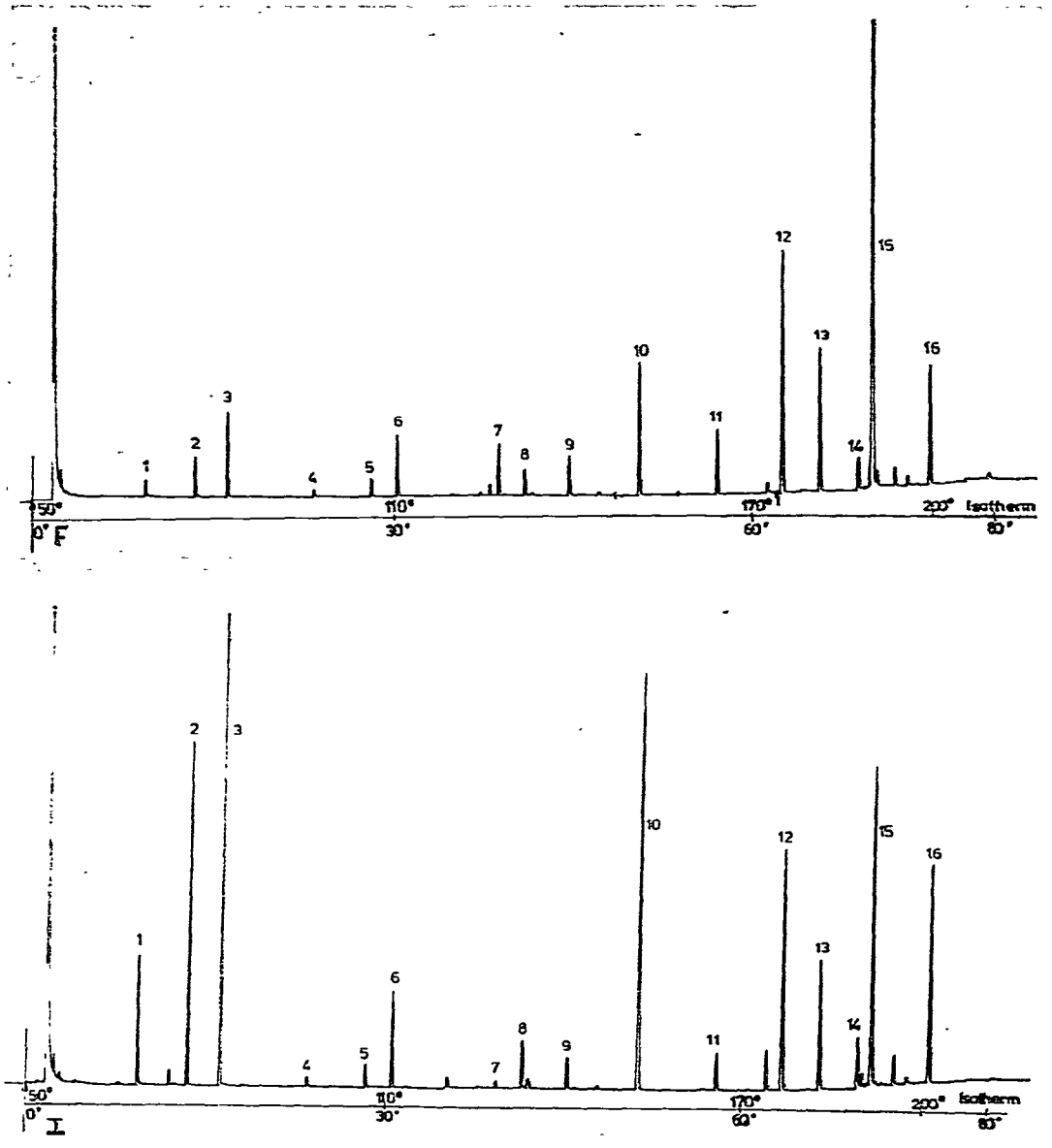

Fig. 3. Chromatograms of French (F) and Italian (I) jasmin oil on a 30 m × 0.5 mm HTS OV-1 glass capillary column. Peaks: 1 = benzyl alcohol, 1a = *p*-cresol, 2 = linalool, 3 = benzyl acetate, 4 = indole, 5 = eugenol, 6 = jasmone, 6a = 5-(*cis*-2-pentenyl)-5-pentanolide, 6b = α-bergamotene, 7 = α-farnesene, 8 = *cis*-3-hexenylbenzoate, 8a = unknown, 9 = methyl jasmonate, 10 = benzyl benzoate, 11 = 6,10,14-trimethylpentadecan-2-one, 11a = methyl palmitate, 12 = isophytol, 13 = geranyllinalool, 14 = isophytyl acetate, 14a = unknown, 15 = phytol, 15a, 15b, 15c = unknown, 16 = phytyl acetate.

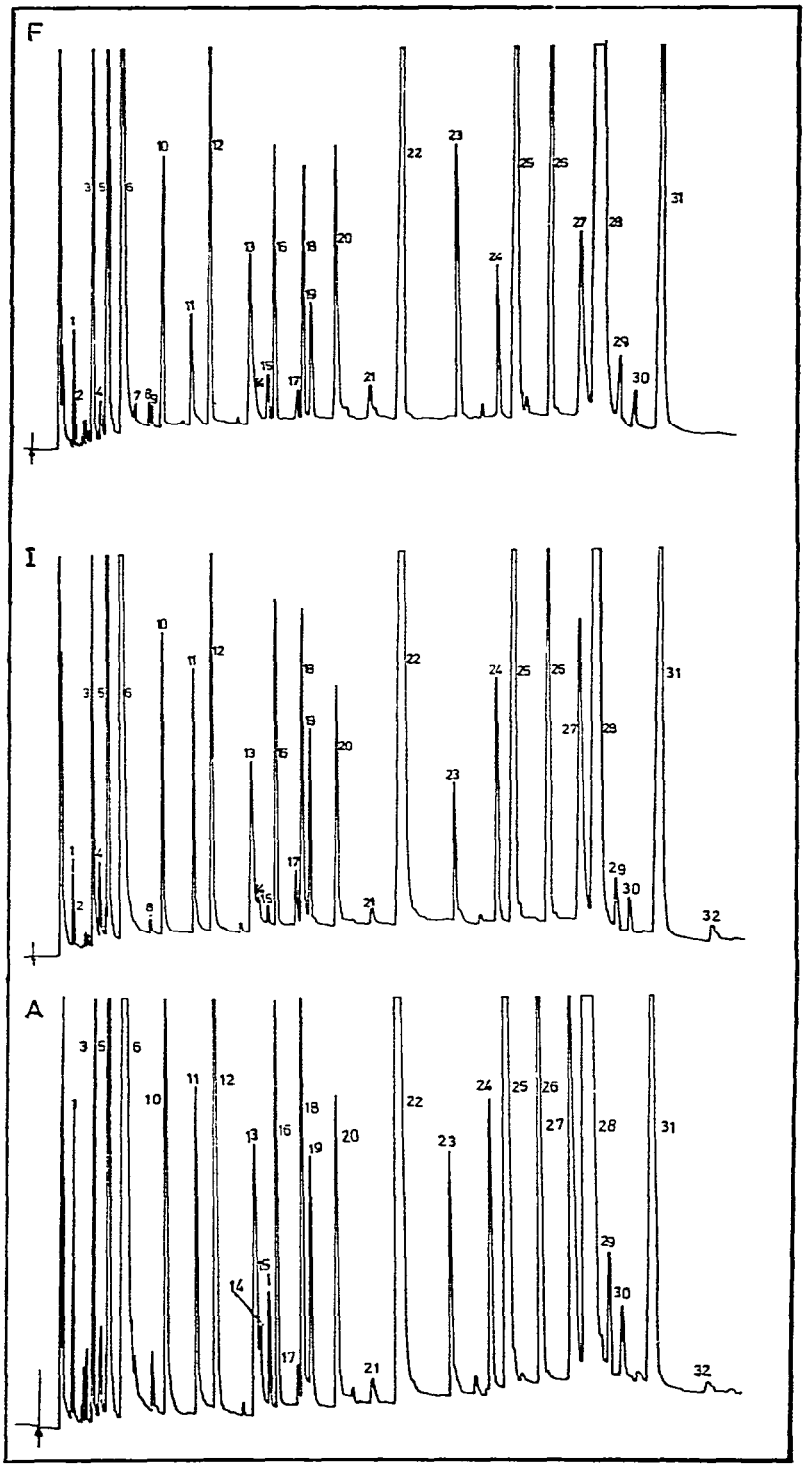

Fig. 4. CGC traces of French (F), Italian (I) and Algerian (A) jasmin oil samples (2 μl, pure) on a 75 m × 0.85 mm SE-30 glass capillary column. Start temperature 125°C, then programmed at 2°C/min to 225°C. Micro-katharometer detection in Varian Aerograph 1400. Bridge at 180 mA, carrier gas (hydrogen) flow-rate 18 ml/min. For peak designations, see Table II.

TABLE II

QUALITATIVE AND QUANTITATIVE COMPOSITION OF SOME JASMIN OILS

Peak No. in Fig. 4	*Name*	*% in mixture*		
		French oil 1972	*Italian oil 1972*	*Algerian oil 1972*
1	*cis*-3-Hexenol	0.4	0.7	—
2	*trans*-2-Hexenol	0.2	0.3	—
3	Benzyl alcohol	0.9	3.0	2.0
4	*p*-Cresol	0.3	0.7	1.0
5	Linalol	1.0	3.6	4.0
6	Benzyl acetate	10.7	25.1	8.5
7	?	—	—	—
8	2-Phenylethyl acetate	0.2	0.2	0.5
9	Linalyl acetate	—	—	—
10	Indole	0.5	0.2	3.7
11	Eugenol	1.1	0.8	3.5
12	Jasmone	1.4	3.0	5.2
13	Jasmin lactone	1.4	1.5	5.5
14	Farnesane	—	—	—
15	Bergamotene	0.9	0.3	1.4
16	Farnesene	0.9	0.8	3.4
17	δ-Laurolactone	—	—	—
18	*cis*-3-Hexenyl benzoate	1.9	1.9	3.9
19	Methyl N-acetyl anthranilate	0.9	0.7	3.5
20	Methyl jasmonate	0.9	1.7	4.0
21	Nerolidol	—	—	—
22	Benzyl benzoate	6.2	13.1	6.5
23	6,10,14-Trimethyl-2-pentadecanone	1.6	1.5	2.2
24	Methyl palmitate	0.5	0.6	0.8
25	Isophytol	1.7	7.5	1.7
26	Isophytyl acetate	7.7	4.0	7.3
27	Geranyllinalool	6.5	3.1	8.0
28	Phytol	52.2	13.6	20.0
29	Ethyl oleate	—	1.1	2.7
30	*n*-Hexadecyl acetate	0.7	0.7	1.7
31	Phytyl acetate	—	7.2	2.6
32	Ethyl linolenate	—	1.1	1.5

the following peaks contribute directly to jasmin oil smell: *cis*-3-hexenol; *trans*-2-hexenol; *p*-cresol; linalool; benzyl acetate; indole; eugenol; jasmone; 5-(*cis*-2-pentenyl)-5-pentanolide; *cis*-3-hexenyl benzoate and methyl jasmonate (numbers 1, 2, 4, 5, 6, 10, 11, 12, 13, 18 and 20 of Fig. 4 and Table II).

The low boiling fraction by vacuum evaporation

Volatiles were obtained by vacuum evaporation and collection as described in Instrumental details. After identical 6-h vacuum evaporation experiments on French and Italian 1972 jasmin oil the weight of condensate obtained is three times greater for the Italian than for the French oil. This clearly reflects the greater volatility of the Italian oil. The composition of the condensates is given in Table III. About 25 peaks each integrating for less than 0.1% in *both* oils are not mentioned in this table. Practically all the peaks in the table are present in both chromatograms. If not indicated, the content is below 0.1%.

TABLE III

LOW BOILING FRACTION OF FRENCH AND ITALION JASMIN OIL

Compound	*Content (%)*	
	French oil	*Italian oil*
Ethanol	1.3	14
Acetone	1.0	—
3-Methylpentane	1.0	—
Butyl methyl ether	0.1	—
3-Penten-1-ol	0.1	—
Penten-3-ol	0.1	—
n-Heptene	0.2	—
Pyridine	0.1	—
4-Methyl-3-hexanol	0.1	—
3-Pentanol	—	0.5
2-Methyl-2-pentanol	—	0.4
3-Methyl-3-pentanol	—	0.8
4-Methyl-2-pentanol	—	0.2
2-Methyl-3-pentanol	—	0.2
Hexanal	—	0.2
3-Hexanol	—	0.1
2-Hexanol	—	0.2
cis-3-Hexenal	0.1	0.1
cis-3-Hexenol	2.0	5.1
trans-2-Hexenol	0.4	3.5
trans-3-Hexenol	—	0.6
n-Heptanal	—	0.2
cis-4-Hexenol	—	0.1
cis-3-Methyl hexenoate	—	0.4
Sabinene	—	0.1
Benzaldehyde	0.3	0.1
Aromatic hydrocarbons	—	0.5
2-Methyl-2-heptenen-6-one	1.1	2
5-Methyl-2-hexenol	0.1	—
cis-3-Hexenyl acetate	0.1	2.5
trans-2-Hexenyl acetate	0.1	1.0
Limonene	0.2	0.2
Benzyl alcohol	11.0	7.0
Neral	—	0.7
Benzyl formate	—	0.3
Terpenol (?)	—	0.4
cis-Linalool oxide	—	1.0
trans-Linalool oxide	—	2.0
Methyl benzoate	0.4	1.0
Linalool	13.0	14.0
Nonanol	1.0	0.6
Benzyl acetate	49.0	37.8
Methyl salicylate	0.1	0.4
2-Phenylethyl acetate	1.4	—
Indole	2.0	—
Eugenol	1.4	—
Jasmone	1.5	—
6-Hydroxyheptenylcyclopentane (?)	0.7	—
Jasmin lactone	1.0	
Farnesane	1.0	—
Bergamotene	1.5	—
Farnesene	3.0	—
cis-3-Hexenyl benzoate	1.0	—
Methyl jasmonate	0.2	—
Benzyl benzoate	0.2	1.3

It is striking that after benzyl acetate (about the middle of the chromatographic run) the Italian oil volatile fraction shows all the peaks but they total only about 2%. The French oil volatile fraction has more than 15% after this benzyl acetate peak! This part of the chromatogram is furthermore the most important part where indole, jasmone, eugenol, jasmin lactone, *cis*-3-hexenyl benzoate and methyl jasmonate appear. In the total oils the sum of the concentrations of these components is reversed, being only 7.2% in the French oil and 9.1% in the Italian oil. Although there are less of the important compounds in the French oil, their concentration in the head space (where it counts!) is much greater than for Italian oil. We attribute this unexpected result to the enhancing and fixating effects of the odourless high boiling components of the oil. This aspect was studied on equilibrium head space mixtures obtained with the instrument in Fig. 1B and also as described in the next paragraph.

ANALYSIS OF ENHANCING AND FIXATING EFFECTS

Our panel found that smell differences were neutralized by adding phytol to Italian oil or benzyl benzoate to French oil. To establish analytically the reasons for this observation, peak areas for jasmone (a polar compound) and farnesene (an apolar compound), both present in about the same amount, were followed as a function of time with the device in Fig. 1B in the head space after adding different non-volatile compounds. These experiments on the influence of the non-volatiles were difficult. For example, collection and transfer of head space vapours to the analysis column was often erratic and quantitatively much more difficult than expected. For this reason we approached the problem from another angle. Instead of looking at the volatiles, we analysed the remaining oil as a function of time. Equal amounts of 10% diethyl ether solutions (100 μl) were spotted on a number of filter strips (8 $\times$ 0.8 cm) and the solvent was allowed to evaporate. The strips were extracted in a small test-tube at the appropriate time by adding methylene chloride (1 ml) containing an internal standard (tridecane). Glass CGC then gave the amounts of remaining jasmone or farnesene for the oils and for oils to which phytol, benzyl benzoate and squalane had been added. Phytol as a medium polar compound and benzyl benzoate as a polar compound are obvious choices as they are both present in large but greatly variable concentrations in the jasmin oils. Squalane was included to determine the effect of an apolar compound. The strips were placed in a large room, but no efforts were made to control temperature, air circulation or other factors that might influence the evaporation process. Still the results were fairly reproducible as shown in Fig. 5 for a repeat experiment following the jasmone peak of French 1972 oil. Similar traces were obtained for the other peaks, other oils and oils to which the same amount of fixator-enhancer had been added (10% oil, 10% fixator-enhancer in diethyl ether). An analysis for a strip coated with French 1972 oil with added benzyl benzoate after 5-h strip evaporation is shown in Fig. 6.

The effect of the fixator-enhancer compounds is only revealed clearly when the values from the addition experiments are divided by the blank values for the unadulterated oils. At time zero this ratio is of course 1, but after evaporation the ratio either increases (fixation) or decreases (enhancement). Curves for jasmone and farnesene in Italian and French 1972 oil are shown in Figs. 7–10.

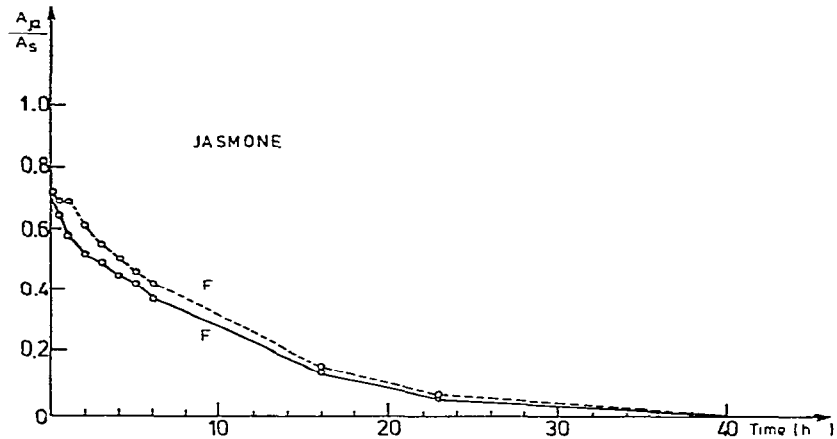

Fig. 5. Evaporation curves for jasmone in jasmin oil. A_{ja} = area of jasmone peak. A_s = area of tridecane internal standard. Test of reproducibility; see text for details.

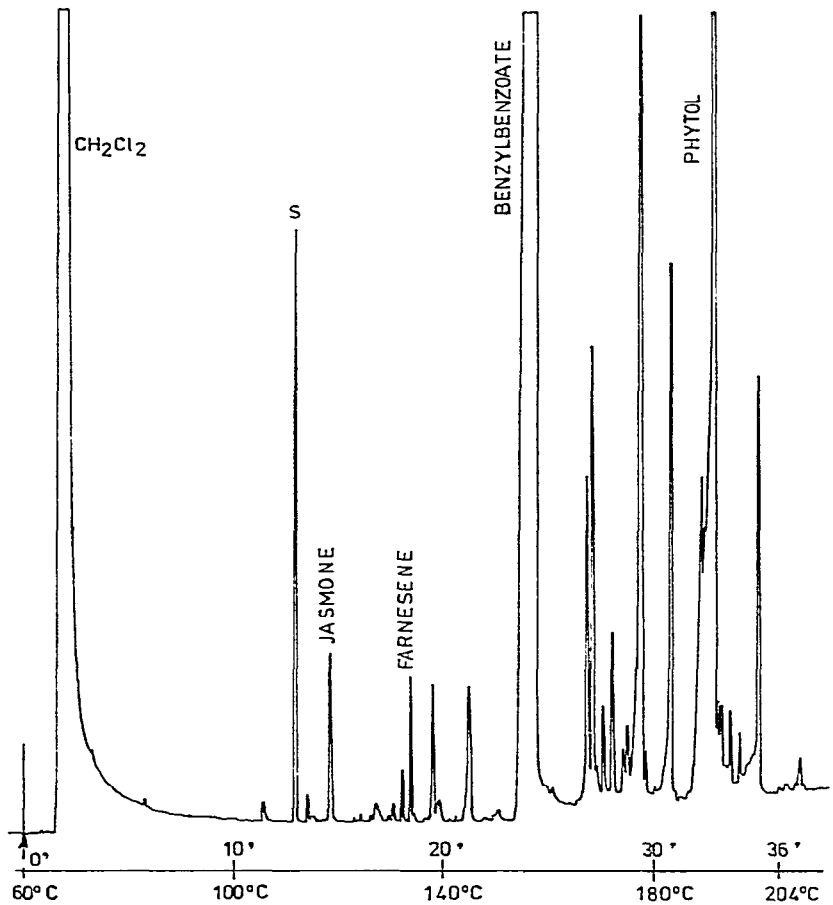

Fig. 6. Example of a chromatogram from an enhancing-fixating experiment as described in the text. French jasmin oil with added benzyl benzoate. Column and conditions as in Fig. 3.

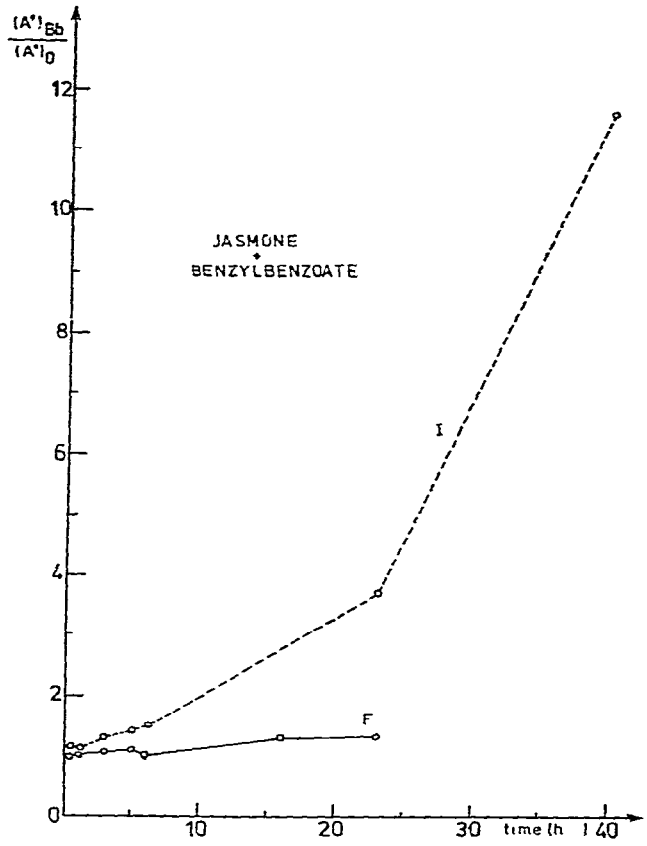

Fig. 7. Evaporation experiment as explained in the text: French (F) and Italian (I) oil with added benzyl benzoate. $(A')_0$ and $(A')_{Bb}$ are the area ratios of the jasmone peak to that of the tridecane (internal standard) peak before and after the addition of benzyl benzoate, respectively.

It is clear that benzyl benzoate fixes (suppresses) jasmone and enhances farnesene while squalane does the opposite. Why addition of benzyl benzoate has a stronger effect on Italian than on French oil is not so clear however. Benzyl benzoate is already present in larger amounts in Italian oil! The very different effect of phytol on both oils is also unexplained. Considering its large content in French oil and the high jasmone concentration in the head space, we had expected an enhancing effect, but the opposite behaviour is observed. Clearly the method described here is suitable for demonstrating enhancing and fixating effects, but essential (jasmin) oils are still too complex for such a simple approach. These are the first results however and hopefully the described approach will provide more significant data in the future. It is clear that benzyl benzoate fixes polar compounds, that other esters like benzyl acetate must act similarly and that their high concentration in Italian oil contributes to lower head space concentrations of polar compounds, at least in the early stages of evaporation.

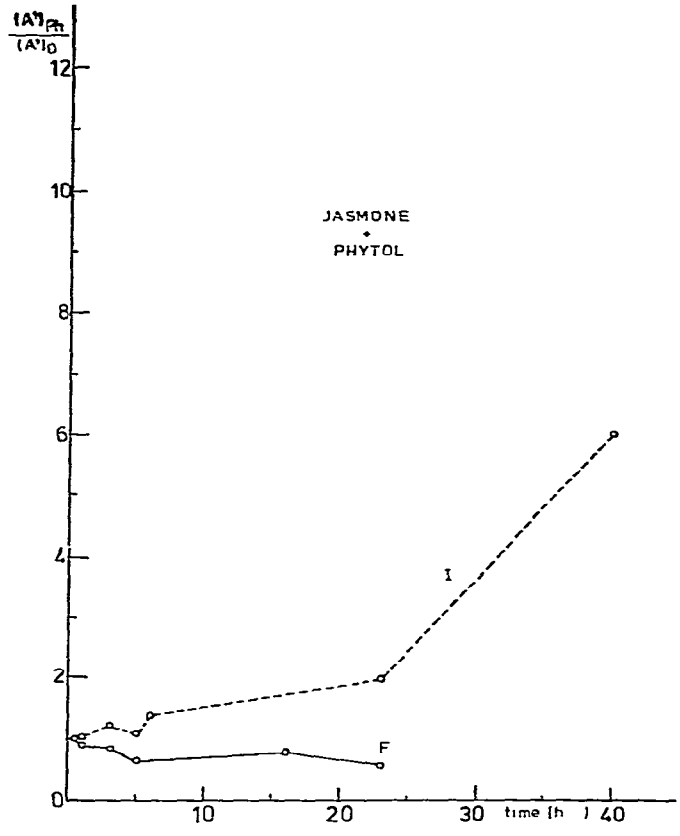

Fig. 8. Evaporation experiment as in Fig. 7 for French (F) and Italian (I) oil with added phytol.

COMPOUNDS OF JASMIN OILS

In the preceding paragraphs it was emphasized that jasmin oils contain only a small number of smell contributing compounds and that minor compounds probably have no influence. Still, in the course of our investigations, a number of compounds were identified from fractions obtained either by partial evaporation as described or by preparative scale GC and by chemical methods.

Large scale preparative GC was optimized for this separation[35] and leads to the chromatogram of Fig. 11. The peaks are numbered as in Fig. 4 and the patterns in both figures are clearly identical. Some of the collected peaks or parts of peaks were almost pure [benzyl alcohol (3), linalool (5), benzyl acetate (6), indole (10), eugenol (11), jasmone (12), farnesene (14), *cis*-3-hexenyl benzoate (18), methyl jasmonate (20), benzyl benzoate (22), isophytol (25), geranyllinalool (27), phytol (28) and phytyl acetate (31)] and easily identified by MS. Other fractions were complex and were further analysed by capillary GC–MS.

Chemical group separations yielded still more detailed information. Hydrocarbons can usually be isolated from essential oils by silica gel column chromatography with a pure hydrocarbon as eluting solvent. This procedure failed with jasmin

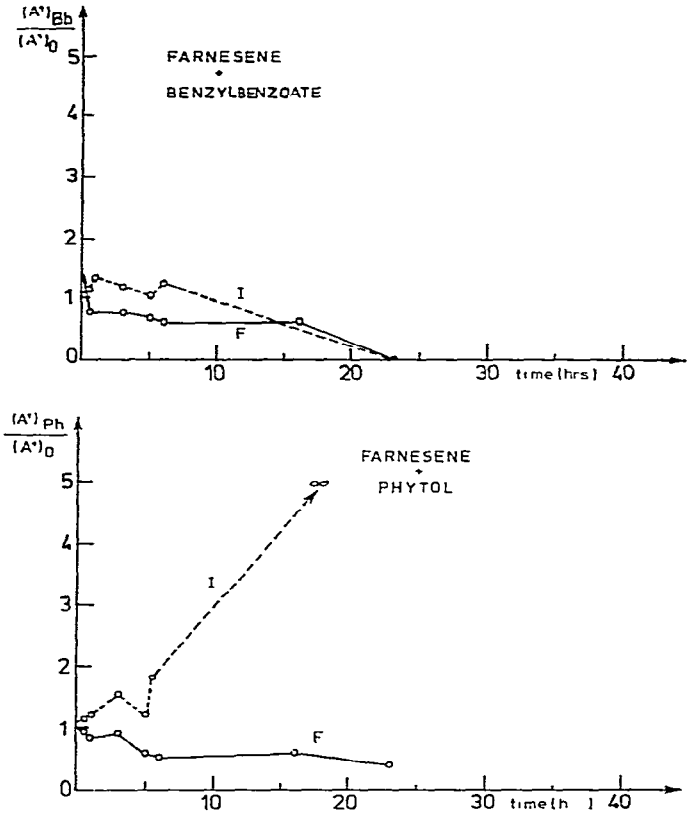

Fig. 9. Evaporation experiments as in Fig. 7 for French (F) and Italian (I) oil with added benzyl benzoate (upper) and phytol (lower).

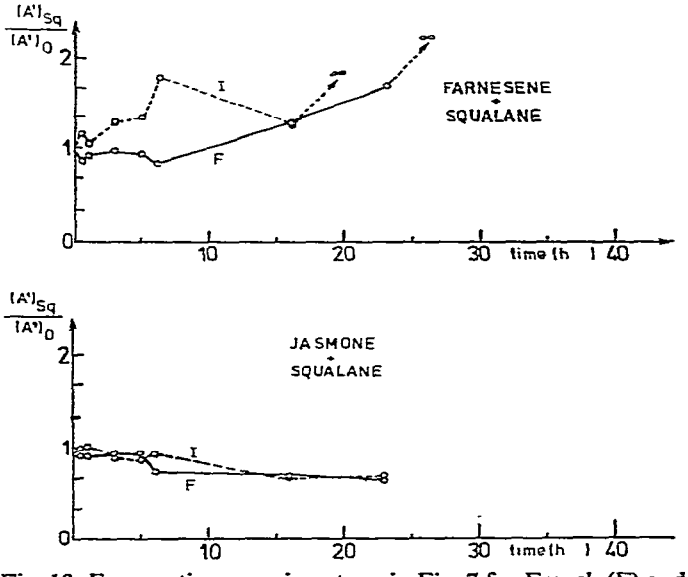

Fig. 10. Evaporation experiments as in Fig. 7 for French (F) and Italian (I) oil with added squalane. Measurements for farnesene and jasmone.

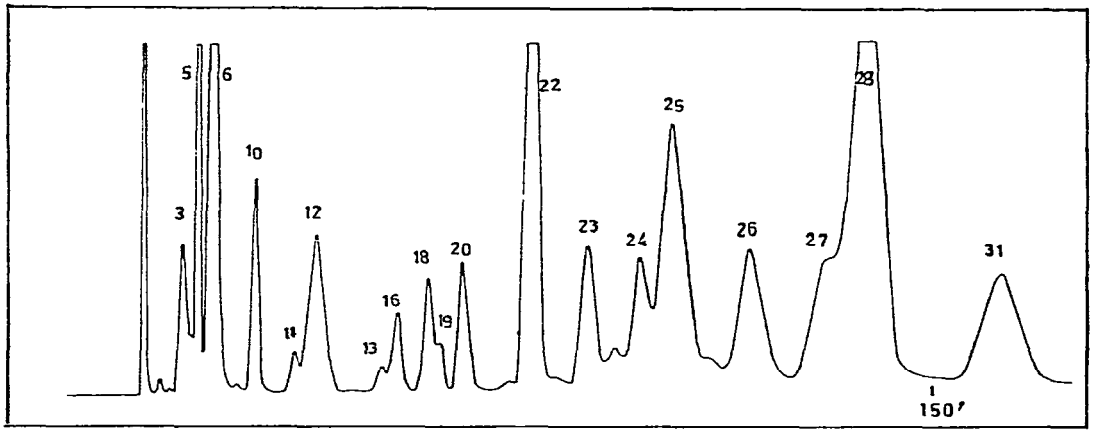

Fig. 11. Large scale preparative GC trace for French jasmin oil. Glass column (12 m × 13 mm) filled with glass beads (60–70 mesh) coated with 1 g SE-30 per 100 ml support. Sample size 200 μl. Hydrogen flow-rate 350 ml/min. Start temperature 120°C, then programmed at 4°C/min to 230°C. Varian Aerograph 713 preparative gas chromatograph.

oil, probably because the hydrocarbon content is too low. Free acids are extracted with alkali. More acids can be obtained in this way after a preliminary ester hydrolysis. Ketones are isolated by extraction with Girard T reagent, alcohols in a similar way by reaction with trichloroacetyl isocyanate. The residue after these treatments consists mainly of ethers and also hydrocarbons which were not separated in the first step. Full experimental details for chemical group separations along these lines have already been published[36]. Identification of the compounds was achieved by CGC, retention data, co-chromatography with authentic material, MS, CGC–MS and even by NMR spectroscopy when possible. Spectral data for particular compounds are avaiable from the authors. The 112 compounds identified by these efforts are listed in Table IV. The 64 compounds marked with an asterisk have not, to our knowledge, been found before in jasmin oil. Many of these are estimated to be artefacts of the extraction procedure.

SYNTHESIS OF SOME JASMIN OIL COMPONENTS

Methyl 2-pyridylacetate was prepared as described by Clarke[37] and 6,10,14-trimethyl-2-pentadecanone was obtained by ozonization of phytol as described[38]. *cis*-3-Hexenal was prepared by ethylation of 1-methoxy-1-buten-3-yne, addition of methanol, partial hydrogenation and acetal scission as described[39]. *cis*-3-Hexenol was obtained by hydrogenation of the above aldehyde. *cis*-3-Hexenyl acetate and benzoate were prepared by esterification of the above alcohol.

5-(cis-2-Pentenyl)-5-pentanolide or jasmin lactone

This lactone is probably a most important aroma-bearing compound in jasmin oil. Intensive synthesis efforts were therefore directed at this target. A method developed by our laboratory has been published[40]. That paper mentions earlier literature. The following approaches were also thoroughly explored.

The Bayer–Villiger ring expansion of pentenylated cyclopentanone was

TABLE IV

COMPOUNDS OF JASMIN OIL IDENTIFIED IN THIS WORK

Hydrocarbons
Isobutane*
Isopentane*
2-Methyl-1,3-butadiene*
Benzene*
3-Methylpentane*
Toluene*
n-Heptane*
Ethylbenzene*
p-Xylene*
Sabinene*
Limonene*
Cumene*
Myrcene*
Diethylbenzene*
Farnesane
α-Bergamotene
α-Farnesene

Alcohols
Ethanol*
2-Methylbuten-3-ol*
3-Methylbutanol*
Pentanol*
3-Pentenol*
Penten-3-ol*
2-Ethylbutanol*
2,3-Dimethyl-2-butenol*
2-Methyl-2-pentanol*
3-Methyl-3-pentanol*
4-Methyl-2-pentanol*
2-Methyl-3-pentanol*
Hexan-3-ol*
Hexan-2-ol*
Octanol*
2-Octanol*
4-Octanol*
cis-3-Hexenol
trans-2-Hexenol
cis-2-Hexenol*
trans-3-Hexenol*
cis-4-Hexenol
4-Methyl-3-hexanol*
5-Methyl-2-hexanol*
Benzyl alcohol
β-Phenylethanol
Linalool
cis-Linalool oxide
trans-Linalool oxide
Nonanol*
6-Nonen-2-ol*
3-Decanol*
2-Hydroxyhexenylcyclopentane* (?)
2-Undecanol*
1,1-Dimethyl-3-hydroxypentenylcyclopentane* (?)
7-Hydroxyheptenylcyclopentane* (?)
3-Methyl-6-hydroxyhexenylcyclopentane* (?)
6-Hydroxyheptenylcyclopentane* (?)
Nerolidol
Geranyllinalool
Isophytol
Phytol
β-Sitosterol*

Esters
cis-3-Methyl hexenoate*
cis-3-Hexenyl acetate
trans-2-Hexenyl acetate
Benzyl formate*
Methyl benzoate
Benzyl acetate
Methyl salicylate
β-Phenylethyl acetate
Linalyl acetate
5-(*cis*-2-pentenyl)-5-pentanolide
δ-Laurolactone*
cis-3-Hexenyl benzoate
trans-2-Hexenyl benzoate
n-Hexyl benzoate
Methyl jasmonate
Methyl dehydrojasmonate
Benzyl benzoate
Methyl palmitate
Isophytyl acetate
Ethyl oleate*
n-Hexadecyl acetate*
Phytyl acetate
Ethyl linolenate*

Carbonyl compounds
Acetone*
cis-3-Hexenal
trans-2-Hexenal
n-Heptanal
Pentan-2-one*
Furfuraldehyde*
Benzaldehyde
2-Methyl-2-hepten-6-one
Neral
Jasmone
n-Hexanal*
6,10,14-Trimethyl-2-pentadecanone

Phenols
p-Cresol
Eugenol

Ethers
Butyl methyl ether*
Ethyl butyl ether*
Ethyl *sec.*-butyl ether*
1,1-Dipropoxyethane*
2,3-Dimethoxypropanol*

N-compounds
Pyridine*
Nitrosobenzene*
Methyl 2-pyridylacetate*
Methyl anthranilate
Methyl N-acetylanthranilate
Indole

Miscellaneous
Chloroform*
1,2-Dichloro-2-methylpropane*
tert.-Butyl chloride
Diethyl sulphide*
Benzoic acid
Ursolic acid

* Not found before in jasmin oil.

investigated by Demole and Winter[41] who reported some success via a dibromo derivative. We studied the same ring expansion via a Beckmann approach. Enamine alkylation of cyclopentanone is no problem and neither is the oxime formation. The ring expansion is however not successful under various conditions and the conversion of the obtained amide into the lactone is also a problem.

The Grignard type coupling reaction of *cis*-3-hexenal and γ-halogenobutyric acid was also investigated. *tert.*-Butyl esters, acetals and oxazolines were used, but all to no avail. Use of 2-lithio-1,3-dithianes in a nucleophilic acylation was also unsuccessful.

Traces of the lactone could often be detected, but we failed to develop a method whereby larger amounts could be prepared reproducibly. This is also true of the published method[40]. Jasmin lactone in a pure state seems to be very unstable. This is probably due to intermolecular polycondensation. However, when the lactone is diluted, as in the case of jasmin oil, this reaction is less likely to occur.

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