New constituents in Egyptian jasmine absolute

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Jasmine absolute, prepared from *Jasminum grandiflorum L.* has been described as one of the most important, if not the most important, natural perfume materials. It has become a most expensive ingredient, as its price, depending on its source, ranges up to more than two thousand dollars per pound.

Extensive research has been done on the identification of the odoriferous constituents of jasmine absolute. A review on its chemical composition from 1899 to 1965 was done by Van der Gen (1972). Since then, a number of valuable constituents have been identified in jasmine by Polak (1973); Stoffelsma and coworkers (1973); Mookherjee and coworkers (1974); Kaiser and Lamparsky (1974); Toyoda and coworkers (1978); and Cheng (1979). However, the total number of compounds reported amounts only to approximately sixty. Although the composition of jasmine oil has been studied for about eighty years, there is still neither agreement on it, nor a completely satisfactory replacement for this natural material.

Jasmine flowers are cultivated in Egypt on a large scale to produce jasmine concrete and its absolute. Egypt is considered one of the major exporting countries of these natural products. However, no detailed analysis of Egyptian jasmine absolute could be found in the literature. The present study is an attempt to identify new and interesting constituents of a high quality Egyptian jasmine absolute.

Experimental

Material used

Fresh flowers of jasmine (*Jasminum grandiflorum L.)* were extracted with perfumery grade purified n-hexane. The extracts were collected, mixed, filtered, and distilled under vacuum to obtain jasmine concrete. Jasmine absolute was then prepared from the concrete by the technique described by Guenther (1960).

Isolation of volatile compounds

The jasmine absolute, 250 g, was distilled at 100°C for one hour under a vacuum of 0.01 mm Hg. The distillate was collected in a series of four traps, which were cooled with dry ice and acetone. The condensate was washed with

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anhydrous reagent grade ethyl ether and then concentrated to approximately 5.81 g using a spinning band distillation apparatus.[a] The distillate amounted to 20.6% of the starting jasmine absolute and is coded JVC I.

The distillation was continued for another hour at 200°C. The distillate thus obtained was coded JVC II. It represented approximately 17% of the jasmine absolute. the residue of the distillation (62.4%) was considered to be jasmine nonvolatile compounds (JNVC).

Gas chromatographic fractionation of volatile compounds

JVC I and JVC II were separated into 22 and 23 broad fractions, respectively, by gas chromatography (figs. 1 and 2). A gas chromatograph, equipped with a flame ionization detector and a 12 foot × ⅛ in OD stainless steel column packed with 10% OV-101 on 60/80 mesh Chromosorb W, was used.[b] The flow rate was 30 ml/min. The column temperature was programmed at 4°C/min from 50-260°C for JVC I and from 100-260°C at 3°C/min for JVC II. Each of the broad fractions was collected in "hairpin" traps made of 3 mm OD borosilicate glass (Thompson and coworkers, 1978). Each of the fractions was sensory evaluated by a highly experienced perfumer from Firmenich, Inc., Princeton, New Jersey.

The broad fractions, which were determined by the perfumer as an interesting aroma to jasmine oil, were each gas chromatographed for a second time using a 12 foot × ⅛ in OD stainless

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[a] K-500 400, Kontes Glass Co.

[b] Perkin-Elmer Sigma 3

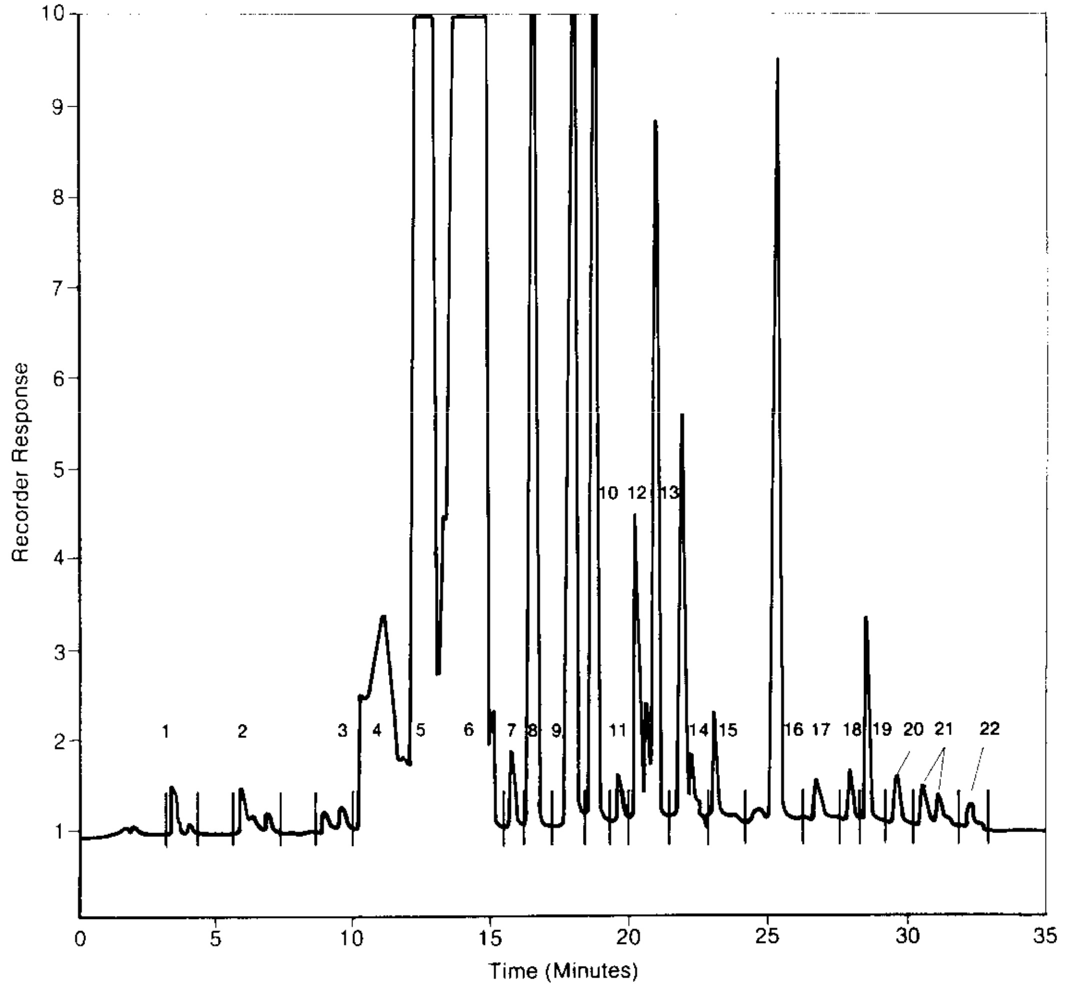

Figure 1. Gas chromatogram of distillate of jasmine absolute (JVC-I).

steel column packed with 10% Carbowax 20M on 50/60 mesh Anakrom ABS. The column temperature was programmed at 100°C, held for 5 min, then 4°C/min to a holding temperature of 215°C for the fractions of JVC I. The column was programmed with a 5 minute isothermal period at 120°C (for Fractions 2 and 3), 140°C (for Fractions 6 and 8), 150°C (for Fractions 12, 16, and 17) of JVC II and then increased at 3°C/min to 215°C and held. The subfractions obtained were accumulatively collected by the method of Thompson and coworkers (1978).

Identification of subfractions

Subfractions were identified by comparing their IR and mass spectra obtained with the reference spectra in the literature, which include the "Eight Peak Index of Mass Spectra" by the Mass Spectrometry Data Center, AWRE, Aldermaston, Reading, UK, and "Sadtler Standard Spectra of IR" by Sadtler Research Laboratories, Philadelphia, Pennsylvania. Their relative percentages were calculated automatically by an integrator.[c]

Infrared spectroscopy was analyzed on an infrared spectrophotometer.[d] The sample was transferred from the collection trap into a 0.1 mm pathlength NaCl microcavity cell using spectroquality grade CCl_4 as the solvent. After IR analysis, the sample solution was recovered for the GC-MS spectrometry.

GC-mass spectral analyses were carried out with a mass spectrometer[e] with a jet separator

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[c] Hewlett-Packard GC, Model 5840A

[d] Beckman Aculab 4, Beckman Instruments, Inc.

[e] DuPont Model 21-490

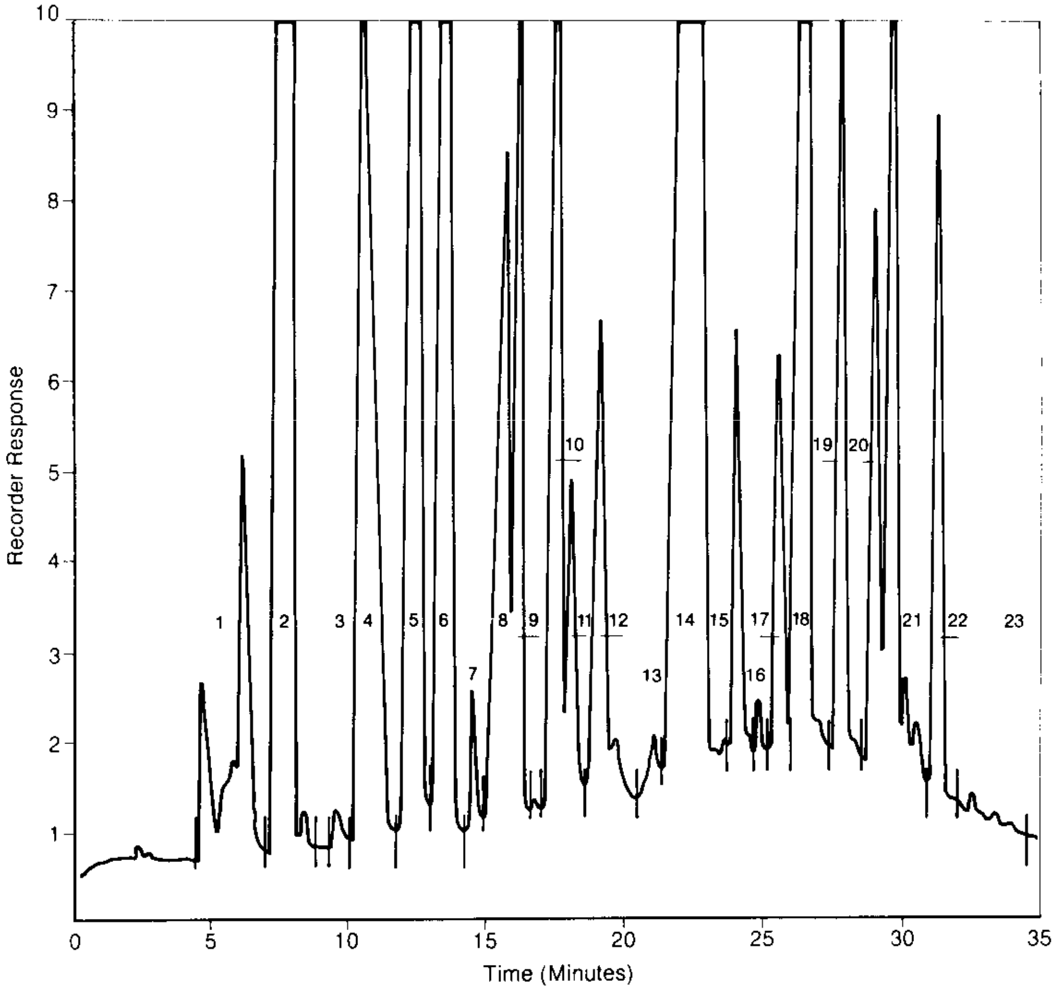

Figure 2. Gas chromatogram of distillate of jasmine absolute (JVC-II).

interfaced with a gas chromatograph[f] with a flame ionization detector. A 12 ft × ⅛ in OD stainless steel column packed with 3% OV-17 on 70/80 mesh. Anakrom ABS was used. The flow rate was 25 ml/min and the column temperature was programmed to provide minimum analysis time with maximum resolution of each subfraction analyzed. Conditions for the mass spectral scans were: ionization voltage—70 ev; ion source temperature—230°C; ion source pressure—10^{-6} Torr; and jet separator temperature—260°C. Chart speed was 5 in/sec and scan speed was 4 sec/decade.

HPLC of nonvolatile compounds

The nonvolatile distillation residue of jasmine absolute was separated into seven broad fractions by high performance liquid chromatography (fig. 3).[g] A reverse μ Bondapack C_{18} column, 3.9 mm ID × 30 cm, particle size 10 microns, was used. The solvent was 70% methanol + 30% water (V/V) with flow rate of 1.0 ml/min. The instrument was equipped with a UV detector and the absorption was recorded at

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[f] Varian Moduline 2700

[g] Model 6000A, Waters Associates, Inc.

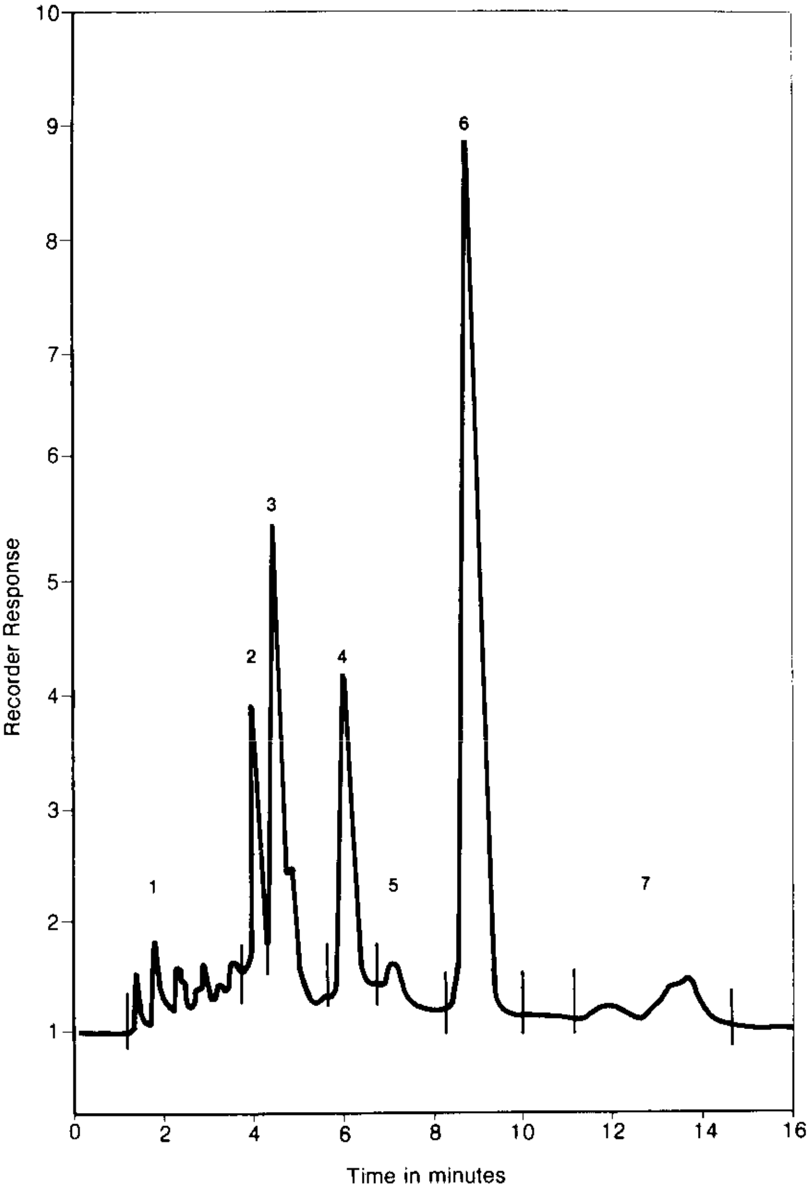

Figure 3. HPLC of the residue of distillation of jasmine absolute (JNVC).

254 nm at a sensitivity of 0.1 A.U.F.S. The recorder chart speed was 1 cm/min. The fractions obtained were collected, extracted with anhydrous reagent grade ethyl ether and then concentrated using a spinning band distillation apparatus.

The seven collected fractions were sensory evaluated by the experienced perfumer. Only Peak No. 6 was found to have an interesting and pleasant aroma. This fraction was rechromatographed with a gas chromatograph[h] fitted with a 12 ft × ⅛ in OD stainless steel column packed with 10% Carbowax 20 M on 50/60 mesh Anakrom ABS. Subfractions obtained (fig. 4) were collected and identified in the same manner as the JVC.

Results and discussion

An Egyptian jasmine absolute prepared from fresh flowers (*Jasminum grandiflorum L.*) was vacuum distilled to yield a distillate at 100°C (JVC-I) 20.6%, a distillate at 200°C (JVC-II) 17%, and a residue of distillation (JNVC) 62.4%.

JVC-I and JVC-II were each gas chromatographed to yield 22 and 23 broad fractions respectively. Sensory evaluation of these fractions by a highly experienced perfumer indicated that Fractions 4, 7, 17, and 20 of JVC-I and Fractions 2, 3, 6, 8, 12, 16, and 17 of JVC-II had an aroma of importance to jasmine absolute (Tables I and II). These fractions were gas chromatographed for a second time and the subfractions thus obtained were collected and identified.

The JNVC were first fractionated by HPLC. The seven fractions obtained were sensory evaluated by the same experienced perfumer.

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[h] Perkin-Elmer Sigma 3

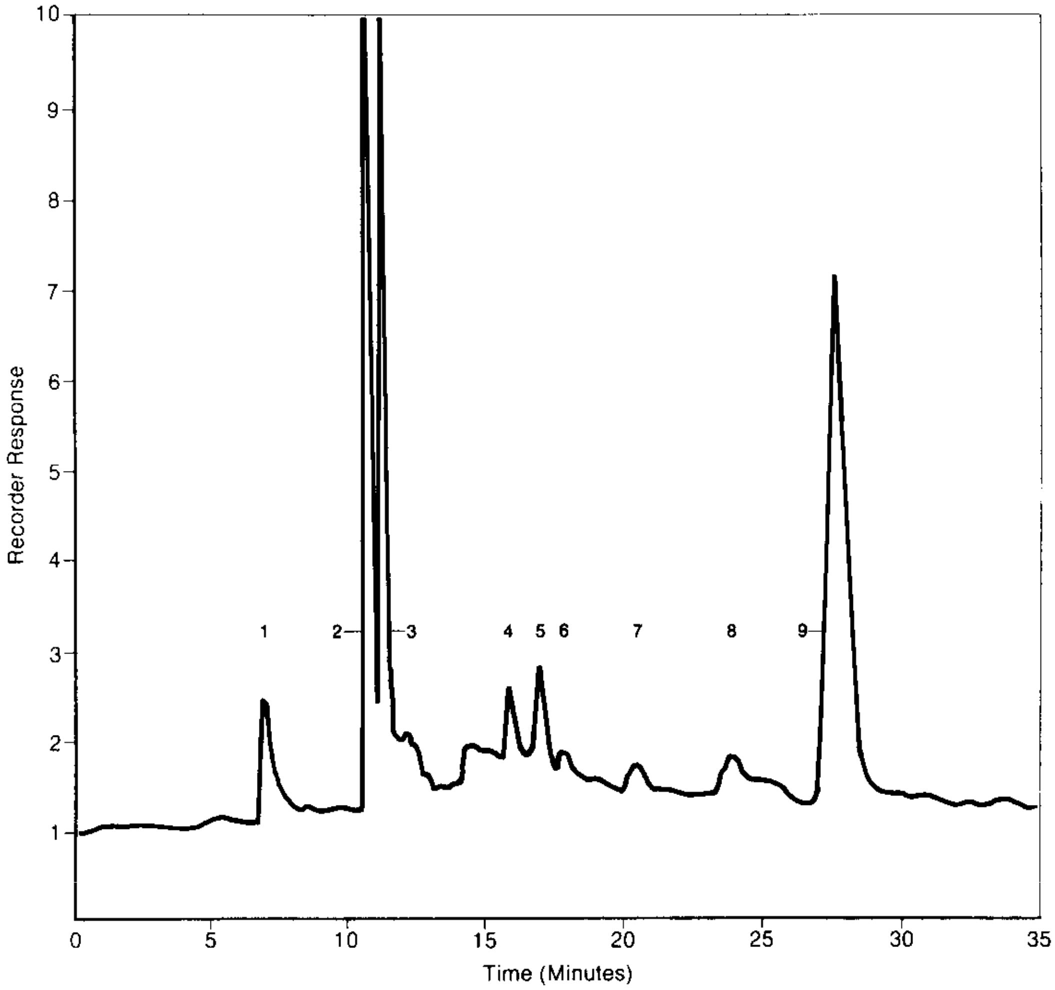

Figure 4. Gas chromatogram of Fraction C obtained from HPLC of the JNVC.

Table I. Description of Aroma of Broad Gas Chromatographic Fractions of JVC I

Broad Fraction No.	Rel. % in Absolute	Odor Description
1	< 0.01	Very volatile fruity
2	0.01	Very volatile off-odor
3	0.03	Very volatile off-odor
4*	3.60	Interesting amber-civet note
5	4.77	Floral, linalool-animal note
6	8.00	Fatty, fruity-animal note
7*	0.03	Fatty, floral jasmine
8	0.66	Indole-like
9	0.83	Eugenol-like
10	0.65	Natural acetates-like
11	0.02	Animal-note
12	0.25	Mushroom-like
13	0.36	Jasmine, lactone, fruity
14	0.27	Detergent-cinnamic note
15	0.07	Pleasant jasmine
16	0.52	Odorless
17*	0.03	Interesting burnt jasmine
18	0.04	Floral-animal note
19	0.13	Pleasant jasmine
20*	0.03	Very light natural jasmine
21	0.08	Weak normal jasmine
22	0.02	Fatty acidic note

*Fractions of importance to jasmine aroma.

Table II. Description of Aroma of Broad Gas Chromatographic Fractions of JVC II

Broad Fraction No.	Rel. % in Absolute	Odor Description
1	0.46	Linalool-animal note
2*	2.38	Burnt jasmine
3*	0.01	Phenolic jasmine
4	1.04	Naphthaline-like
5	1.24	Eugenol-like
6*	1.15	Interesting absolute note
7	0.08	Earthy jasmine
8*	1.09	Nice jasmine, fruity "peach-like"
9	0.04	Odorless
10	0.77	Fishy
11	0.20	Odorless
12*	0.53	Warm jasmine "methyl-jasmonate-like"
13	0.16	Cinnamic aldehyde-like
14	3.40	Weak herbal note
15	0.38	Odorless
16*	0.10	Interesting natural jasmine
17*	0.40	Slightly burnt jasmine
18	1.40	Unpleasant "very burnt, metallic - fishy note"
19	0.55	
20	0.45	
21	0.80	Unpleasant metallic - fishy note
22	0.33	
23	0.02	Burnt animal jasmine

*Fractions of importance to jasmine aroma.

Fraction 6 was found to have an aroma of importance to jasmine absolute. It was further fractionated by gas chromatography and the subfractions collected and identified.

A total of 53 compounds were identified as constituents of Egyptian jasmine absolute. Out of these compounds, 41 have not been reported previously (Table III).

It appears that most major constituents of jasmine absolute have been reported in the literature. However, many minor constituents, which may make important contributions to the total aroma of jasmine absolute, were identified only in the present study, probably due to the improved methodology. For example, among alcohols, benzyl alcohol has previously been found in jasmine (Lederer, 1960) at approximately 1.73% of the jasmine absolute. However, 2,7-dimethylocta-2,7-dienol and 2,4,6-trimethyl-dodeca-11-en-ol were present in jasmine absolute in trace amounts and were identified only in this study. Another example is the esters. The two major constituents, benzyl acetate and cis-methyl jasmonate, were identified previously in jasmine (Demole, 1962; Peyron and Acchiardi, 1979), while the other seven esters that were present in trace amounts (Table III) were identified only in the present study. Among the ketones, jasmone and cis-jasmone were reported previously by Calvarano (1966) and Mookherjee and coworkers (1973). However, the other ke-

Table III. Compounds Identified in Egyptian Jasmine Absolute

Number of Peaks*	Identified As	Identified by MS	Identified by IR	Relative % in Jasmine Absolute
From JVC-I				
	Ester			
4-7-2	** Benzyl formate	x	x	0.56
	Alcohols			
4-7-1	Benzyl alcohol	x	x	1.73
4-4-3	** 2,7-Dimethylocta-2,7-dienol	x	x	< 0.01
17-5-3	** 2,4,6,-Trimethyldodec-11-en-1-01	x		< 0.01
	Ketone			
17-5-4	** 2-Undecanone	x	x	< 0.01
	Nitrogen Compounds			
17-7-1	** 1-Phenyl-2-propylamine	x	x	< 0.01
17-1-1	** 2-Butylpyridine	x		< 0.01
17-2-1	** 1-Phenylpyrrole	x	x	< 0.01
17-6-2	** 4-Phenylbutylamine	x		< 0.01
17-3-2	** 2-(beta-methoxy-alpha-methylethyl)-pyridine	x		< 0.01
	Aldehyde			
4-2-2	Benzaldehyde	x	x	0.01
	Hydrocarbons			
4-4-5	** 2-Methyldecalin	x	x	0.04
17-5-2	** 2,6,10-Trimethyldodecane	x		< 0.01
From JVC-II				
	Esters and Lactones			
2-2-1	Benzyl acetate	x	x	2.27
2-1-2	** Cyclohexyl butyrate	x		< 0.01
8-10-2	** 2-Methylbutyl hexanoate	x	x	0.01
8-14-2	** Benzyl acetoacetate	x		< 0.01
8-12-3	** Citronellyl propionate	x	x	< 0.01
12-3-1	cis-Methyl jasmonate	x	x	0.45
17-7-2	** Methyl myristate	x	x	0.26
17-1-2	** Methyl pentadecanoate	x	x	0.02
17-8-1	** Methyl stearate	x	x	0.01
8-9-2	** delta-decalactone	x	x	0.04

Table Continued

Table III. Compounds Identified in Egyptian Jasmine Absolute (Continued)

Number of Peaks*	Identified As	Identified by MS	Identified by IR	Relative % in Jasmine Absolute
	Alcohols			
2-1-1	Linalool	x	x	< 0.01
8-5-2	** Tridecanol	x	x	0.04
8-6-1	Nerolidol	x	x	0.32
8-13-1	Farnesol	x	x	0.36
8-4-1	6,7-Dihydro-2t-farnesol	x	x	0.12
	Ketones			
2-1-3	** 2,2-Dimethyl-8-oxabicyclo (3,2,1)oct-6-en-3-one	x		< 0.01
16-3-2	** Ethyl 2-methylcyclohex-2-enyl ketone	x		0.02
6-7-1	3-Methyl-2-(2-cis-pentenyl) -2-cyclopenten-1-one or "Jasmone"	x	x	1.13
17-7-1	3-Methyl-2-(2-trans-pentenyl)-2-cyclopenten-1-one or "Jasmone"	x	x	0.01
8-15-1	** 6,7-Diketododecane	x	x	0.05
	Nitrogen Compounds			
3-4-2	** 2-n-Pentylpyridine	x		< 0.01
3-4-1	** 2-Phenylpyridine	x	x	< 0.01
17-2-1	** 2-(5-Nonyl)pyridine	x		< 0.01
16-3-1	** n-Heptadecylamine	x		< 0.01
	Phenol			
8-8-1	** 2-(Pentyl-3)-Phenol	x	x	0.01
	Ether			
8-8-2	** t-Butyl benzyl ether	x		< 0.01
	Hydrocarbons			
8-11-1	** 3-Methyldicyclohexylmethane	x		< 0.01
6-1-2	** n-Tetradecane	x		< 0.01
8-14-3	** Bisabolene	x	x	0.02
8-7-1	** alpha-Farnesene	x	x	< 0.01
8-3-2	** n-Hexadecane	x	x	0.08
From JNVC				
	Esters			
6-1-1	Methyl benzoate	x	x	-
6-1-2	** trans-2-Hexen-1-yl caproate	x		-
6-6-6	Benzyl benzoate	x	x	-
	Alcohol			
6-2-1	Phytol	x	x	-
	Nitrogen Compounds			
6-5-3	** Hippuric acid	x	x	-
6-6-5	** 2-Acetylamino-6-oxo-purine	x		-
6-3-2	** Benzyl-2-(4-anisoyl)-pyrrole	x	x	-
	Phenol			
6-5-2	** 4-Methyl-2, 6-di-t-butyl-phenol	x		-
	Hydrocarbon			
6-1-3	** 1-Cyclohexyl-3-cyclopentylpropane	x		-

* The first, second and third numerals indicate the number of GC peaks during the first, second and third chromatography respectively. For JNVC, the first, second and third numerals indicate the number of HPLC peak and the first and the second GLC respectively.

** Compound not previously identified in jasmine absolute.

tones (Table III) were present in trace amounts and were identified in the present study.

Among the compounds identified, those containing nitrogen are of particular interest. From JVC-I, five nitrogen compounds were identified (Table III). They may contribute to the burnt note of jasmine absolute. All of these compounds were identified from broad Fraction No. 17, which was originally described as having an interesting burnt aroma that contributes one of the important aroma notes to the jasmine absolute.

Five pyridine compounds were identified in this study, namely, 2-butylpyridine, 2-(β-methoxy-α-methylethyl)-pyridine, 2-phenylpyridine, 2-(5-nonyl)pyridina, and 2-n-pentylpyridine. None of them has been reported previously as a minor constituent of jasmine absolute. These pyridine compounds are powerful odorants. For example, 2-n-pentylpyridine has an odor threshold of 0.6 ppb in water. Therefore, these pyridine compounds may be important to the total aroma of jasmine absolute.

A group of compounds that has not been reported previously in jasmine absolute is the lactones. The importance of lactones to the flavor of foods has been reported by May and coworkers (1978). The δ-decalactone found in this study is a powerful odorant and may contribute to the total aroma of jasmine absolute.

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