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Note

Characterization of volatile components in apricot purées by gas chromatography–mass spectrometry

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The characterization of the volatile components in apricot purée has been carried out as part of a study dealing with the definition of the quality level of foods on the basis of analytical data. Volatile substances are the main factors responsible for aroma, which, together with other factors such as taste and physical and psychological factors, contributes to the "flavour".

Apricot purées are semi-manufactured products from the industrial production of fruit juices. Some studies dealing with the characterization of apricot aroma have been reported and different procedures for the sampling of the volatiles have been proposed. In one of the earliest studies, Tang and Jennings [1,2] used absorption on charcoal and gas chromatographic (GC) separation for their identification on fruits belonging to the Blenheim variety Terpenic hydrocarbons, terpenic alcohols, lactones and organic acids were identified. Rodriguez *et al.* [3] studied the volatile compounds of the Rouge de Rousillon cultivar, starting both from fresh fruits and from industrially manufactured purées. In their work two different extraction procedures were used. By means of GC–mass spectrometry (GC–MS), terpenes, terpenic alcohols, lactones and methyl and ethyl esters of fatty acids were identified. Chairote *et al.* [4] studied the volatile components of apricot purées of the same variety using two different isolation techniques: a trapping technique, using a Chromosorb 105 trap for the enrichment of the samples, and a vacuum steam distillation followed by fractionation on a silica column. Several compounds were identified for the first time in these products including 3-nonen-2-one, *p*-hydroxybenzaldehyde, damascenone, *β*-ionone, dihydroactinidiolide and 2-phenylethanol.

More recently, Guichard and Souty [5] determined the relative amounts of aroma compounds in fresh fruits of six different varieties having different organoleptic properties. The most abundant substances were found to be terpenic alcohols, lactones, phenolic aldehydes and sesquiterpenic ketones. The volatile components were isolated by vacuum distillation at room temperature, extraction of the distillate with dichloromethane and fractionation of the extracts on a silica column.

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The results of the quantification of twelve volatile components of apricot, obtained by adding known amounts of the single components before the extraction, were compared by Guichard [6] with those obtained with the internal standard method. Considerable differences were observed using the two methods. A selection and classification of 56 volatile components of apricot were achieved by Schlich and Guichard [7] using statistical methods; the components were grouped according to their chemical class.

In this work, the aroma components of apricot purées, industrially manufactured, were characterized using the purge and trap technique for the extraction of the volatile substances with the aim of obtaining a GC profile of the volatile fraction of the different samples and identifying new compounds in this fraction. Using capillary GC–MS 105 compounds were identified.

EXPERIMENTAL

Samples

Twenty purée samples derived from different batches supplied by fruit-juice producers (Eckes, Trento and Zipperle, Merano, Italy) were examined. These purées were obtained from fruits of different varieties and origin, cultivated in Italy. The apricot purées were heated at 115–120°C for 1 min and then frozen and maintained at −18°C until the analysis.

Extraction procedure for volatile substances

The volatile components of the apricot purées were isolated by means of the purge and trap technique, using Tenax as adsorbing material.

To 40 g of purée, 40 g of water were added, followed by 4.5 μg of methyl salicylate, to be used as internal standard to check the reproducibility of the sampling procedure for the different samples. The sample, thermostated at 50°C, was purged with purified helium for 10 min at a flow-rate of 50 ml/min, then the aroma components were stripped out with the same flow of helium and adsorbed on a Tenax trap. To eliminate the adsorbed water, which could interfere in the GC analysis, the trap was flushed with helium for 10 min.

The substances trapped on Tenax were thermally desorbed and injected into the gas chromatograph using a Chrompack TCT thermal desorption cold trap; the Tenax trap was heated at 240°C for 10 min under a helium flow (flow-rate 10 ml/min). The desorbed compounds were cryofocused in a silica capillary, cooled at −108°C; the capillary was then quickly heated to 200°C for injection into the column. The traps for adsorption, purchased from Chrompack, consisted of glass tubes (16 cm × 4 mm I.D.) filled with Tenax (90 mg, 20–35 mesh).

Gas chromatography and mass spectrometry

For GC analysis a Dani 3865 chromatograph, equipped with a flame ionization detector was used with injector and detector temperatures of 250°C.

GC–MS analysis was carried out using a Finnigan system consisting of a Hewlett-Packard Model 5890 gas chromatograph, an Incos 50 quadrupole mass spectrometer and a Data General computer. Ionization was effected by electron impact (70 eV). The gas chromatograms were recorded by monitoring the total ion current in the 35–350 u range; below these values it was not possible, with the sampling device used, to avoid interferences from peaks derived from air. The temperatures of the interface and of the ion source were 240 and 140°C, respectively.

Using both flame ionization and mass detection, chromatographic separations were carried out on a DB-WAX bonded-phase column (J. & W. Scientific) (30 m × 0.25 mm I.D., film thickness 0.25 μm. The column temperature was held at 40°C for 6 min, then increased from 40 to 60°C at 2.5°C/min and from 60 to 220°C at 7.5°C/min, holding this temperature for 6 min.

The compounds used as reference substances in the GC analysis were obtained from Aldrich.

RESULTS AND DISCUSSION

Table I lists the substances identified in the apricot purées by means of GC/MS following the described procedure. The third column lists the literature sources which report the corresponding substances among the volatile components of apricot and the fourth column indicates the number of samples out of 20 in which the substances were found in this work. The identifications were obtained by mass spectrometry and, where possible, were confirmed by comparison with authentic substances used as references. Fig. 1 shows the chromatograms obtained with flame ionization detection for two samples having considerably different aromatic profiles and Fig. 2 shows a chromatogram obtained by GC–MS; the peaks are numbered according to Table I.

Using the purge and trap technique, more than 150 compounds were isolated; among these, 105 were identified, 44 of which have not been reported previously. The identified compounds are 14 hydrocarbons, 33 carbonyl derivatives, 30 alcohols, 1 phenol, 4 carboxylic acids, 17 esters, 3 lactones, 2 furans and 1 pyran. Among these are substances that are considered to be typical components of apricot aroma [4] such as benzaldehyde, linalol, α-terpineol, geraniol, linalol oxides, γ-octalactone and γ-decalactone.

Nerol, geraniol and oxides of terpenic alcohols are known to be formed via thermal decomposition of hydroxylic derivatives of linalol [9]. These compounds were found in all the samples and their presence may be due to the blanching undergone by these apricot purées during industrial production, or to the effects of heating in the extraction steps.

Among the compounds identified for the first time as volatile constituents of the apricot purées are methyl acetate, ethyl butanoate, α-phellandrene, α-terpinene, (*E*)-ocimene, acetyl methyl carbinol acetoin, α-farnesene, geranylacetone, phenol, nerolidol I and II and isopropyl myristate and palmitate. With regard to the last two compounds, in a previous study [3] the methyl and ethyl esters of fatty acids were identified as volatile components in frozen apricot fruits.

In addition to the cited compounds, 1,1,6-trimethyl-1,2-dihydronaphthalene and 1,5,8-trimethyl-1,2-dihydronaphthalene were identified; these compounds have structures related to that of β-ionone. The first has been found in peaches, strawberries and in red wine and is probably formed by oxidation of (6-*trans*-2′-*trans*)-6-(but-2′-enylidene)-1,5,5-trimethylcyclohex-1-ene by the following mechanism [10]:

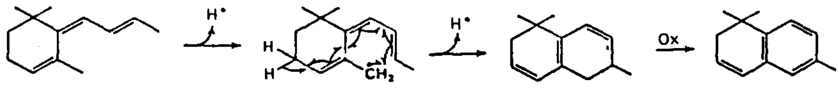

TABLE I

VOLATILE COMPOUNDS IDENTIFIED IN APRICOT PURÉES

No.	Aroma compound	Ref.	Occurrence	Method of identification[a]
1	Acetone	3	20	MS
2	Methyl acetate		19	MS
3	2-Methylfuran		15	MS
4	Butanal	5	12	RT, MS
5	Ethyl acetate	5	20	RT, MS
6	2-Butanone	5	16	MS
7	2-Methylbutanal	5	19	MS
8	Ethanol	5	5	RT, MS
9	Ethyl propanoate	5,8	10	MS
10	Pentanal	3,5	18	MS
11	2-Pentanone	5	4	MS
12	Isobutyl acetate	5	20	MS
13	3-Methyl-2-pentanone		5	MS
14	Toluene	5	20	MS
15	Ethyl butanoate		18	MS
16	1-Propanol	8	14	MS
17	2-Methyl-3-buten-2-ol		20	MS
18	Butyl acetate	5	20	MS
19	Hexanal	3,5	20	RT, MS
20	2-Methyl-2-butenal		2	MS
21	2,6,6-Trimethyl-2-vinyltetrahydro-2*H*-pyran		20	MS
22	2-Methyl-1-propanol	8	18	RT, MS
23	2,4-(8-*p*-Menthadiene)	3	10	MS
24	3-Methylbutyl acetate	5	10	MS
25	α-Phellandrene		4	MS
26	β-Myrcene	1,3,4	20	RT, MS
27	α-Terpinene		20	RT, MS
28	Isobutyl butanoate		1	MS
29	Limonene	1,3,4	20	RT, MS
30	Amyl acetate	5	6	RT, MS
31	1-Butanol	5,8	20	RT, MS
32	Heptanal	5	17	RT, MS
33	1-Penten-3-ol		13	RT, MS
34	2-Heptanone	5	12	MS
35	Eucalyptol	5	18	RT, MS
36	2-Pentylfuran		12	MS
37	(*E*)-Ocimene		7	MS
38	(*E*)-2-Hexenal	3	5	RT, MS
39	γ-Terpinene	3,4	11	RT, MS
40	2-Methyl-1-butanol		15	MS
41	3-Methyl-1-butanol	8	11	RT, MS
42	Ethyl hexanoate	5,8	1	MS
43	*p*-Cymene	3,4	20	MS
44	3-Octanone		5	MS
45	3,7,7-Trimethylbicyclohept-2-ene		20	MS
46	1-Pentanol	3,5,8	19	RT, MS
47	Hexyl acetate	5,8	20	MS
48	Octanal	5	14	MS
49	Acetyl methyl carbinol acetoin		16	MS
50	2,6,6-Trimethylcyclohexanone		20	MS
51	(*Z*)-4-Hexenyl acetate		17	MS
52	(*Z*)-2-Heptenal		17	MS
53	2,3-Octanedione		20	MS

TABLE I *(continued)*

No.	Aroma compound	Ref.	Occurrence	Method of identification[a]
54	(*E*)-2-Hexenyl acetate		17	MS
55	6-Methyl-5-hepten-2-one	3,5	20	RT, MS
56	1-Hexanol	3,4,5,8	20	RT, MS
57	(*E*)-3-Hexen-1-ol		6	RT, MS
58	Nonanal	5	18	RT, MS
59	3,5,5-Trimethyl-2-cyclohexen-1-one		10	MS
60	(*Z*)-3-Hexen-1-ol	3,5	20	RT, MS
61	Buthyl hexanoate		5	MS
62	(*Z*)-2-Hexen-1-ol		18	MS
63	(*E*)-2-Decenal		3	MS
64	Epoxydihydrolinalol I	1,2,3,4	19	MS
65	1-Hepten-3-ol		11	MS
66	Furfural	8	20	MS
67	6-Methyl-5-hepten-2-ol		2	MS
68	Epoxydihydrolinalol II	1,2,3,4	20	MS
69	(*E*,*E*)-2,4-Heptadienal	5	2	MS
70	Decanal	5	6	MS
71	Benzaldehyde	3,4,5	20	MS
72	3-Nonen-2-one	4	1	MS
73	Linalol	1,2,3,4,5,8	20	RT, MS
74	1-Octanol	8	18	RT, MS
75	Terpinen-4-ol	3,4,5	6	RT, MS
76	2,6,6-Trimethyltetrahydrobenzaldehyde		20	MS
77	Butanoic acid		3	MS
78	2,6,6-Trimethyldihydrobenzaldehyde		20	MS
79	α-Terpineol	1,2,3,4,5	20	RT, MS
80	Ethyl benzoate	5,8	2	MS
81	1,1,6-Trimethyl-1,2-dihydronaphthalene		20	MS
82	1,5,8-Trimethyl-1,2-dihydronaphthalene		1	MS
83	α-Farnesene		14	MS
84	Geranial	1,3	7	MS
85	1-Decanol	8	3	MS
86	Nerol	3,4	20	MS
87	Damascenone	4	8	RT, MS
88	Hexanoic acid	2	4	MS
89	Geraniol	3,4,8	20	RT, MS
90	Geranyl acetone		19	RT, MS
91	2-Phenylethanol	4,5,8	3	RT, MS
92	γ-Octalactone	1,2,3,4,5	3	RT, MS
93	β-Ionone	4,5	20	RT, MS
94	1-Dodecanol		7	MS
95	2,4,4-Trimethyl-3-(2-butenyl-2-cyclohexen-1-one)		9	MS
96	Phenol		19	MS
97	Isopropyl myristate		20	MS
98	Nerolidol I		5	MS
99	γ-Decalactone	1,2,3,4,5	20	RT, MS
100	Isopropyl palmitate		6	MS
101	Nerolidol II		2	MS
102	γ-Dodecalactone	2,4	6	RT, MS
103	Myristic acid		7	MS
104	Palmitic acid		8	MS
105	Farnesol	3,4	3	RT, MS

[a] MS = Identified by means of mass spectrometry. RT = identified by comparison with retention time of authentic reference compounds.

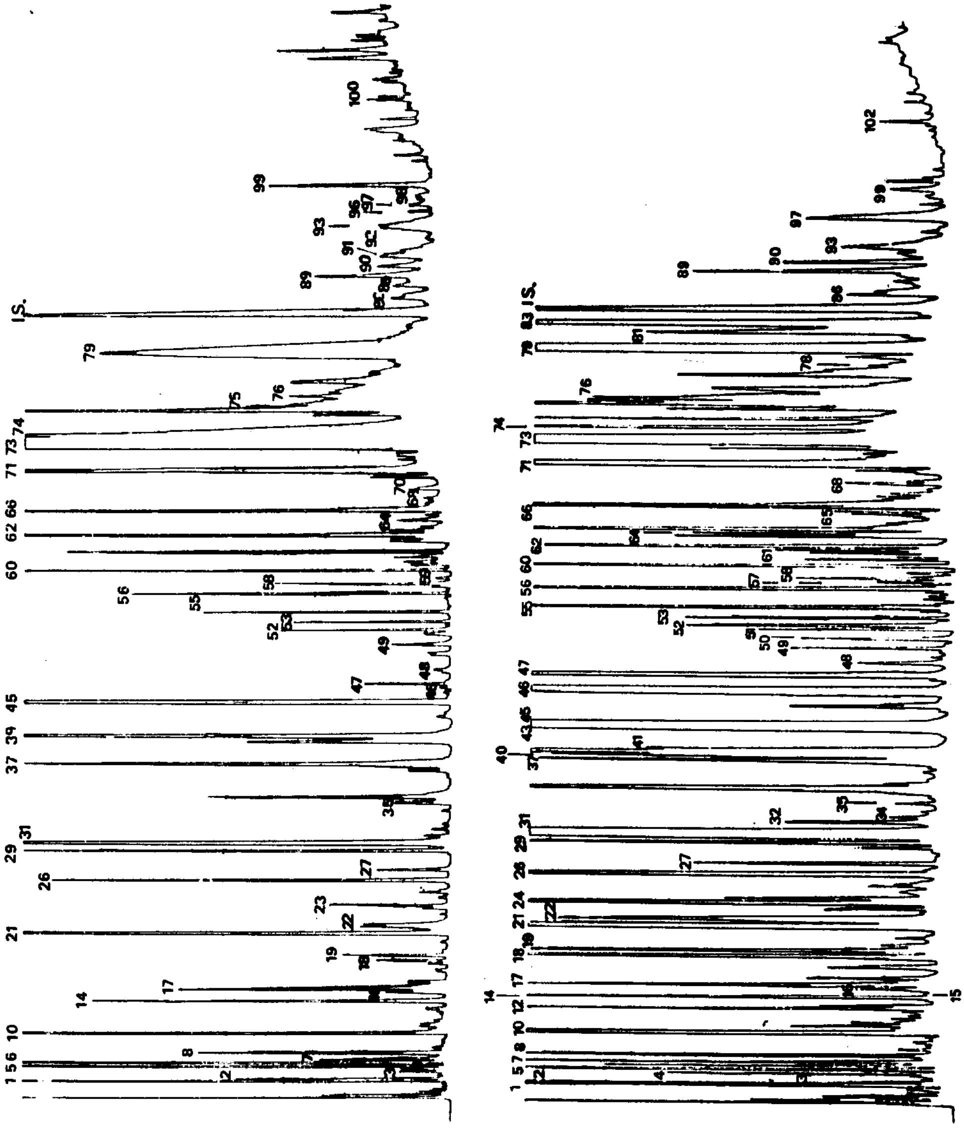

Fig. 1. Gas chromatograms of volatile compounds of two apricot purée samples obtained by means of flame ionization detection. For peak numbers, see Table I.

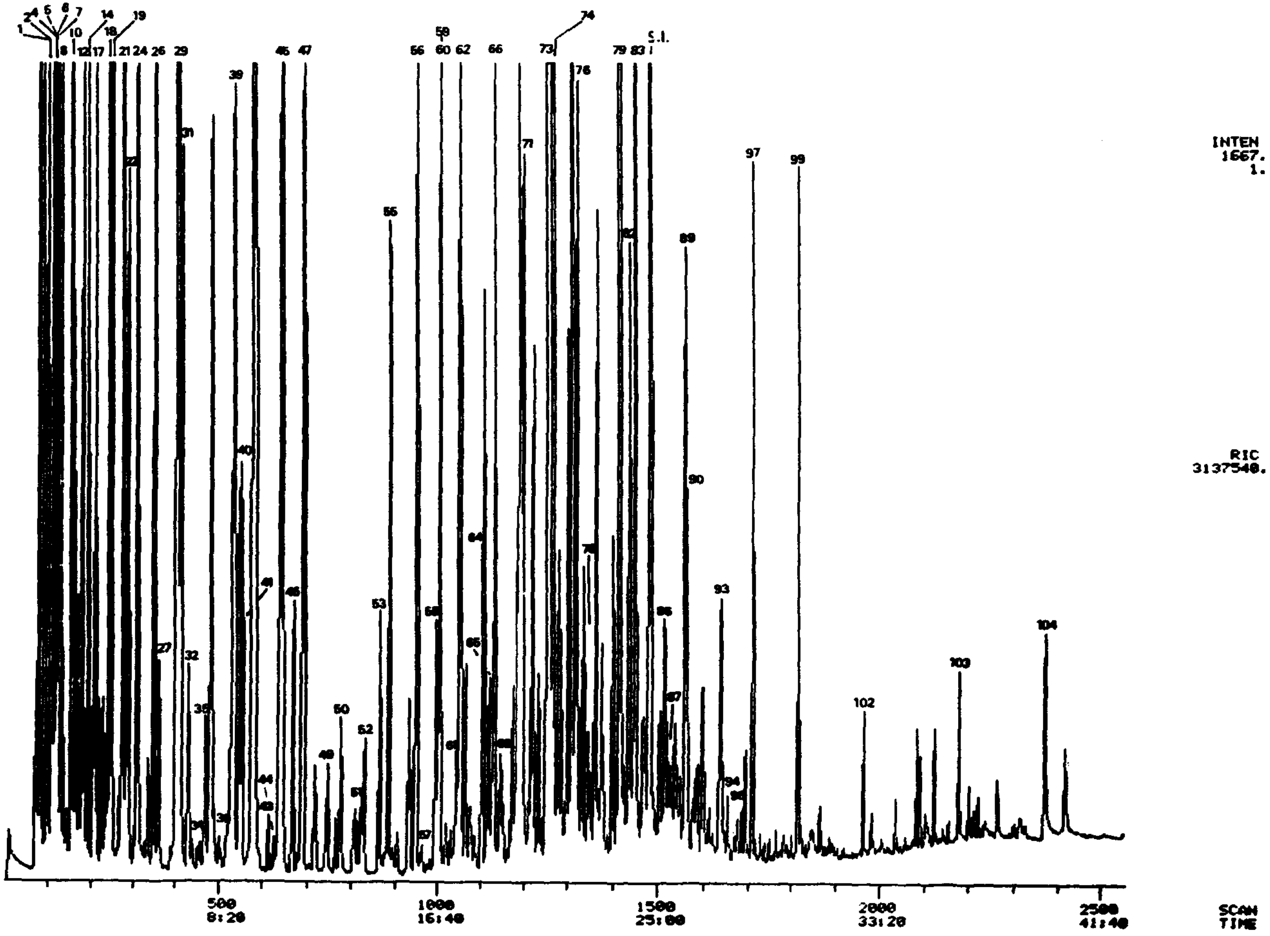

Fig. 2. Gas chromatogram of volatile compounds of a purée sample obtained by means of GC–MS; the signal was obtained by monitoring the total ion current in the range 35–350 u. For peak numbers, see Table I.

Moreover, the mass spectra indicate the presence of a series of compounds which are positional isomers of *x,y,z*-trimethyl-1,2,3,4-tetrahydronaphthalene (TTN), having a structure related to that of α- or β-ionone. These compounds have similar mass spectra, with the parent peak at *m/z* 159 and the molecular peak $M^+ = 174$, relative abundance 30–40%; Fig. 3 shows the mass spectrum of a trimethyltetrahydronaphthalene. Some of these substances have been found in some varieties of ruhm [11,12] and could be derived from the thermal degradation of β-carotene [13,14].

The two unsaturated ketones, 6-methyl-5-hepten-2-one and 6,10-dimethyl-5,9-undecadien-2-one, known as geranylacetone, may be derived from the oxidation of carotenoids, both having licopene as aroma precursor [10]. Other identified degradation products of carotenoids are β-ionone and damascenone; these compounds have already been found in several products such as tea [15], tobacco [16] and grape [17]. Damascenone, together with linalol oxides, is considered to be responsible for the overcooked note of the aroma and can form in the industrial manufacture of apricot purées [4].

A series of substances were extracted and separated, but it was not possible to give them a definite attribution; however, because of the presence in the mass spectra of fragments at *m/z* 136, 121, 93 and 68, a monoterpenic structure can be attributed to these substances.

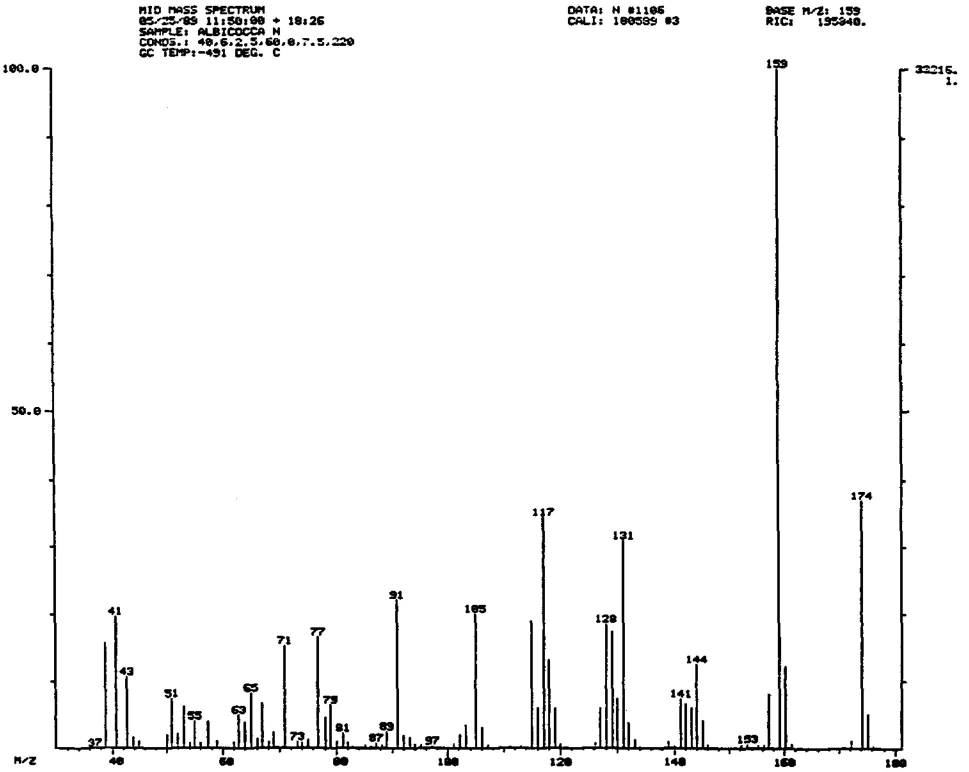

Fig. 3. Mass spectrum of a trimethyltetrahydronaphthalene.

As shown by the list of compounds in Table I, with purge and trap sampling it was possible to extract both very volatile compounds such as methyl and ethyl acetate and poorly volatile compounds such as the lactones; these compounds determine the fruity note of the apricot aroma [5], but cannot be detected with static and dynamic headspace techniques [18,19]. Moreover, the use of cryoconcentration permits fast injection of the sample into the column and contributes to the high efficiency of the chromatographic separation.

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