The Composition of the Volatile Fraction of the Italian Citrus Essential Oils

By Giovanni Dugo, Università di Messina, Italy

The annual production of citrus fruits in Italy amounts to about 3,500,000 tons, 31% of which goes to the transformation industries. Table I reports the production data, the quantity transformed and the essential oil obtained from each fruit.[1]

Unfortunately, it is difficult to find accurate information about bitter orange and its essential oil because the production of this type of orange is very limited.

The contribution of Sicily and Calabria to citrus production in Italy reaches 90% at least, which makes them the most important suppliers of Italian citrus products. In particular, Sicily produces about 70% of the total amount of citrus, and 90% of lemon fruit produced in Italy.

Figure 1 shows the Sicilian and Calabrian fruit-growing areas for each fruit. The transformation industries are situated in the same areas.

In Italy the citrus fruit season starts in October-November. Production and processing periods of different *Citrus* species differ remarkably (Figure 2). The lemon season lasts the entire year; in the first part of the season, "primofiore" lemons are processed, from then, up to spring, "winter" lemons, then "bianchetti" and finally, in summer, "verdelli" lemons.

The productive season of the other citrus fruits is more limited. For example, mandarin season starts in October

A. Cotroneo, R. Del Duce, M.G. Donato, Giacomo Dugo, P. Dugo, G. Lamonica, G. Licandro, L. Mondello, I. Stagno d'Alcontres, A. Trozzi and A. Verzera have taken part in the research which allowed this report.

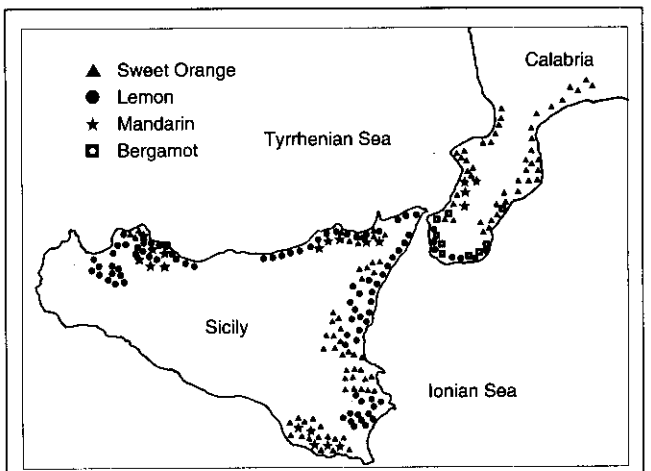

Figure 1. Citrus growing areas in Sicily and Calabria

Table I. Production of citrus fruits and their essential oils during the 1991/1992 season

Fruit type	Fruit Produced tons	Transformed tons	Essential oil tons
Lemon	860,000	195,000	775
Sweet orange	2,004,000	790,000	1,350
Mandarin and other small fruit	523,000	63,000	315
Bergamot	18,000	18,000	100

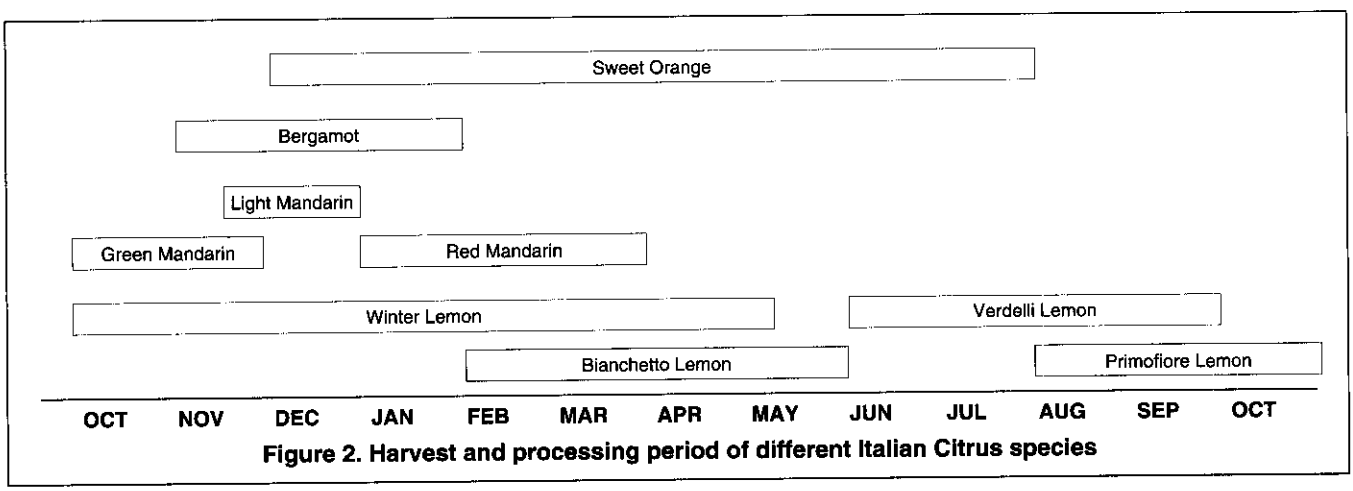

Figure 2. Harvest and processing period of different Italian Citrus species

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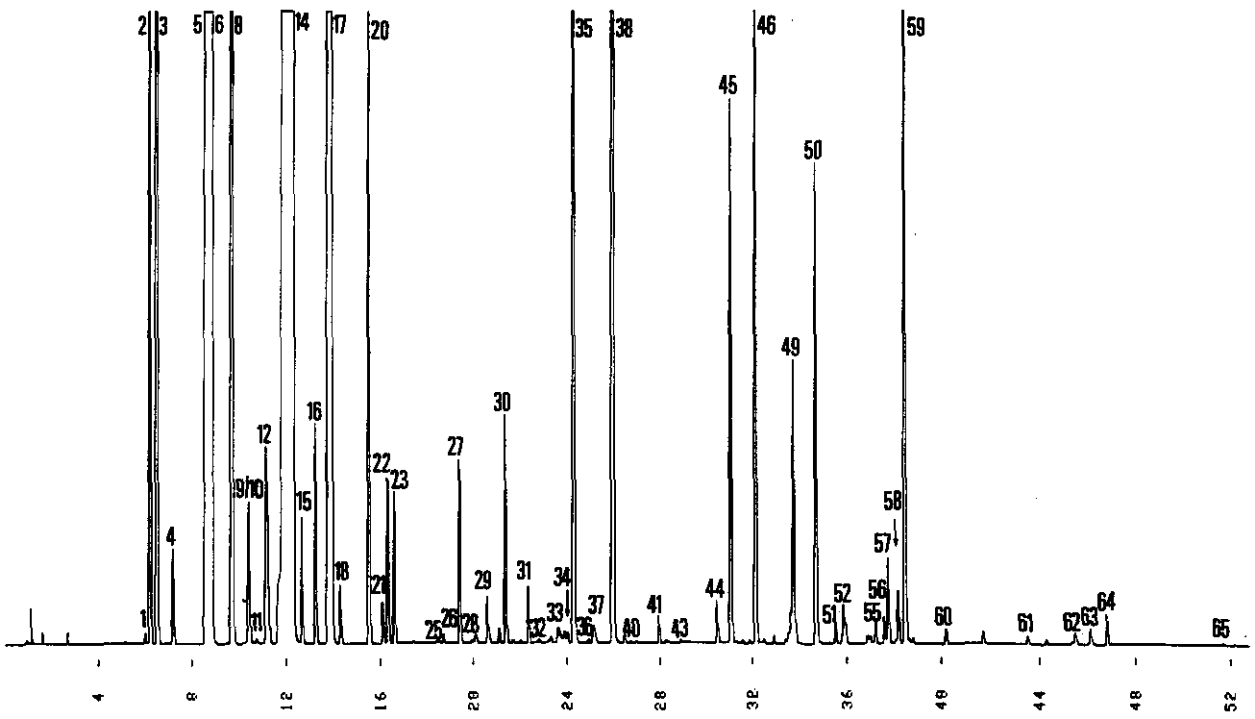

Figure 3. Gas chromatogram of a lemon essential oil

Experimental: gas chromatograph Fisons Series Mega 5160, equipped with a Shimadzu data processor C-3RA; detector FID; a silica capillary column 25 m x 0.32 mm i.d. coated with SE-52; column temperature 60°C (8') to 100°C at 3°C/min, to 130°C at 2.5°C/min, to 180°C at 3°C/min; injector and detector temperature, 280°C; injection mode, split; carrier gas H_2, 0.50 kg/cm². For identification of components, see Table II.

and lasts until the beginning of March; in the early season unripe fruits (green mandarins) are processed, after which processing of ripe fruits (red mandarins) begins.

The sweet orange season is between December and July; in Italy 70% of the transformed oranges possess blond-pulp while the remaining 30% are blood-pulp. In the early season (from December to January) the industries process ripe blond-pulp oranges; in the mid-season, from February to April, overall blood-pulp oranges and in late season blond-pulp oranges which ripen late.

The most important cultivars transformed are:

Early season: Biondo comune, Navelina, Washington navel, Moro and Tarocco (less ripe);

Mid season: Biondo comune, Moro, Tarocco, Sanguinello;

Late season: Sanguinello, Ovale, Valencia late.

This list should only be considered as a general guideline of which oranges are processed at what time. It should be remembered that during the period when only blond fruits are usually picked, it is possible for blood oranges also to be processed. The contrary could also happen during the period when blood oranges are principally picked.

Finally, the bitter orange productive season lasts from October to March, while that of bergamot from November to February.

The methods employed to obtain cold-pressed essential oils in Italy are: "Sfumatrice," "Pelatrice," "Torchi" and "FMC."

As one might expect from their names, the first three technologies were developed in Italy while the "FMC" process was developed in the United States. Presently, the FMC process is widespread, representing about 15-20% of the transformation machines working in Italy.

Modern mechanical systems for cold extraction of citrus oils require the following fundamental steps:

1. Mechanical action on fruits or on rind in order to cause utricles to break so that the essential oil can be released.
2. The use of an aqueous phase in which the citrus oil forms an emulsion so that it can be moved away from the oil release. In some situations the aqueous phase is recycled to limit the loss of oxygenated compounds.
3. Emulsion centrifugation to obtain pure essential oil.

"Sfumatrice" machines work on rinds without pulp; now these are not widely used and are replaced by "Torchi" which work on the entire fruits too. Both technologies, especially "Sfumatrice," yield essential oils that possess acceptable olfactive properties.

In contrast, "Pelatrice" machines work on the entire fruit, and the essential oil is obtained by rasping the fruit epicarp in order to cause utricles to break. "FMC" machines

Table II. Composition of the volatile fraction of lemon oil

		$\bar{X}$	s	Min	Max
1	tricyclene	0.006	0.001	0.003	0.008
2	α-thujene	0.443	0.026	0.370	0.543
3	α-pinene	1.979	0.095	1.496	2.403
4	camphene	0.060	0.004	0.046	0.081
5	sabinene	2.009	0.202	1.128	2.794
6	β-pinene	12.747	1.452	9.453	17.794
7	6-methyl-5-hepten-2-one	0.004	0.003	0.001	0.017
8	myrcene	1.480	0.094	1.053	1.860
9	octanal	0.053	0.016	0.021	0.137
10	α-phellandrene	0.055	0.018	0.013	0.127
11	δ-3-carene	0.004	0.002	0.001	0.010
12	α-terpinene	0.188	0.024	0.049	0.251
13	p-cymene	0.154	0.085	0.025	0.675
14	limonene	65.367	1.900	59.570	71.060
15	(Z)-β-ocimene	0.069	0.023	0.031	0.149
16	(E)-β-ocimene	0.119	0.025	0.070	0.204
17	γ-terpinene	9.523	0.423	6.586	11.275
18	trans-sabinene hydrate	0.039	0.009	0.014	0.074
19	octanol	0.003	0.002	0.001	0.008
20	terpinolene	0.382	0.025	0.205	0.438
21	cis-sabinene hydrate	0.030	0.010	0.010	0.072
22	linalool	0.100	0.018	0.049	0.179
23	nonanal	0.106	0.020	0.044	0.194
24	cis-limonene oxide	0.005	0.004	0.002	0.024
25	trans-limonene oxide	0.006	0.003	0.002	0.019
26	camphor	0.007	0.002	0.003	0.015
27	citronellal	0.096	0.019	0.040	0.166
28	borneol	0.005	0.003	0.001	0.017
29	terpinen-4-ol	0.029	0.011	0.010	0.080
30	α-terpineol	0.156	0.040	0.058	0.276
31	decanal	0.038	0.011	0.012	0.082
32	octyl acetate	0.004	0.002	0.001	0.011
33	nerol + citronellol	0.035	0.024	0.006	0.179
34	carbonyl compound	0.016	0.013	0.002	0.090
35	neral	0.864	0.140	0.455	1.333
36	piperitone	0.004	0.002	0.001	0.012
37	geraniol	0.022	0.009	0.004	0.059
38	geranial	1.461	0.238	0.602	2.252
39	perillaldehyde	t			
40	bornyl acetate	0.004	0.002	0.002	0.014
41	undecanal	0.021	0.005	0.002	0.046
42	nonyl acetate	0.005	0.002	0.002	0.019
43	methylgeranate	0.003	0.001	0.002	0.011
44	citronellyl acetate	0.028	0.009	0.005	0.082
45	neryl acetate	0.398	0.081	0.228	0.883
46	geranyl acetate	0.408	0.128	0.163	0.809
47	dodecanal	t			
48	decyl acetate	t			
49	β-caryophyllene	0.229	0.028	0.107	0.334
50	trans-α-bergamotene	0.354	0.038	0.211	0.579
51	α-humulene	0.016	0.003	0.007	0.030
52	β-santalene + cis-β-farnesene	0.046	0.007	0.007	0.074
53	γ-muurolene	0.009	0.003	0.004	0.023
54	germacrene D	0.008	0.003	0.003	0.019
55	sesquiterpene	0.018	0.003	0.003	0.038
56	valencene	0.023	0.017	0.001	0.088
57	germacrene B	0.063	0.014	0.023	0.120
58	sesquiterpene	0.043	0.007	0.013	0.134
59	β-bisabolene	0.529	0.067	0.295	0.916
60	γ-elemene	0.015	0.002	0.006	0.028
61	tetradecanal	0.010	0.002	0.004	0.018
62	2,3-dimethyl-3-(4-methyl-3-pentenyl)-2-norbornanol	0.018	0.004	0.009	0.038
63	campherenol	0.018	0.003	0.007	0.034
64	α-bisabolol	0.022	0.003	0.009	0.030
65	nootkatone	0.004	0.002	0.001	0.010
	hydrocarbons	95.847	0.463	93.668	97.677
	monoterpenes	94.510	0.526	92.183	96.644
	sesquiterpenes	1.337	0.145	0.811	2.174
	oxygenated compounds	3.920	0.411	2.303	5.470
	carbonyl compounds	2.657	0.364	1.371	3.798
	alcohols	0.423	0.106	0.186	0.748
	esters	0.836	0.183	0.419	1.583

t = trace

also process the entire fruit providing the contemporaneous extraction of juice and oil and give good quality products.

The aqueous phase that carries the essential oil is easily recycled when oil is produced using the "Pelatrice" and "FMC" processes. The ability to recycle the aqueous phase is more difficult for "Sfumatrice" and "Torchi" because of the rapid increase of pectins in the aqueous phase.

Genuine Italian essential oils, for several reasons, are offered on the international market at prices which are considerably higher than those of the essential oils produced in other citrus-growing countries. The main reason for this is the lack of efficient coordination between the citrus processors and citrus growers. However, despite the disadvantage of the higher cost, cold-pressed Italian essential oils, namely lemon, mandarin and bergamot, are highly valued and are able to find an outlet on the basis of superior quality of their olfactory characteristics.

It has always been our opinion that, in order to defend its position on the international market, the Italian citrus-processing industry must base its economic policy on the genuineness and high quality of its products, without trying to meet its competitors at their price levels.

Therefore, in order to provide fundamental information on the quality and genuineness of Italian citrus oils, we have performed research on the chemical composition of the volatile fractions of lemon,[2-6] mandarin,[7,8] bergamot,[9,10] sweet orange[11] and bitter orange[12] oils. The samples analyzed were undoubtedly genuine, produced with the usual industrial techniques and representative of entire productive seasons and of all productive areas.

Lemon Oil

Lemon oil is produced with the usual industrial techniques: "Pelatrice," "Sfumatrice," "Torchi," "FMC;" in summer it is mostly obtained by "Pelatrice." In fact the oil obtained from summer lemons is worse than that of winter lemons, so it is preferable to use a less expensive technology such as "Pelatrice."

The volatile fraction of lemon oil constitutes about 96-98% of the whole oil.

Figure 3 shows the chromatogram of a lemon oil analyzed by gas chromatography (GC) using an SE-52 column. Table II reports its composition as single components and classes of substances.

The results reported in Table II refer to 1,546 industrial samples, absolutely genuine lemon oil, which are representative of entire productive seasons from 1982 to 1992 and of all productive areas. As can be seen, limonene is the main component: its percentage lies between 60% and 71%. Among the other monoterpenes, there is a high proportion of β-pinene (9-18%) and γ-terpinene (8-11%). Oxygenated compounds are found in amounts between 2.3% and 6.3%. Aldehydes are the class of substances which mainly contribute to the total content of oxygenated compounds. In particular, the main oxygenated components of the oil are neral and geranial (in time past called Citral A and Citral B). The so-called "Citral" (total content of carbonyl compounds)

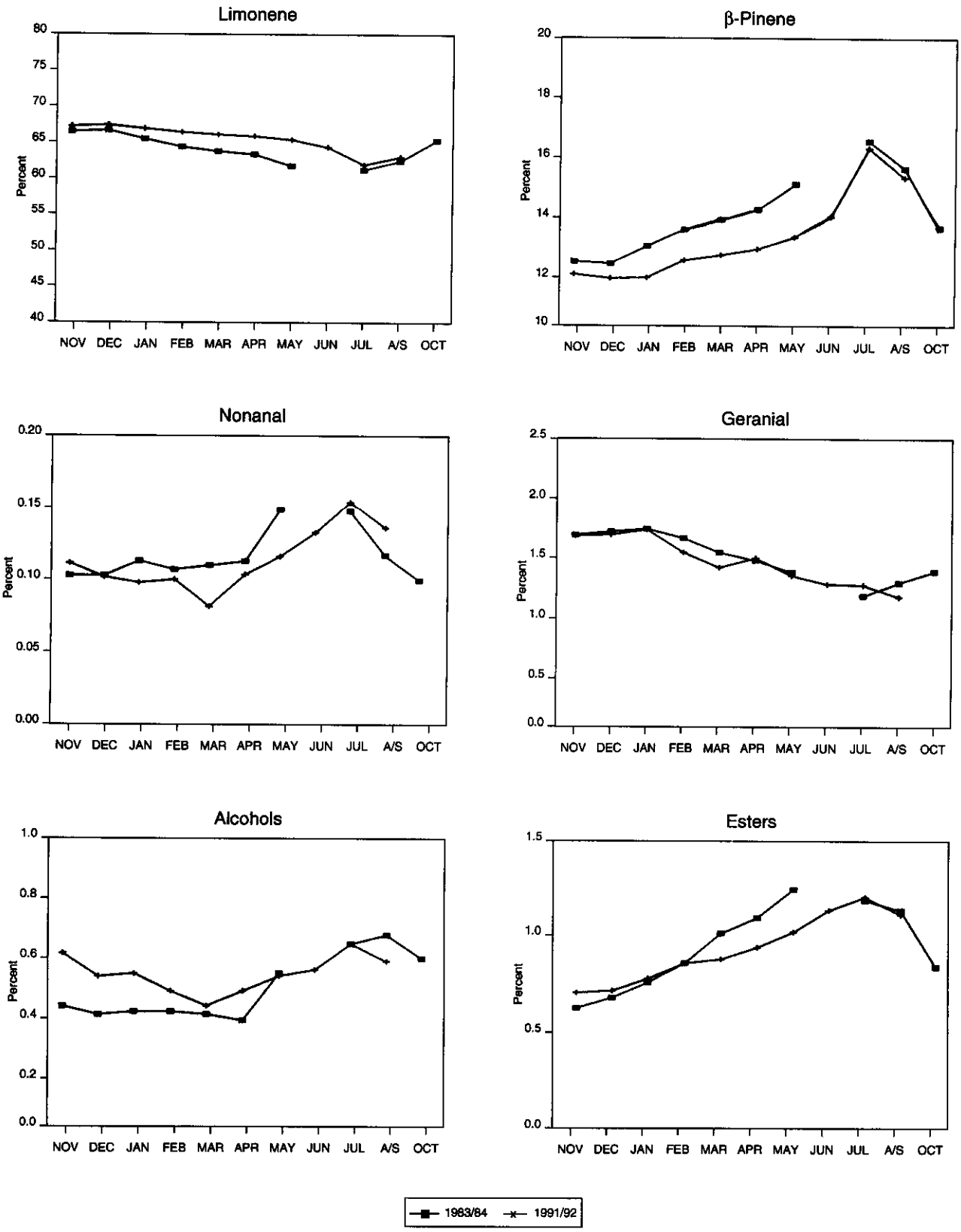

Figure 4. Variation in average content of limonene, β-pinene, geranial, nonanal, esters and alcohols for lemon oils produced during two different seasons

Table III. Composition of the volatile fraction of winter (November-March) and summer (June-September) lemon oils

		Winter		Summer	
		$\bar{X}$	s	$\bar{X}$	s
1	tricyclene	0.006	0.001	0.007	0.001
2	α-thujene	0.449	0.024	0.414	0.017
3	α-pinene	1.982	0.097	1.982	0.083
4	camphene	0.059	0.004	0.066	0.004
5	sabinene	1.954	0.189	2.264	0.198
6	β-pinene	12.179	1.122	15.209	1.300
7	6-methyl-5-hepten-2-one	0.003	0.002	0.005	0.003
8	myrcene	1.515	0.084	1.359	0.058
9	octanal	0.050	0.009	0.062	0.029
10	α-phellandrene	0.051	0.012	0.083	0.026
11	δ-3-carene	0.004	0.002	0.005	0.002
12	α-terpinene	0.191	0.023	0.169	0.028
13	p-cymene	0.146	0.090	0.180	0.071
14	limonene	66.019	1.628	62.651	1.487
15	(Z)-β-ocimene	0.064	0.022	0.078	0.018
16	(E)-β-ocimene	0.111	0.020	0.135	0.027
17	γ-terpinene	9.483	0.415	9.491	0.462
18	trans-sabinene hydrate	0.038	0.009	0.047	0.011
19	octanol	0.002	0.001	0.005	0.001
20	terpinolene	0.386	0.025	0.359	0.030
21	cis-sabinene hydrate	0.030	0.010	0.038	0.011
22	linalool	0.101	0.017	0.104	0.016
23	nonanal	0.100	0.016	0.136	0.021
24	cis-limonene oxide	0.005	0.003	0.006	0.002
25	trans-limonene oxide	0.005	0.003	0.006	0.002
26	camphor	0.008	0.002	0.007	0.002
27	citronellal	0.095	0.017	0.089	0.019
28	borneol	0.006	0.003	0.005	0.004
29	terpinen-4-ol	0.026	0.009	0.045	0.012
30	α-terpineol	0.150	0.036	0.206	0.035
31	decanal	0.032	0.006	0.060	0.010
32	octyl acetate	0.003	0.002	0.006	0.002
33	nerol + citronellol	0.027	0.011	0.070	0.052
34	carbonyl compound	0.016	0.014	0.020	0.015
35	neral	0.910	0.124	0.705	0.115
36	piperitone	0.004	0.002	0.004	0.001
37	geraniol	0.021	0.009	0.026	0.006
38	geranial	1.547	0.205	1.154	0.179
39	perillaldehyde	t		t	
40	bornyl acetate	0.004	0.002	0.005	0.003
41	undecanal	0.020	0.004	0.030	0.004
42	nonyl acetate	0.004	0.002	0.006	0.002
43	methylgeranate	0.004	0.001	0.003	0.001
44	citronellyl acetate	0.026	0.007	0.030	0.009
45	neryl acetate	0.378	0.054	0.538	0.095
46	geranyl acetate	0.357	0.103	0.535	0.079
47	dodecanal	t		t	
48	decyl acetate	t		t	
49	β-caryophyllene	0.229	0.028	0.238	0.024
50	trans-α-bergamotene	0.349	0.035	0.375	0.025
51	α-humulene	0.016	0.003	0.015	0.003
52	β-santalene + cis-β-farnesene	0.046	0.007	0.046	0.009
53	γ-muurolene	0.009	0.004	0.009	0.002
54	germacrene D	0.007	0.001	0.009	0.004
55	sesquiterpene	0.018	0.003	0.020	0.003
56	valencene	0.016	0.009	0.040	0.023
57	germacrene B	0.061	0.012	0.075	0.016
58	sesquiterpene	0.042	0.006	0.046	0.005
59	β-bisabolene	0.521	0.060	0.571	0.043
60	γ-elemene	0.015	0.002	0.016	0.002
61	tetradecanal	0.009	0.002	0.012	0.002
62	2,3-dimethyl-3-(4-methyl-3-pentenyl)-2-norbornanol	0.016	0.003	0.022	0.005
63	campherenol	0.018	0.003	0.021	0.002
64	α-bisabolol	0.022	0.003	0.025	0.002
65	nootkatone	0.003	0.001	0.006	0.002
	hydrocarbons	95.843	0.458	95.753	0.439
	monoterpenes	94.528	0.511	94.309	0.466
	sesquiterpenes	1.315	0.131	1.444	0.092
	oxygenated compounds	3.940	0.408	3.940	0.389
	carbonyl compounds	2.771	0.330	2.258	0.293
	alcohols	0.402	0.093	0.565	0.081
	esters	0.764	0.138	1.110	0.122

t = trace

has become an important parameter to establish the price of the oil and today, too, it represents a reference of quality. Esters are present in quantities which vary from 0.4% to 1.6% while the content of alcohols varies from 0.2% to about 0.7%.

The volatile fraction composition of lemon oil shows cyclic variations during the year. These variations are especially due to the different type of lemons processed during the productive season.

The characteristic trends of all components and classes of substances are almost identical in the several years investigated and also their average values are almost equal in the same period of different productive seasons.

The greatest quantitative differences registered for identical periods of different years can be explained by the presence of different proportions of lemon type processed and to a lesser extent by the area from where lemons were grown.

The reproducibility of the annual cyclic variations of lemon oil composition is shown in Figure 4, in which the results of some parameters for two different productive seasons are compared.

As can be seen in the same figure, the composition of the high quality winter oils is different from that of summer oils. In fact, from the beginning of the season to March-April, the content of single components and of the classes of substances is almost the same, while from April to August the composition of lemon oil changes remarkably. Esters, alcohols, β-pinene, sabinene and aliphatic aldehydes reach their maximum in the oils produced in summer when neral, geranial and limonene show their lowest levels.

Table III shows the quantitative differences between "winter" (November-March) and "summer" (May-September) oils.

Oils obtained from "Primofiore" lemons, which often constitute a high percentage of the total lemons processed in October and November, show some characteristics in their composition: namely, a very low content of the esters (up to 0.42%) and a high content of linalool (up to 0.18%).

The extraction technology influences the volatile fraction composition of lemon oils. The oils obtained from "Pelatrice" and "FMC" machines generally show a higher content of oxygenated compounds (carbonyl compounds and esters) and a lower content of hydrocarbons than those obtained from "Sfumatrice" and "Torchi" for the same period of the year.

As discussed above, because of the difficulty in recycling the aqueous phase when a higher aqueous phase/essential oil ratio is used, a heavier loss of the oxygenated compounds is experienced with the "Sfumatrice" and "Torchi" technologies than the "Pelatrice" and "FMC" processes.

Table IV and Figure 5 show the quantitative differences in the composition of the "winter" oils obtained by different processes. "Sfumatrice" also includes the oils produced by the "Torchi" process because both produce oils with similar compositions.

Italian lemon oils show an average aldehyde content included in the range shown by California oils but higher

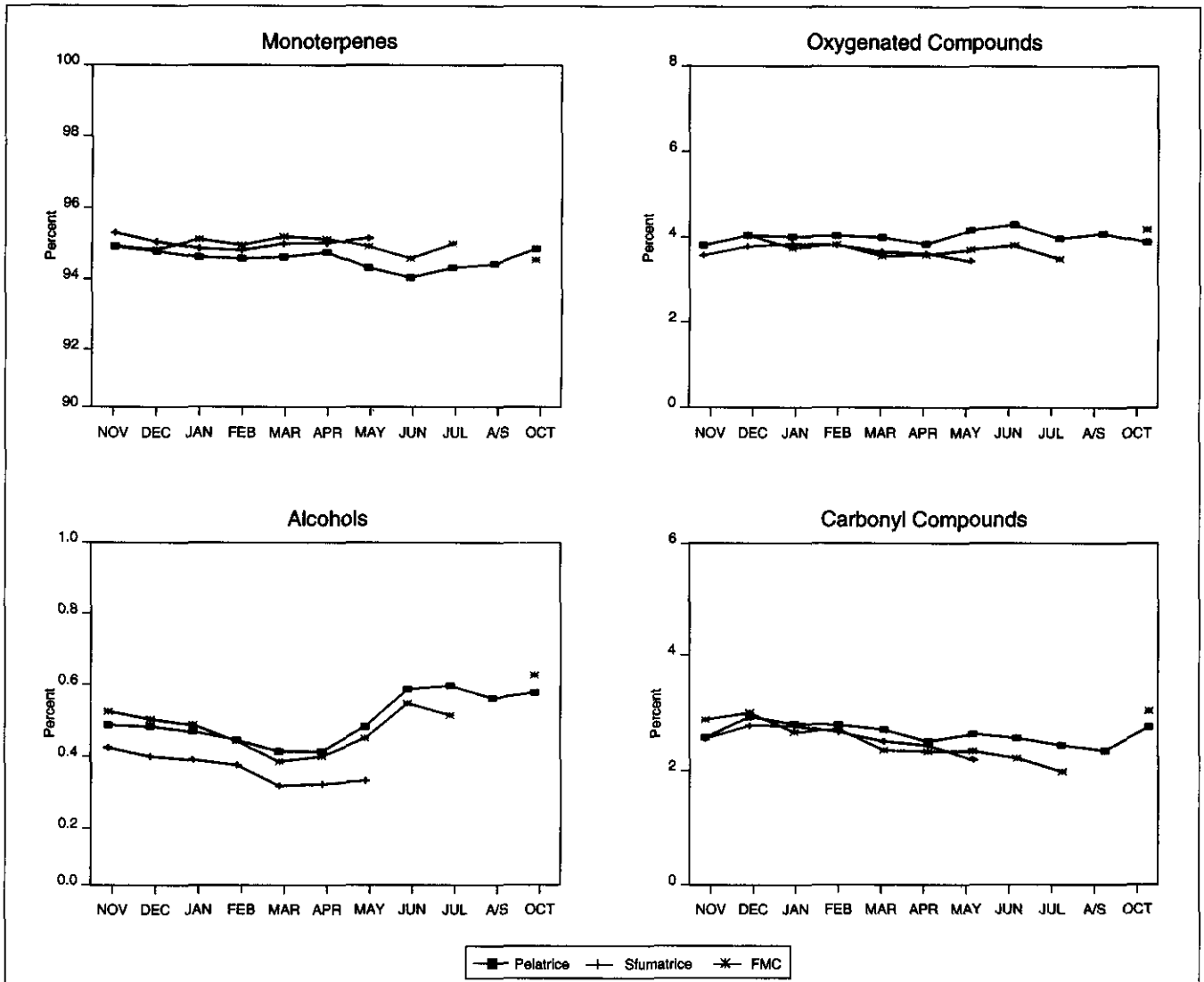

Figure 5. Variation in average content of monoterpenes, oxygenated compounds, carbonyl compounds and alcohols for lemon oils processed by different industrial technologies

than that of Arizona oils. Among them the "winter" Italian oils possess an aldehyde content similar to that of California oils, while "summer" oils show a value nearer to that of Arizona oils.

The average ester content for the "summer" Italian oils is near to the California value. For the "winter" Italian oils, the ester value is very similar to that of the Arizona oils.

The average alcohol content is similar to the minimum values shown by the California oils (early oils) and to the maximum alcohol values of the Arizona oils (early oils).[13]

Italian lemon oils have a composition very similar to that of Uruguayan oils, particularly of the south of Uruguay,[14] while they have a higher content of oxygenated compounds (aldehydes, esters, alcohols) than Argentinian oils.[15,16]

The comparison of Italian and Spanish oils is difficult since the results by Boelens for the Spanish oil differ for each year from 1987 to 1990. The aldehyde values reported for 1987 are lower than the average values reported for the "summer" Italian oils, while for 1990 the values of the aldehyde content are sometimes higher than those for the "winter" Italian oils. Alcohol and ester contents also show remarkable differences.[17,18]

Mandarin Oil

Mandarin oil is obtained by "Pelatrice," "Torchi" and "FMC" processes. The volatile fraction of mandarin oil represents about 96-98% of the whole oil.

Figure 6 shows a chromatogram of a mandarin oil obtained using an SE-52 capillary column, while Table V reports its composition as single components and classes of substances. These results refer to about 400 genuine industrial samples, which are representative of entire productive seasons, from 1982 to 1992.

The main component is limonene; its percentage varies from 65% to 75%, while γ-terpinene is also present in a high percentage (16-23%). Oxygenated compounds vary from

Table IV. Composition of the volatile fraction of "Pelatrice," "Sfumatrice" and "FMC" winter lemon oils

		Pelatrice		Sfumatrice		FMC	
		$\bar{X}$	s	$\bar{X}$	s	$\bar{X}$	s
1	tricyclene	0.006	0.000	0.006	0.000	0.006	0.000
2	α-thujene	0.446	0.025	0.458	0.021	0.446	0.025
3	α-pinene	1.955	0.099	2.023	0.089	1.955	0.099
4	camphene	0.058	0.004	0.060	0.004	0.058	0.004
5	sabinene	1.933	0.205	1.969	0.188	1.933	0.205
6	β-pinene	12.065	1.171	12.246	1.146	12.065	1.171
7	6-methyl-5-hepten-2-one	0.003	0.003	0.002	0.002	0.003	0.003
8	myrcene	1.513	0.080	1.531	0.086	1.513	0.080
9	octanal	0.048	0.008	0.049	0.010	0.048	0.008
10	α-phellandrene	0.053	0.012	0.052	0.012	0.053	0.012
11	δ-3-carene	0.005	0.002	0.004	0.002	0.005	0.002
12	α-terpinene	0.189	0.026	0.193	0.019	0.189	0.026
13	p-cymene	0.149	0.095	0.155	0.082	0.149	0.095
14	limonene	65.789	1.721	66.183	1.682	65.789	1.721
15	(Z)-β-ocimene	0.066	0.022	0.063	0.023	0.066	0.022
16	(E)-β-ocimene	0.114	0.019	0.108	0.020	0.114	0.019
17	γ-terpinene	9.597	0.379	9.379	0.412	9.597	0.379
18	trans-sabinene hydrate	0.044	0.007	0.031	0.006	0.044	0.007
19	octanol	0.001	0.000	0.001	0.000	0.001	0.000
20	terpinolene	0.388	0.028	0.385	0.021	0.388	0.028
21	cis-sabinene hydrate	0.036	0.008	0.024	0.006	0.036	0.008
22	linalool	0.107	0.013	0.092	0.015	0.107	0.013
23	nonanal	0.100	0.015	0.100	0.016	0.100	0.015
24	cis-limonene oxide	0.005	0.002	0.005	0.004	0.005	0.002
25	trans-limonene oxide	0.005	0.003	0.005	0.003	0.005	0.003
26	camphor	0.009	0.002	0.007	0.001	0.009	0.002
27	citronellal	0.096	0.016	0.096	0.016	0.096	0.016
28	borneol	0.007	0.002	0.005	0.002	0.007	0.002
29	terpinen-4-ol	0.026	0.007	0.024	0.008	0.026	0.007
30	α-terpineol	0.172	0.025	0.123	0.025	0.172	0.025
31	decanal	0.032	0.006	0.032	0.006	0.032	0.006
32	octyl acetate	0.003	0.002	0.003	0.001	0.003	0.002
33	nerol + citronellol	0.032	0.010	0.022	0.008	0.032	0.010
34	carbonyl compound	0.016	0.014	0.017	0.014	0.016	0.014
35	neral	0.967	0.123	0.864	0.108	0.967	0.123
36	piperitone	0.004	0.002	0.004	0.002	0.004	0.002
37	geraniol	0.026	0.009	0.016	0.006	0.026	0.009
38	geranial	1.640	0.206	1.479	0.179	1.640	0.206
39	perillaldehyde	t		t		t	
40	bornyl acetate	0.003	0.001	0.003	0.002	0.003	0.001
41	undecanal	0.020	0.004	0.019	0.004	0.020	0.004
42	nonyl acetate	0.004	0.002	0.004	0.001	0.004	0.002
43	methylgeranate	0.004	0.001	0.004	0.001	0.004	0.001
44	citronellyl acetate	0.026	0.007	0.026	0.007	0.026	0.007
45	neryl acetate	0.387	0.056	0.376	0.053	0.387	0.056
46	geranyl acetate	0.371	0.107	0.348	0.101	0.371	0.107
47	dodecanal	t		t		t	
48	decyl acetate	t		t		t	
49	β-caryophyllene	0.232	0.031	0.225	0.025	0.232	0.031
50	trans-α-bergamotene	0.358	0.035	0.349	0.034	0.358	0.035
51	α-humulene	0.016	0.003	0.015	0.002	0.016	0.003
52	β-santalene + cis-β-farnesene	0.048	0.007	0.046	0.006	0.048	0.007
53	γ-muurolene	0.011	0.004	0.009	0.004	0.011	0.004
54	germacrene D	0.007	0.002	0.007	0.001	0.007	0.002
55	sesquiterpene	0.019	0.003	0.018	0.003	0.019	0.003
56	valencene	0.018	0.009	0.014	0.009	0.018	0.009
57	germacrene B	0.060	0.011	0.061	0.011	0.060	0.011
58	sesquiterpene	0.043	0.006	0.042	0.006	0.043	0.006
59	β-bisabolene	0.535	0.062	0.520	0.059	0.535	0.062
60	γ-elemene	0.015	0.002	0.015	0.002	0.015	0.002
61	tetradecanal	0.009	0.002	0.009	0.002	0.009	0.002
62	2,3-dimethyl-3-(4-methyl-3-pentenyl)-2-norbornanol	0.015	0.002	0.016	0.002	0.015	0.002
63	campherenol	0.018	0.002	0.018	0.002	0.018	0.002
64	α-bisabolol	0.021	0.002	0.022	0.001	0.021	0.002
65	nootkatone	0.002	0.002	0.002	0.001	0.002	0.002
	hydrocarbons	95.609	0.413	96.057	0.395	95.609	0.413
	monoterpenes	94.265	0.468	94.751	0.444	94.265	0.468
	sesquiterpenes	1.345	0.139	1.306	0.126	1.345	0.139
	oxygenated compounds	4.157	0.383	3.745	0.345	4.157	0.383
	carbonyl compounds	2.921	0.326	2.656	0.287	2.921	0.326
	alcohols	0.450	0.070	0.336	0.069	0.450	0.070
	esters	0.785	0.140	0.751	0.137	0.785	0.140

t = trace

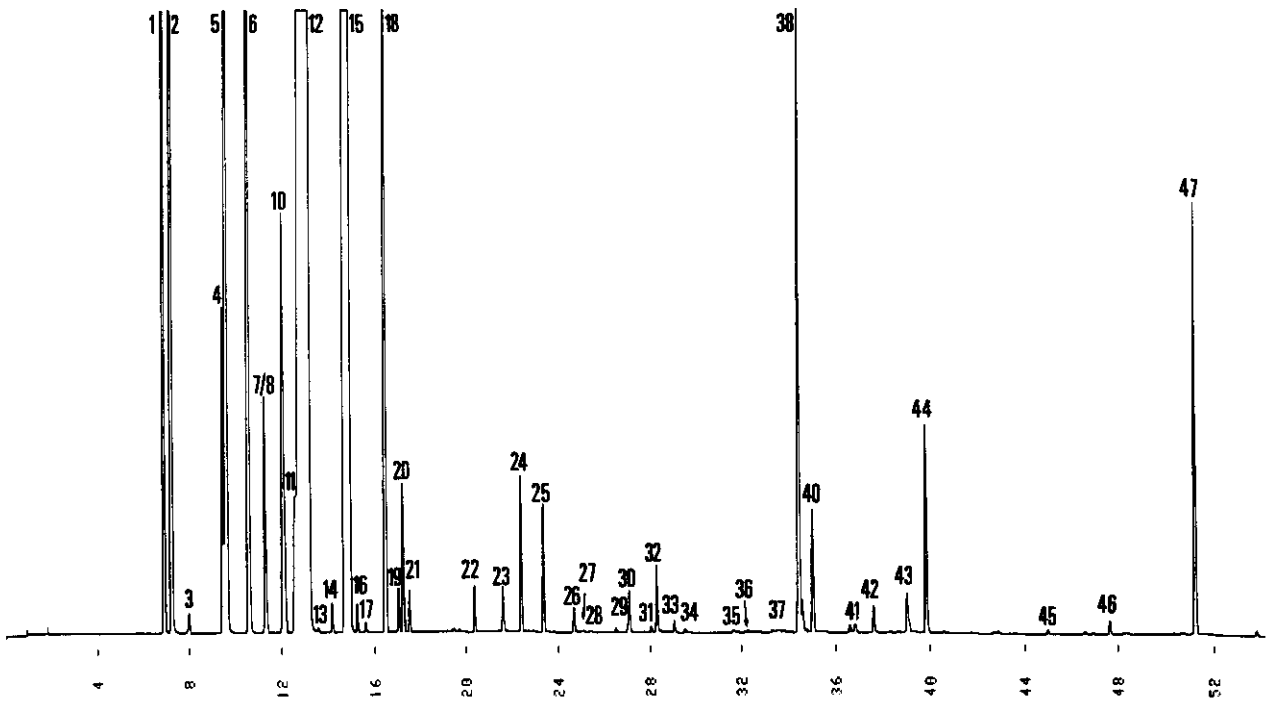

Figure 6. Gas chromatogram of a mandarin essential oil. Experimental condition: see Figure 3. For identification of components, see Table V

0.8% to 2.2%. The aldehydes are the main class of the oxygenated compounds followed by alcohols and esters.

The esters are comprised mainly of methyl N-methyl anthranilate.

The composition of mandarin oil varies during the whole productive season in relation to the ripeness of the fruits processed.

The reproducibility of the annual cyclic variations of mandarin oil composition for two different productive seasons is shown in Figure 7 and 8.

Because of the changes in the oil composition, it is possible to distinguish the oils obtained in the early season, when unripe mandarins (green mandarins) are processed, from those of the second part of the productive season, when ripe mandarins (red mandarins) are being processed.

Monoterpenes show the highest values at the end of the season (red mandarins), while oxygenated compounds (alcohols, esters, carbonyl compounds) show an average content decrease during the season from the beginning (green mandarins) to the end (red mandarins). Between October and February there is a variation in total oxygenated compounds from 2% to less than 1% respectively. Similar variations occur for some oxygenated classes of compounds, such as carbonyl compounds 0.7% to 0.4%, esters 0.5% to 0.3% and alcohols 0.6% to ca. 0.1%.

Each monoterpene hydrocarbon identified reveals a different behavior. For example, the limonene content increases during the season from 68% in October to 73-74% in February, the myrcene content remains almost the same while the content of α-pinene, β-pinene and γ-terpinene decreases during the season.

Both alcohols and aldehydes decrease during the season so that their content can be useful in establishing the production period of a mandarin oil.

Table VI reports the composition of early-season oils (October-November) obtained from unripe fruits, of mid-season oils (December) obtained from almost ripe fruits, and of late-season oils (January-February) obtained from ripe fruits. This table shows the different composition of the oil as fruits are ripening.

Italian mandarin oil shows a higher content of γ-terpinene, methyl N-methyl anthranilate, thymol and α-sinensal than Spanish oil,[18] and a definitely lower limonene content.

Brazilian mandarin oils[19] show a limonene content similar to that of the Italian late season oils (red oils), and a lower content of γ-terpinene; moreover, they show a high content of methyl N-methyl anthranilate and thymol than Italian oils.

The Argentinian oils[16] can be distinguished from Italian oils by a definitely higher content of limonene, and a lower content of γ-terpinene and methyl N-methyl anthranilate.

However, for a commercial sample of Argentinian mandarin oil, Wilson and Shaw[20] reported that the methyl N-methyl anthranilate and thymol contents were 0.65% and 0.18%. The values are higher than the average values of the Italian oils, which are 0.45% and 0.05% respectively.

Bergamot Oil

The production of bergamot is limited to a small area of

Table V. Composition of the volatile fraction of mandarin oil

		$\bar{X}$	s	Min	Max
1	α-thujene	0.879	0.063	0.716	1.065
2	α-pinene	2.341	0.130	2.000	2.745
3	camphene	0.018	0.002	0.011	0.022
4	sabinene	0.258	0.014	0.228	0.338
5	β-pinene	1.667	0.110	1.388	2.096
6	myrcene	1.708	0.050	1.566	1.958
7	octanal	0.139	0.047	0.032	0.199
8	α-phellandrene	0.066	0.014	0.034	0.113
9	δ-3-carene	0.002	0.001	0.001	0.005
10	α-terpinene	0.439	0.038	0.264	0.519
11	p-cymene	0.317	0.127	0.125	0.782
12	limonene	69.684	1.851	65.303	74.528
13	(Z)-β-ocimene	0.004	0.002	0.001	0.011
14	(E)-β-ocimene	0.020	0.004	0.013	0.031
15	γ-terpinene	19.722	1.260	16.227	22.751
16	trans-sabinene hydrate	0.025	0.011	0.006	0.059
17	octanol	0.004	0.002	0.001	0.012
18	terpinolene	0.869	0.053	0.722	1.009
19	cis-sabinene hydrate	0.044	0.023	0.008	0.107
20	linalool	0.115	0.034	0.037	0.189
21	nonanal	0.028	0.006	0.008	0.042
22	citronellal	0.032	0.005	0.016	0.048
23	terpinen-4-ol	0.040	0.014	0.012	0.082
24	α-terpineol	0.137	0.052	0.038	0.270
25	decanal	0.089	0.011	0.054	0.123
26	nerol + citronellol	0.020	0.005	0.007	0.034
27	carbonyl compound	0.010	0.004	0.003	0.020
28	neral	0.008	0.005	0.001	0.028
29	geraniol	0.004	0.002	0.001	0.013
30	geranial + perillaldehyde	0.048	0.012	0.005	0.120
31	alcohol	0.007	0.003	0.001	0.020
32	thymol	0.052	0.020	0.013	0.096
33	undecanal	0.009	0.002	0.001	0.019
34	nonyl acetate	0.004	0.002	0.001	0.012
35	citronellyl acetate	0.004	0.002	0.001	0.015
36	neryl acetate	0.004	0.002	0.001	0.012
37	geranyl acetate	0.005	0.002	0.001	0.013
38	methyl N-methyl-anthranilate	0.447	0.086	0.263	0.657
39	dodecanal	0.026	0.004	0.016	0.036
40	β-caryophyllene	0.097	0.012	0.066	0.143
41	α-humulene	0.010	0.002	0.003	0.017
42	2-dodecenal	0.020	0.005	0.005	0.033
43	α-selenene	0.041	0.007	0.024	0.064
44	α-farnesene	0.154	0.044	0.071	0.261
45	tetradecanal	0.005	0.001	0.001	0.009
46	(Z,E)-farnesol	0.011	0.003	0.002	0.017
47	α-sinensal	0.283	0.060	0.120	0.526
	hydrocarbons	98.278	0.333	97.162	99.080
	monoterpenes	97.977	0.374	96.791	98.851
	sesquiterpenes	0.301	0.056	0.182	0.448
	oxygenated compounds	1.581	0.309	0.854	2.219
	carbonyl compounds	0.683	0.118	0.351	0.999
	alcohols	0.446	0.150	0.136	0.805
	esters	0.452	0.085	0.263	0.657

the south Calabrian coast, around the Tyrrhenian and Ionian seas, between Villa S. Giovanni and Brancaleone.

Bergamot oil is almost exclusively obtained by the "Pelatrice" process with the exception of a small amount still being produced by the ancient "Calabrese" process.

Its volatile fraction represents 93-96% of the oil.

Figure 9 shows the chromatogram of a bergamot oil obtained using an SE-52 column; Table VII reports the composition as single components and classes of substances.

These results are relative to about 1,000 industrial genu-

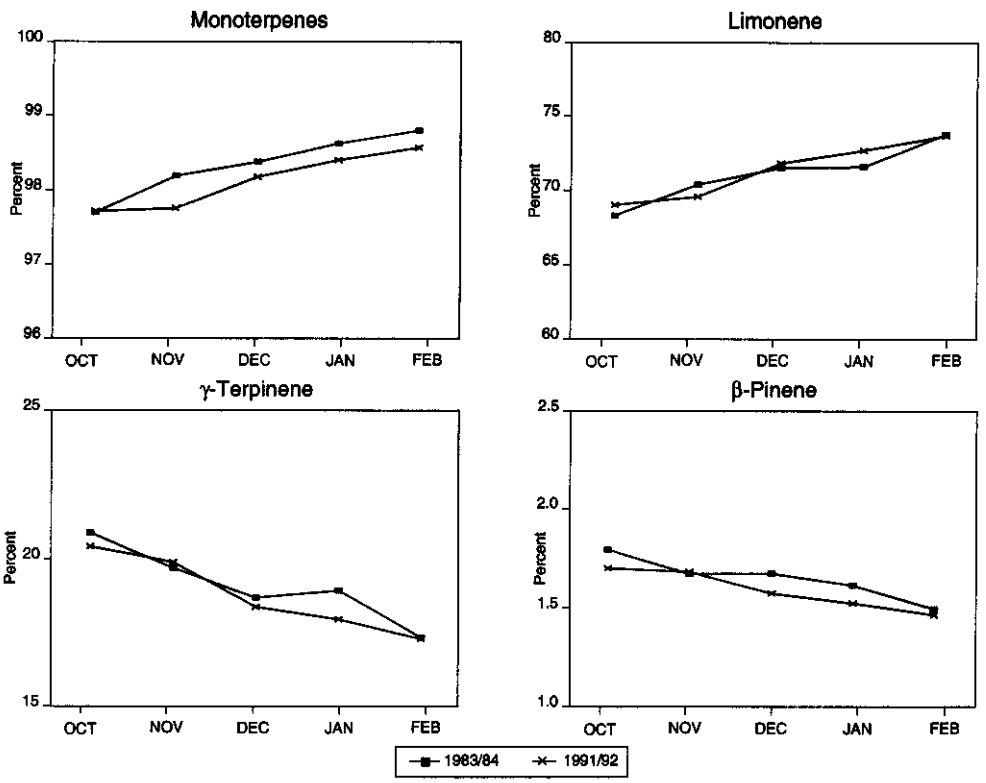

Figure 7. Variation in average content of total monoterpenes, limonene, γ-terpinene and β-pinene for mandarin oils produced during two different seasons

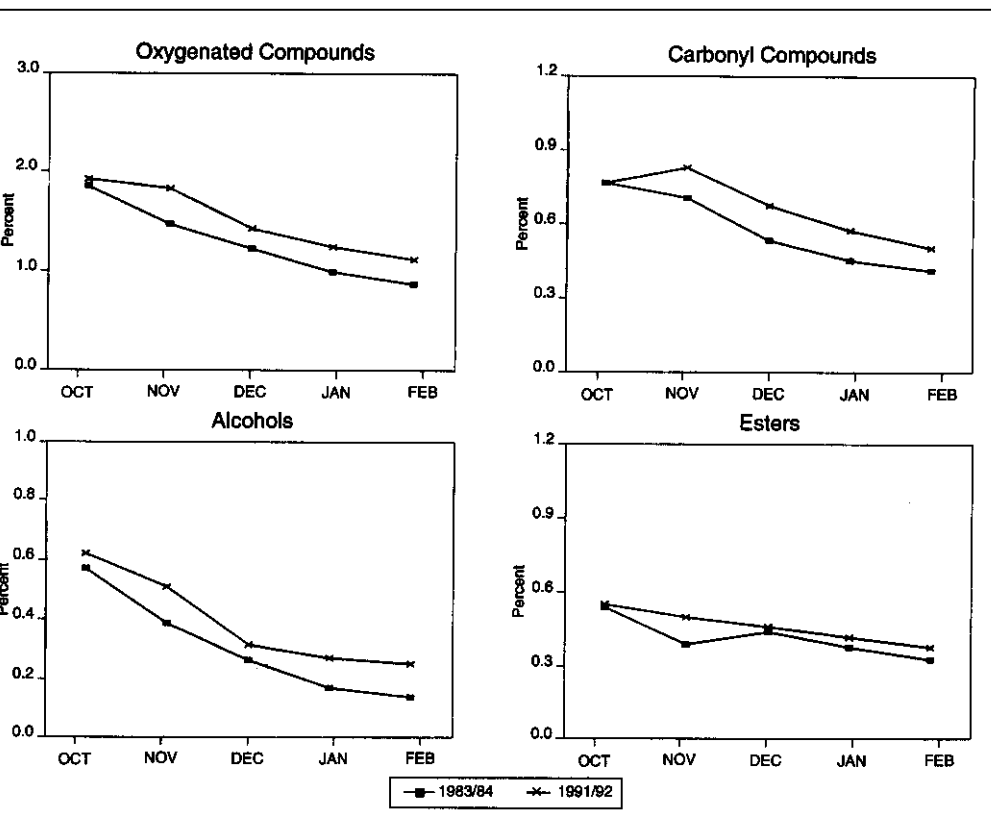

Figure 8. Variation in average content of oxygenated compounds, carbonyl compounds, alcohols and esters for mandarin oils produced during two different seasons

Table VI. Composition of the volatile fraction of green (October-November), light (December) and red (January-February) mandarin oils

		Green		Light		Red	
		$\bar{X}$	s	$\bar{X}$	s	$\bar{X}$	s
1	α-thujene	0.904	0.045	0.854	0.050	0.790	0.053
2	α-pinene	2.389	0.095	2.286	0.109	2.173	0.118
3	camphene	0.018	0.002	0.017	0.002	0.017	0.001
4	sabinene	0.259	0.012	0.263	0.024	0.248	0.008
5	β-pinene	1.702	0.083	1.654	0.115	1.524	0.088
6	myrcene	1.705	0.043	1.689	0.068	1.737	0.051
7	octanal	0.166	0.018	0.092	0.022	0.058	0.019
8	α-phellandrene	0.061	0.010	0.075	0.019	0.080	0.015
9	δ-3-carene	0.002	0.001	0.001	0.000	0.002	0.001
10	α-terpinene	0.453	0.029	0.419	0.033	0.389	0.028
11	p-cymene	0.289	0.117	0.421	0.122	0.366	0.115
12	limonene	68.904	1.244	70.464	1.402	72.470	1.375
13	(Z)-β-ocimene	0.004	0.002	0.004	0.002	0.005	0.002
14	(E)-β-ocimene	0.021	0.004	0.019	0.004	0.016	0.002
15	γ-terpinene	20.226	0.855	19.237	1.073	17.904	1.035
16	trans-sabinene hydrate	0.030	0.010	0.018	0.007	0.013	0.004
17	octanol	0.004	0.002	0.003	0.002	0.003	0.002
18	terpinolene	0.891	0.039	0.839	0.043	0.797	0.039
19	cis-sabinene hydrate	0.054	0.020	0.027	0.011	0.017	0.006
20	linalool	0.130	0.025	0.093	0.022	0.066	0.016
21	nonanal	0.030	0.004	0.024	0.007	0.020	0.005
22	citronellal	0.032	0.005	0.031	0.006	0.029	0.006
23	terpinen-4-ol	0.046	0.012	0.028	0.008	0.023	0.007
24	α-terpineol	0.161	0.041	0.093	0.023	0.069	0.023
25	decanal	0.091	0.009	0.083	0.013	0.083	0.012
26	nerol + citronellol	0.022	0.004	0.018	0.003	0.016	0.004
27	carbonyl compound	0.012	0.004	0.008	0.001	0.007	0.002
28	neral	0.009	0.005	0.007	0.004	0.006	0.003
29	geraniol	0.004	0.002	0.005	0.003	0.001	0.000
30	geranial + perillaldehyde	0.052	0.010	0.041	0.015	0.039	0.011
31	alcohol	0.008	0.002	0.004	0.002	0.005	0.002
32	thymol	0.060	0.016	0.042	0.011	0.026	0.010
33	undecanal	0.009	0.002	0.009	0.002	0.008	0.002
34	nonyl acetate	0.003	0.001	0.004	0.001	0.005	0.002
35	citronellyl acetate	0.002	0.001	0.002	0.000	0.006	0.002
36	neryl acetate	0.003	0.001	0.004	0.000	0.006	0.002
37	geranyl acetate	0.004	0.001	0.007	0.001	0.007	0.002
38	methyl N-methyl-anthranilate	0.473	0.082	0.410	0.066	0.361	0.039
39	dodecanal	0.025	0.003	0.025	0.003	0.029	0.005
40	β-caryophyllene	0.101	0.011	0.093	0.012	0.082	0.007
41	α-humulene	0.010	0.002	0.009	0.002	0.009	0.002
42	2-dodecenal	0.019	0.004	0.020	0.004	0.024	0.006
43	α-selenene	0.043	0.005	0.041	0.007	0.034	0.006
44	α-farnesene	0.163	0.043	0.150	0.035	0.116	0.032
45	tetradecanal	0.005	0.001	0.006	0.000	0.006	0.001
46	(Z,E)-farnesol	0.010	0.003	0.011	0.002	0.012	0.003
47	α-sinensal	0.302	0.054	0.260	0.036	0.216	0.046
	hydrocarbons	98.136	0.260	98.510	0.199	98.714	0.192
	monoterpenes	97.820	0.298	98.217	0.205	98.472	0.202
	sesquiterpenes	0.316	0.052	0.293	0.042	0.241	0.039
	oxygenated compounds	1.728	0.214	1.329	0.150	1.137	0.165
	carbonyl compounds	0.738	0.078	0.591	0.081	0.517	0.081
	alcohols	0.515	0.115	0.326	0.071	0.243	0.064
	esters	0.476	0.083	0.412	0.066	0.376	0.042

ine samples, which represent whole productive seasons from 1984 to 1992.

Bergamot oil is marked by a content of oxygenated compounds which is higher than that of any other commonly encountered citrus fruit oil. The main oxygenated constituents of bergamot oil are linalool and linalyl acetate. Limonene, which is the main component of the other citrus oils (its percentage is generally more than 60%), never exceeds 55% in bergamot oil. Generally, the limonene and linalyl acetate contents of bergamot oil are similar.

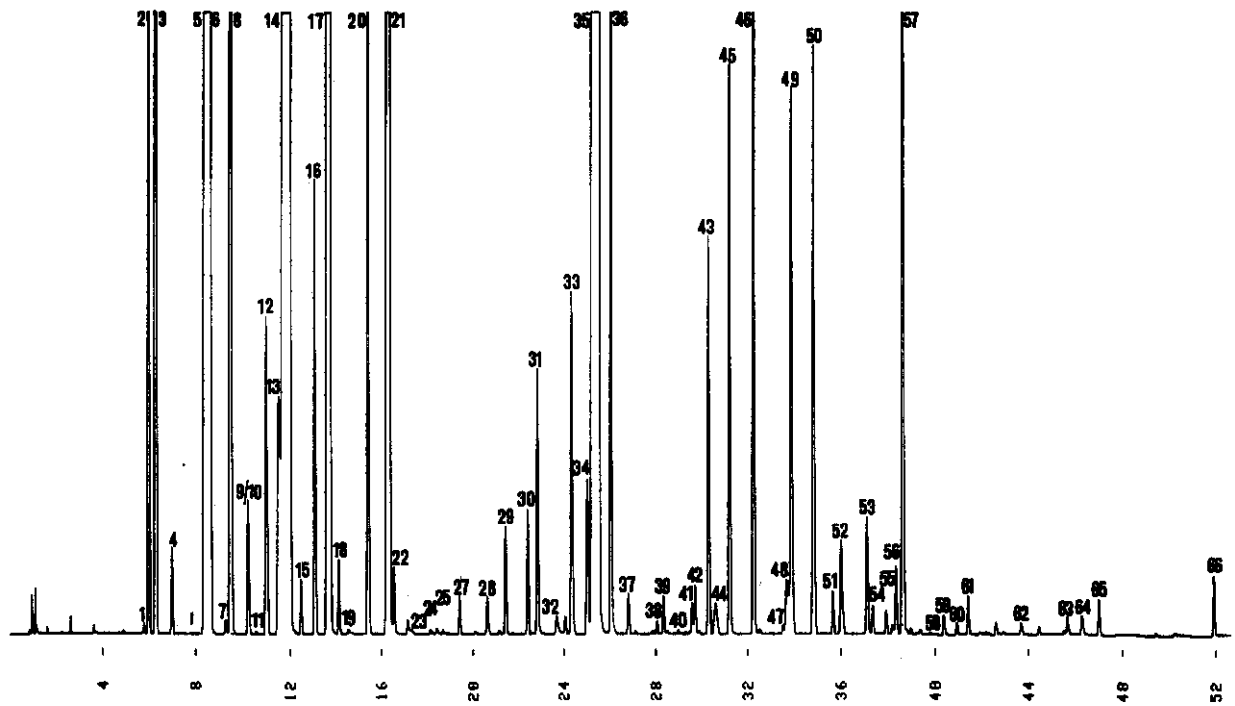

Figure 9. Gas chromatogram of a bergamot essential oil. Experimental condition: see Figure 3. For identification of components, see Table VII

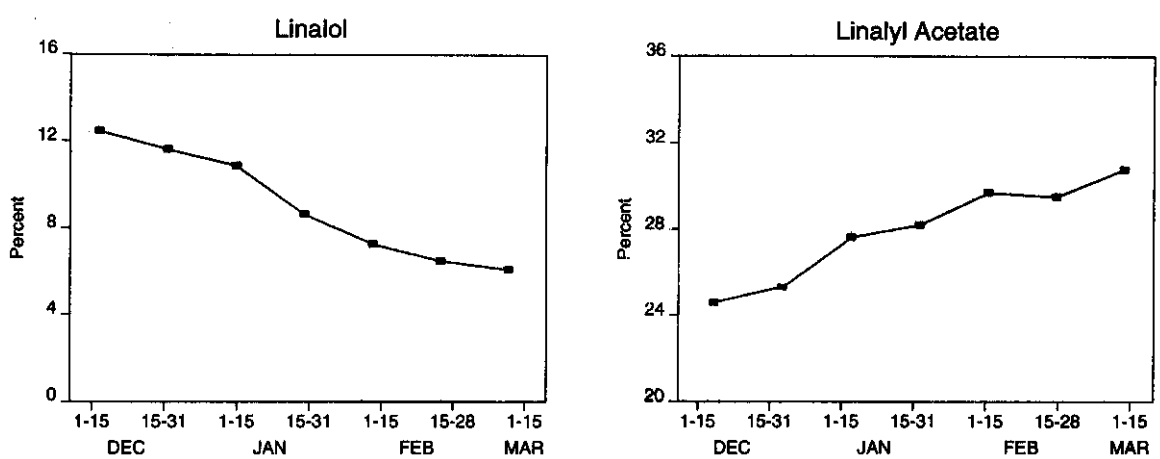

Figure 10. Variation in average content of linalool and linalyl acetate for bergamot essential oil during the productive season

The ranges observed in the oil composition are rather wide, as shown by the standard deviations reported in Table VII, although the oils referred to a narrow period of time and to a limited production area of the fruits.

Oxygenated compounds vary from 19% to 60% even though 75% of the samples possess values between 32% and 46%; alcohols vary from 2% to 20%, even though 80% of the samples are in the range from 5% to 12% and esters vary from 17% to 41% even though 80% of the samples range from 24% to 34%.

These quantitative differences in composition are due to the influence of the area where the fruits are produced and of the production period.

For example, the linalool content is highest at the beginning of the productive season, after which it decreases during the season and reaches the lowest values in March, while linalyl acetate exhibits an opposite behavior. Figure 10 shows the trends of linalool and linalyl acetate during the productive season.

The composition of the essential oil depends on the provenance of the fruits, the latitude but not the altitude being the determining factor.

Table VII. Composition of the volatile fraction of bergamot oil

		$\bar{X}$	s	Min	Max
1	tricyclene	0.004	0.001	0.002	0.005
2	α-thujene	0.357	0.045	0.190	0.491
3	α-pinene	1.354	0.166	0.731	1.844
4	camphene	0.038	0.005	0.022	0.053
5	sabinene	1.278	0.170	0.113	2.044
6	β-pinene	7.517	1.047	4.374	11.024
7	6-methyl-5-hepten-2-one	0.006	0.002	0.002	0.019
8	myrcene	0.998	0.113	0.650	1.810
9	octanal	0.050	0.009	0.025	0.078
10	α-phellandrene	0.030	0.005	0.013	0.043
11	δ-3-carene	0.003	0.001	0.001	0.005
12	α-terpinene	0.171	0.043	0.081	1.167
13	p-cymene	0.236	0.147	0.040	0.843
14	limonene	39.722	4.520	24.073	54.851
15	(Z)-β-ocimene	0.025	0.005	0.017	0.063
16	(E)-β-ocimene	0.253	0.033	0.021	0.418
17	γ-terpinene	8.350	0.956	5.386	11.378
18	trans-sabinene hydrate	0.039	0.005	0.022	0.057
19	octanol	0.002	0.003	0.000	0.031
20	terpinolene	0.350	0.042	0.210	0.475
21	linalool	7.756	3.269	1.578	20.260
22	nonanal	0.035	0.009	0.012	0.067
23	cis-limonene oxide	0.005	0.002	0.002	0.015
24	trans-limonene oxide	0.005	0.001	0.003	0.011
25	isopulegol	0.003	0.001	0.002	0.007
26	camphor	0.003	0.001	0.001	0.007
27	citronellal	0.015	0.004	0.004	0.032
28	terpinen-4-ol	0.022	0.004	0.013	0.042
29	α-terpineol	0.059	0.012	0.030	0.101
30	decanal	0.061	0.008	0.037	0.086
31	octyl acetate	0.114	0.016	0.062	0.223
32	nerol + citronellol	0.038	0.017	0.008	0.111
33	neral	0.228	0.032	0.122	0.718
34	cis-sabinene hydrate acetate	0.089	0.011	0.057	0.124
35	linalyl acetate	27.946	4.128	15.087	40.375
36	geranial	0.363	0.043	0.188	0.537
37	bornyl acetate	0.019	0.003	0.010	0.031
38	undecanal	0.008	0.002	0.000	0.024
39	nonyl acetate	0.018	0.004	0.004	0.035
40	methylgeranate	0.005	0.002	0.002	0.024
41	linalyl propionate	0.032	0.012	0.009	0.073
42	δ-elemene	0.029	0.008	0.016	0.058
43	α-terpinyl acetate	0.172	0.030	0.093	0.272
44	citronellyl acetate	0.027	0.008	0.002	0.058
45	neryl acetate	0.345	0.082	0.136	0.662
46	geranyl acetate	0.381	0.116	0.138	0.840
47	dodecanal	0.031	0.005	0.011	0.051
48	decyl acetate	t			
49	β-caryophyllene	0.352	0.049	0.225	0.551
50	trans-α-bergamotene	0.301	0.036	0.211	0.437
51	α-humulene	0.027	0.004	0.017	0.045
52	(Z)-β-farnesene + (Z)-β-santalene	0.063	0.006	0.043	0.087
53	germacrene D	0.061	0.010	0.039	0.106
54	sesquiterpene	0.016	0.002	0.010	0.027
55	germacrene B	0.015	0.004	0.004	0.040
56	α-farnesene + sesquiterpene	0.039	0.006	0.023	0.093
57	β-bisabolene	0.426	0.054	0.298	0.648
58	tridecanal	t			
59	γ-elemene	0.012	0.002	0.009	0.017
60	β-sesquiphellandrene	0.007	0.002	0.004	0.013
61	(E)-nerolidol	0.019	0.003	0.012	0.027
62	tetradecanal	0.007	0.002	0.004	0.013
63	2,3-dimethyl-3-(4-methyl-3-pentenyl)-2-norbornanol	0.011	0.002	0.006	0.021
64	campherenol	0.015	0.003	0.009	0.025
65	α-bisabolol	0.016	0.003	0.011	0.026
66	nootkatone	0.031	0.015	0.011	0.099
	hydrocarbons	61.984	6.352	39.474	80.446
	monoterpenes	60.679	6.284	38.199	79.042
	sesquiterpenes	1.305	0.144	0.012	1.894
	oxygenated compounds	37.839	6.324	19.389	60.179
	carbonyl compounds	0.769	0.079	0.379	1.236
	alcohols	7.924	3.287	1.693	20.491
	esters	29.143	4.006	16.856	41.411

t = trace

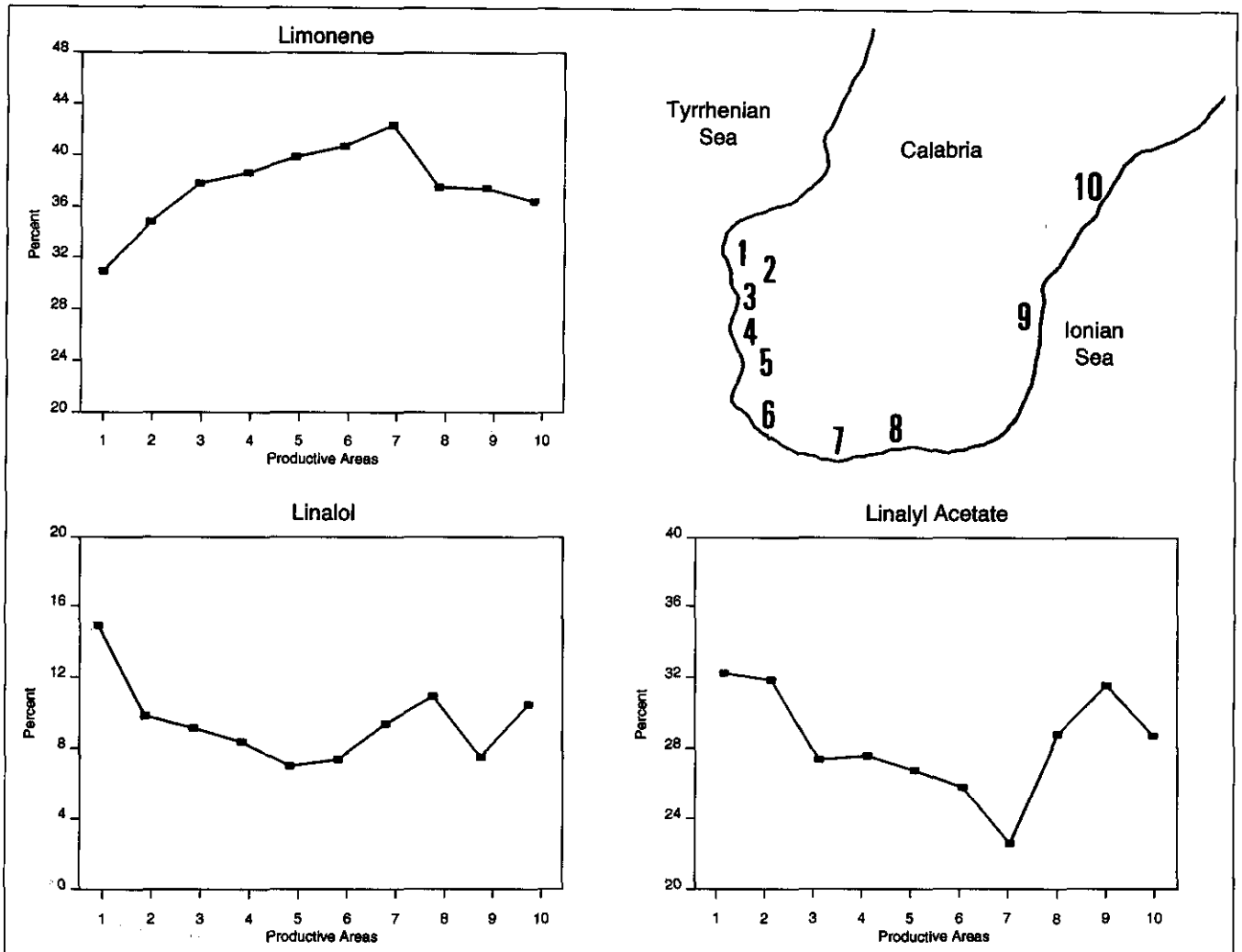

Figure 11. Variation in average content of limonene, linalool and linalyl acetate for bergamot oils in relation to the production areas

In particular the monoterpene and sesquiterpene hydrocarbons show the lowest values at the highest latitudes, both on the Tyrrhenian and Ionian side, while the highest values are shown by the oils obtained from fruits which came from South Calabria. In contrast, oxygenated compounds exhibit an opposite tendency.

Figure 11 shows the behavior of limonene, linalool and linalyl acetate in relation to the origin of the fruits. In this figure the Calabrian productive areas have been grouped into ten homogeneous sectors.

Bergamot oil from Corsica and the Ivory Coast[21] possess linalyl acetate and linalool contents higher than the average content of the Italian oils, in fact the linalool content is sometimes higher than the maximum value found in the Italian oils.

It is opportune to explain that very high levels of linalool and linalyl acetate are not always found in the bergamot oil of the best olfactory characteristics. During our research on bergamot oil,[9,10] we analyzed some samples obtained from fruits harvested in the interior regions of Calabria, where traditionally bergamot is not grown, and they showed high linalyl acetate and linalool contents, but poor olfactory qualities.

Sweet Orange Oil

Sweet orange oil is generally obtained by "Pelatrice" and "FMC" processes. The extraction technology employed depends on the type of the fruits processed and mainly on the quality of the juice required. The juice is the most important product of sweet orange, while the oil represents a less valuable product. The volatile fraction represents about 96-99% of the oil.

Figure 12 shows the chromatograms of an early-season blond orange oil and of a red orange oil obtained using an SE-52 capillary column. The chemical composition of sweet orange oil given as single components and classes of substances can be seen in Table VIII. These results are relative to 190 industrial genuine samples representative of the 1991/1992 productive season.

Limonene is the main component; its content represents about 95% of the volatile fraction. Among the other monoterpene hydrocarbons only myrcene exceeds 1%. Oxygen-

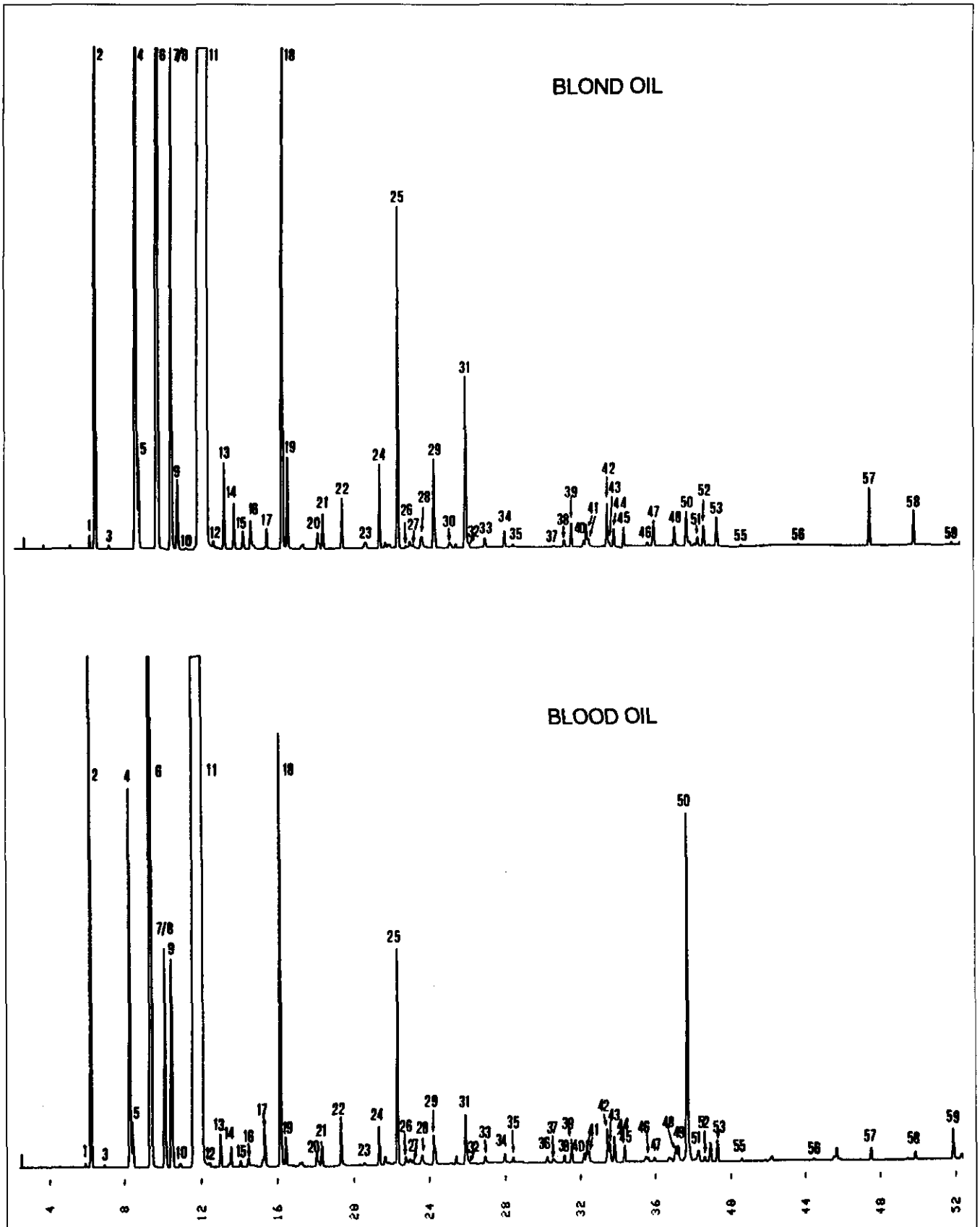

Figure 12. Gas chromatograms of blond and blood sweet orange oils. Experimental condition: see Figure 3. For identification of components, see Table VIII

Table VIII. Composition of the volatile fraction of sweet orange oil

		$\bar{X}$	s	Min	Max
1	α-thujene	0.005	0.002	0.003	0.011
2	α-pinene	0.514	0.031	0.440	0.659
3	camphene	0.003	0.001	0.001	0.004
4	sabinene	0.494	0.198	0.245	1.064
5	β-pinene	0.036	0.016	0.018	0.140
6	myrcene	1.871	0.096	1.711	2.519
7	octanal	0.193	0.086	0.070	0.388
8	α-phellandrene	0.050	0.009	0.026	0.084
9	δ-3-carene	0.125	0.040	0.017	0.251
10	α-terpinene	0.004	0.001	0.001	0.007
11	limonene	95.210	0.483	93.928	95.895
12	(Z)-β-ocimene	0.006	0.002	0.002	0.014
13	(E)-β-ocimene	0.033	0.014	0.014	0.086
14	γ-terpinene	0.021	0.017	0.002	0.098
15	trans-sabinene hydrate	0.007	0.003	0.001	0.016
16	octanol	0.012	0.008	0.002	0.036
17	terpinolene	0.027	0.007	0.012	0.052
18	linalool	0.412	0.081	0.253	0.666
19	nonanal	0.036	0.013	0.016	0.067
20	cis-limonene oxide	0.011	0.005	0.002	0.027
21	trans-limonene oxide	0.018	0.005	0.007	0.036
22	citronellal	0.038	0.008	0.021	0.068
23	terpinen-4-ol	0.005	0.002	0.001	0.013
24	α-terpineol	0.042	0.015	0.025	0.099
25	decanal	0.177	0.059	0.094	0.359
26	octyl acetate	0.007	0.003	0.001	0.016
27	cis-carveol	0.005	0.002	0.001	0.012
28	nerol	0.012	0.004	0.004	0.034
29	neral	0.049	0.018	0.023	0.100
30	geraniol	0.005	0.002	0.001	0.013
31	geranial	0.073	0.026	0.031	0.134
32	perillaldehyde	0.008	0.003	0.004	0.015
33	bornyl acetate	0.010	0.004	0.005	0.024
34	undecanal	0.009	0.002	0.003	0.015
35	nonyl acetate	0.003	0.001	0.001	0.008
36	α-terpinyl acetate	0.003	0.002	0.001	0.009
37	citronellyl acetate	0.005	0.002	0.001	0.010
38	neryl acetate	0.007	0.001	0.003	0.013
39	α-copaene	0.021	0.006	0.013	0.093
40	geranyl acetate	0.008	0.002	0.004	0.014
41	β-cubebene + β-elemene	0.023	0.005	0.007	0.037
42	dodecanal	0.029	0.013	0.010	0.079
43	decyl acetate	0.009	0.006	0.003	0.026
44	β-caryophyllene	0.017	0.004	0.011	0.032
45	α-cadinene	0.016	0.003	0.008	0.028
46	α-humulene	0.005	0.002	0.001	0.014
47	(Z)-β-farnesene	0.012	0.006	0.002	0.031
48	γ-muurolene	0.017	0.003	0.005	0.025
49	germacrene D	0.010	0.006	0.001	0.026
50	valencene	0.124	0.094	0.019	0.409
51	γ-cadinene	0.004	0.001	0.001	0.009
52	α-farnesene	0.010	0.005	0.004	0.028
53	δ-cadinene	0.023	0.003	0.015	0.030
54	tridecanal	t			
55	(Z)-nerolidol	0.003	0.001	0.001	0.008
56	tetradecanal	t			
57	β-sinensal	0.022	0.010	0.003	0.048
58	α-sinensal	0.014	0.007	0.002	0.039
59	nootkatone	0.012	0.007	0.002	0.036
	hydrocarbons	98.549	0.303	97.739	99.048
	monoterpenes	98.398	0.310	97.561	98.939
	sesquiterpenes	0.151	0.020	0.098	0.280
	oxygenated compounds	1.235	0.314	0.783	1.961
	carbonyl compounds	0.654	0.218	0.333	1.184
	alcohols	0.503	0.107	0.321	0.825
	esters	0.050	0.014	0.028	0.103
	aliphatic aldehydes	0.444	0.162	0.209	0.889
	terpenic aldehydes	0.203	0.063	0.085	0.340

t = trace

ated compounds range from 0.8% to 2%; aliphatic aldehydes (the content of which generally represents an important parameter for the quality of the oil) are the main oxygenated class of compounds, then come the alcohols (linalool is the main component), and finally the esters which never exceed 0.1%.

The type of the fruits (with blond or blood pulp), the harvest period and the extraction technology influence the composition of oil. Because of the different ratio of water/oil used in the two extraction machines, the oils obtained by "Pelatrice" generally have a higher content of oxygenated compounds and a lower content of monoterpenes than those processed by "FMC."

Early- and late-season oils obtained by processing blond fruits generally show a similar composition; this composition is different from that of the oils obtained from blood oranges.

The blond oils generally show a higher content of oxygenated compounds, especially aliphatic aldehydes, and a lower content of monoterpenes than blood oils.

Tables IX and X show the differences between "Pelatrice" and "FMC" sweet orange oils and between blond and blood oils, while Figures 13 and 14 report the trends of some components and classes of substances.

As can be observed in Figures 12 and 15, the oils obtained from blond or blood fruits can be distinguished by

Table IX. Composition of the volatile fraction of "Pelatrice" and "FMC" sweet orange oils

		Pelatrice		FMC	
		$\bar{X}$	s	$\bar{X}$	s
1	α-thujene	0.005	0.002	0.004	0.001
2	α-pinene	0.506	0.036	0.523	0.020
3	camphene	0.003	0.001	0.003	0.001
4	sabinene	0.593	0.212	0.382	0.096
5	β-pinene	0.044	0.017	0.028	0.010
6	myrcene	1.862	0.122	1.881	0.053
7	octanal	0.238	0.080	0.144	0.063
8	α-phellandrene	0.051	0.009	0.049	0.009
9	δ-3-carene	0.107	0.036	0.145	0.035
10	α-terpinene	0.004	0.001	0.005	0.001
11	limonene	94.944	0.482	95.508	0.255
12	(Z)-β-ocimene	0.006	0.002	0.006	0.002
13	(E)-β-ocimene	0.040	0.017	0.026	0.006
14	γ-terpinene	0.028	0.018	0.012	0.008
15	trans-sabinene hydrate	0.009	0.003	0.006	0.001
16	octanol	0.017	0.007	0.007	0.004
17	terpinolene	0.023	0.005	0.030	0.006
18	linalool	0.459	0.078	0.359	0.043
19	nonanal	0.041	0.013	0.029	0.008
20	cis-limonene oxide	0.013	0.005	0.008	0.005
21	trans-limonene oxide	0.020	0.005	0.015	0.003
22	citronellal	0.040	0.008	0.036	0.006
23	terpinen-4-ol	0.006	0.003	0.004	0.002
24	α-terpineol	0.051	0.015	0.032	0.005
25	decanal	0.210	0.047	0.141	0.048
26	octyl acetate	0.007	0.003	0.006	0.002
27	cis-carveol	0.005	0.002	0.004	0.001
28	nerol	0.014	0.004	0.010	0.003
29	neral	0.058	0.018	0.038	0.011
30	geraniol	0.006	0.002	0.005	0.001
31	geranial	0.087	0.026	0.057	0.016
32	perillaldehyde	0.010	0.003	0.007	0.002
33	bornyl acetate	0.011	0.004	0.009	0.003
34	undecanal	0.010	0.002	0.008	0.002
35	nonyl acetate	0.004	0.002	0.003	0.001
36	α-terpinyl acetate	0.004	0.002	0.003	0.002
37	citronellyl acetate	0.004	0.002	0.005	0.001
38	neryl acetate	0.007	0.001	0.007	0.001
39	α-copaene	0.020	0.008	0.021	0.002
40	geranyl acetate	0.007	0.002	0.008	0.001
41	β-cubebene + β-elemene	0.022	0.006	0.024	0.005
42	dodecanal	0.034	0.012	0.023	0.013
43	decyl acetate	0.009	0.007	0.009	0.004
44	β-caryophyllene	0.017	0.004	0.017	0.004
45	α-cadinene	0.018	0.003	0.015	0.002
46	α-humulene	0.004	0.002	0.005	0.002
47	(Z)-β-farnesene	0.014	0.007	0.009	0.004
48	γ-muurolene	0.016	0.003	0.017	0.003
49	germacrene D	0.009	0.005	0.011	0.006
50	valencene	0.105	0.080	0.145	0.103
51	γ-cadinene	0.005	0.001	0.004	0.001
52	α-farnesene	0.013	0.005	0.008	0.003
53	δ-cadinene	0.023	0.003	0.023	0.002
54	tridecanal	t		t	
55	(Z)-nerolidol	0.003	0.001	0.003	0.001
56	tetradecanal	t		t	
57	β-sinensal	0.026	0.010	0.017	0.008
58	α-sinensal	0.016	0.008	0.011	0.005
59	nootkatone	0.011	0.005	0.013	0.009
	hydrocarbons	98.369	0.246	98.752	0.221
	monoterpenes	98.216	0.256	98.603	0.225
	sesquiterpenes	0.153	0.024	0.149	0.013
	oxygenated compounds	1.429	0.266	1.017	0.202
	carbonyl compounds	0.776	0.188	0.517	0.160
	alcohols	0.569	0.100	0.428	0.050
	esters	0.050	0.017	0.049	0.009
	aliphatic aldehydes	0.533	0.137	0.344	0.126
	terpenic aldehydes	0.237	0.060	0.165	0.040

t = trace

Table X. Composition of the volatile fraction of blond and blood sweet orange oils

		Blond		Blood	
		$\bar{X}$	s	$\bar{X}$	s
1	α-thujene	0.006	0.002	0.004	0.001
2	α-pinene	0.508	0.035	0.520	0.026
3	camphene	0.003	0.001	0.003	0.001
4	sabinene	0.625	0.215	0.387	0.089
5	β-pinene	0.047	0.017	0.028	0.008
6	myrcene	1.856	0.103	1.884	0.089
7	octanal	0.272	0.061	0.129	0.037
8	α-phellandrene	0.051	0.009	0.050	0.010
9	δ-3-carene	0.101	0.033	0.144	0.036
10	α-terpinene	0.003	0.001	0.005	0.001
11	limonene	94.847	0.423	95.506	0.286
12	(Z)-β-ocimene	0.006	0.002	0.006	0.002
13	(E)-β-ocimene	0.042	0.017	0.026	0.006
14	γ-terpinene	0.029	0.019	0.014	0.010
15	trans-sabinene hydrate	0.009	0.003	0.006	0.001
16	octanol	0.018	0.007	0.008	0.004
17	terpinolene	0.023	0.005	0.030	0.007
18	linalool	0.478	0.070	0.358	0.039
19	nonanal	0.045	0.012	0.028	0.007
20	cis-limonene oxide	0.014	0.005	0.008	0.005
21	trans-limonene oxide	0.020	0.005	0.016	0.004
22	citronellal	0.041	0.010	0.036	0.004
23	terpinen-4-ol	0.007	0.002	0.004	0.002
24	α-terpineol	0.053	0.015	0.034	0.008
25	decanal	0.229	0.044	0.135	0.027
26	octyl acetate	0.008	0.003	0.006	0.002
27	cis-carveol	0.005	0.002	0.004	0.001
28	nerol	0.015	0.004	0.010	0.004
29	neral	0.064	0.015	0.037	0.008
30	geraniol	0.006	0.002	0.004	0.001
31	geranial	0.095	0.021	0.055	0.013
32	perillaldehyde	0.010	0.002	0.006	0.001
33	bornyl acetate	0.012	0.004	0.009	0.002
34	undecanal	0.011	0.002	0.008	0.001
35	nonyl acetate	0.004	0.001	0.003	0.001
36	α-terpinyl acetate	0.003	0.001	0.003	0.002
37	citronellyl acetate	0.004	0.002	0.005	0.002
38	neryl acetate	0.007	0.001	0.007	0.001
39	α-copaene	0.019	0.002	0.022	0.007
40	geranyl acetate	0.007	0.001	0.008	0.002
41	β-cubebene + β-elemene	0.023	0.005	0.023	0.006
42	dodecanal	0.038	0.013	0.021	0.006
43	decyl acetate	0.009	0.007	0.010	0.005
44	β-caryophyllene	0.016	0.002	0.018	0.005
45	α-cadinene	0.018	0.003	0.015	0.002
46	α-humulene	0.004	0.002	0.005	0.002
47	(Z)-β-farnesene	0.015	0.007	0.009	0.004
48	γ-muurolene	0.016	0.003	0.017	0.003
49	germacrene D	0.007	0.003	0.011	0.006
50	valencene	0.078	0.049	0.162	0.104
51	γ-cadinene	0.005	0.001	0.004	0.001
52	α-farnesene	0.013	0.005	0.008	0.003
53	δ-cadinene	0.023	0.003	0.023	0.002
54	tridecanal	t		t	
55	(Z)-nerolidol	0.003	0.001	0.003	0.001
56	tetradecanal	t		t	
57	β-sinensal	0.029	0.009	0.016	0.007
58	α-sinensal	0.018	0.008	0.011	0.005
59	nootkatone	0.010	0.005	0.013	0.008
	hydrocarbons	98.298	0.204	98.754	0.197
	monoterpenes	98.145	0.213	98.604	0.206
	sesquiterpenes	0.153	0.021	0.150	0.019
	oxygenated compounds	1.533	0.196	0.991	0.125
	carbonyl compounds	0.857	0.143	0.488	0.093
	alcohols	0.593	0.088	0.429	0.050
	esters	0.050	0.016	0.049	0.011
	aliphatic aldehydes	0.594	0.108	0.321	0.068
	terpenic aldehydes	0.257	0.048	0.159	0.032

t = trace

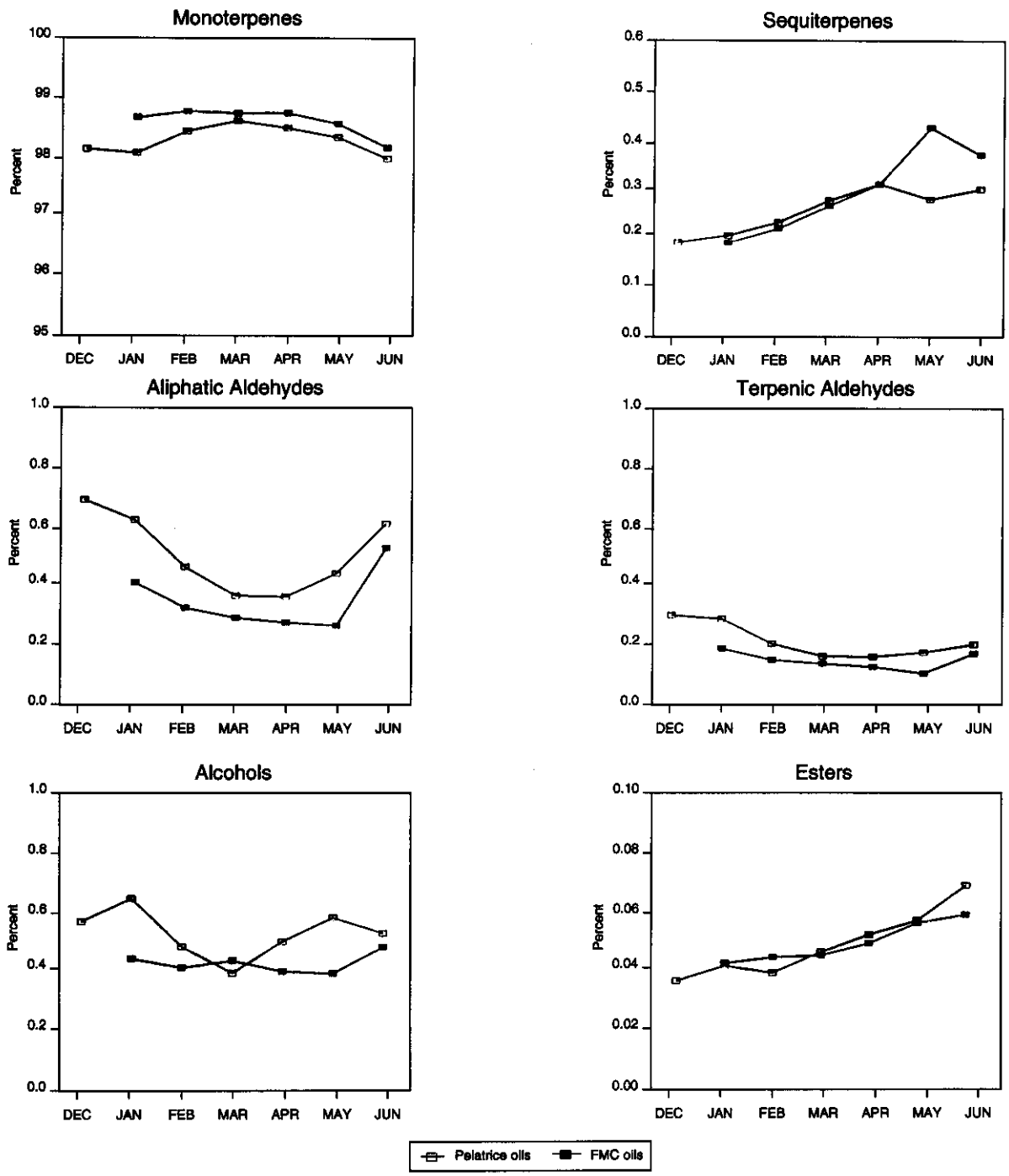

Figure 13. Variation in average content of some classes of substances for sweet orange oils processed by "Pelatrice" and "FMC" machines

their valencene content; it is higher in blood oils, especially late-season oils, and is generally lower in blond oils.

The variation trend of the aldehyde content of Italian sweet orange oils is different from that of North American oils. In these oils the aldehyde content increases during the productive season.[22-24]

The aldehyde content of Italian oils is the same or a little higher than those of Spanish[17,18] and South American oils[16,19,25] but lower than that of Florida, California and Israeli oils.[26,27]

Bitter Orange Oil

Bitter orange oil is produced by the usual industrial techniques such as "Pelatrice," "Sfumatrice," "Torchi," "FMC." The volatile fraction of bitter orange oil represents about 95-97% of the oil.

Figure 16 shows the chromatogram of a bitter orange oil obtained using an SE-52 capillary column. The composition of the oil as single components and classes of substances can be seen in Table XI. The results reported in Table XI are relative to ten absolutely genuine industrial samples obtained during the production season 1991-1992.

The main component is limonene, the content of which always exceeds 93%. Among the minor monoterpene hydrocarbons, only myrcene exceeds 1%.

Linalyl acetate is the main oxygenated compound of bitter orange oil, and it represents the major part of the esters. Linalool is the main alcohol, while octanal and decanal are the main carbonyl compounds.

Oxygenated compounds do not exceed 2.2%. Esters range from 0.8% to 1.4%; carbonyl compounds from 0.35% to 0.63% and alcohols from 0.33% to 0.46%.

Italian bitter orange oil possesses higher contents of aliphatic and terpenic aldehydes, linalyl acetate and linalool than Spanish bitter orange oil, while the content of α-terpineol and nootkatone is lower. In comparison with oils produced in the Ivory Coast, the Italian oil possesses an equivalent linalyl acetate content while the linalool and α-terpineol contents are higher and lower respectively. In both oils nootkatone was either absent or present as a trace constituent. When compared with Brazilian oils, the Italian oil is richer in an aliphatic aldehyde, linalyl acetate and

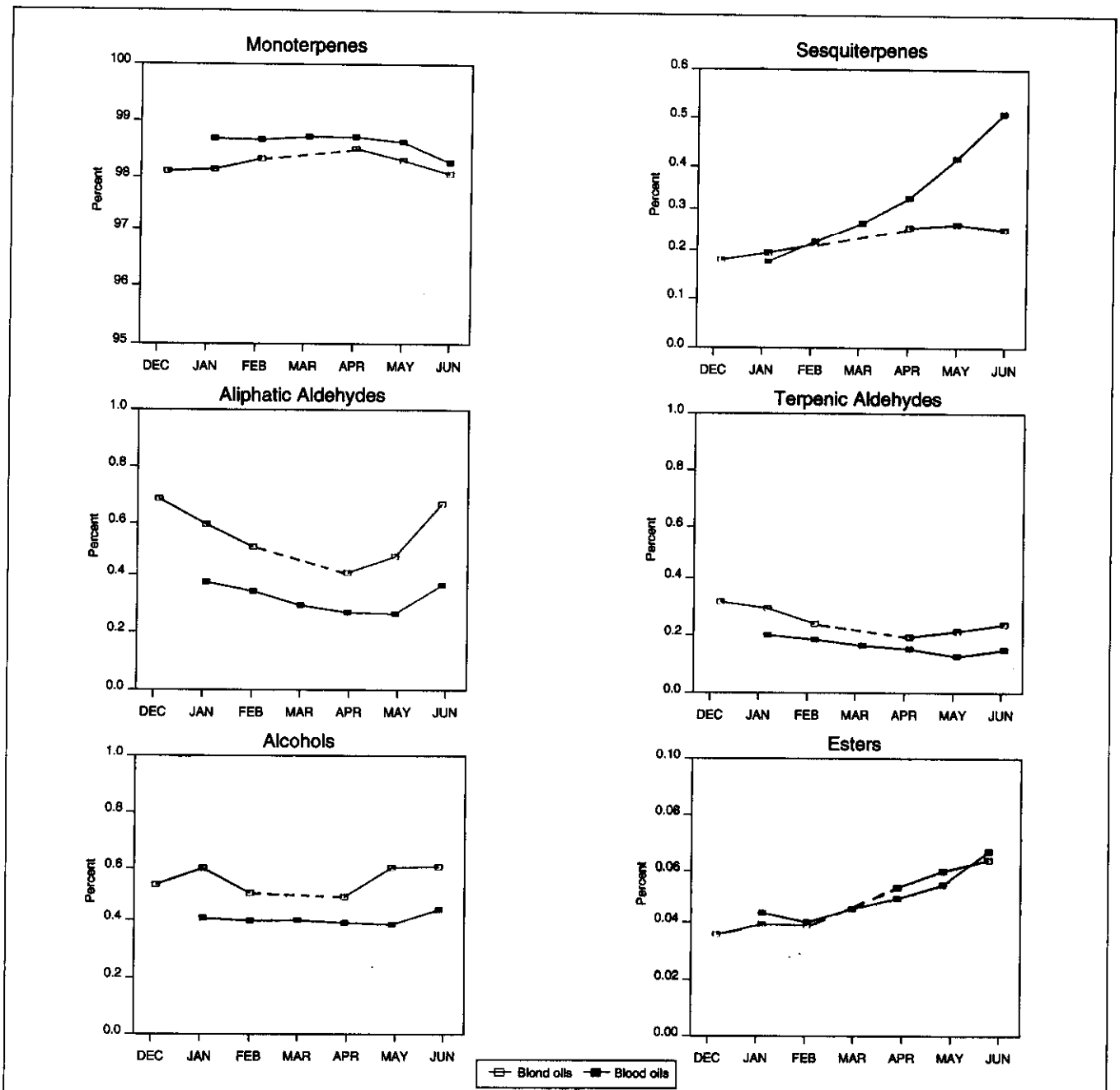

Figure 14. Variation in average content of some classes of substances for blond and blood sweet orange oils

Table XI. Composition of the volatile fraction of bitter orange oil

		$\bar{X}$	s	Min	Max
1	hexanol	0.001	0.001	0.000	0.003
2	α-thujene	0.006	0.002	0.004	0.009
3	α-pinene	0.563	0.019	0.521	0.585
4	camphene	0.007	0.001	0.005	0.007
5	sabinene	0.315	0.064	0.263	0.452
6	β-pinene	0.940	0.159	0.634	1.281
7	myrcene	1.789	0.039	1.705	1.843
8	octanal	0.135	0.024	0.106	0.191
9	α-phellandrene	0.058	0.010	0.045	0.082
10	δ-3-carene	0.003	0.001	0.001	0.005
11	α-terpinene	0.002	0.001	0.001	0.005
12	p-cymene + limonene	93.563	0.218	93.200	93.861
13	(Z)-β-ocimene	0.010	0.003	0.006	0.014
14	(E)-β-ocimene	0.308	0.061	0.187	0.382
15	γ-terpinene	0.056	0.041	0.007	0.127
16	trans-sabinene hydrate	0.003	0.002	0.002	0.008
17	octanol	0.005	0.004	0.001	0.014
18	terpinolene	0.007	0.002	0.004	0.010
19	cis-sabinene hydrate	0.001	0.000	0.000	0.001
20	linalool	0.270	0.042	0.199	0.333
21	nonanal	0.027	0.006	0.015	0.036
22	cis-limonene oxide	0.005	0.004	0.001	0.010
23	trans-limonene oxide	0.003	0.002	0.001	0.006
24	isopulegol	0.003	0.002	0.001	0.006
25	citronellal	0.005	0.004	0.002	0.015
26	borneol	0.002	0.001	0.001	0.005
27	nonanol	0.001	0.000	0.001	0.001
28	terpinen-4-ol	0.004	0.003	0.001	0.008
29	α-terpineol	0.042	0.008	0.030	0.059
30	decanal	0.123	0.026	0.106	0.194
31	octyl acetate	0.038	0.006	0.032	0.050
32	nerol + citronellol	0.004	0.002	0.001	0.007
33	neral	0.045	0.008	0.032	0.055
34	piperitone	0.002	0.001	0.001	0.003
35	linalyl acetate	0.894	0.152	0.642	1.173
36	geranial	0.074	0.017	0.048	0.098
37	perillaldehyde	0.009	0.002	0.005	0.011
38	undecanal	0.008	0.005	0.001	0.015
39	nonyl acetate	0.003	0.002	0.001	0.008
40	ester	0.016	0.007	0.005	0.028
41	α-terpinyl acetate	0.006	0.001	0.004	0.007
42	citronellyl acetate	0.007	0.001	0.005	0.009
43	neryl acetate	0.020	0.003	0.016	0.024
44	geranyl acetate	0.098	0.014	0.075	0.114
45	dodecanal	0.015	0.004	0.010	0.026
46	decyl acetate	0.027	0.007	0.010	0.038
47	β-caryophyllene	0.052	0.010	0.035	0.063
48	trans-α-bergamotene	0.014	0.004	0.009	0.019
49	α-humulene	0.007	0.002	0.004	0.009
50	β-santalene	0.009	0.003	0.003	0.012
51	carbonyl compound	0.012	0.002	0.003	0.015
52	germacrene D	0.108	0.014	0.087	0.134
53	germacrene B	0.009	0.001	0.007	0.011
54	β-bisabolene	0.003	0.002	0.001	0.006
55	β-sesquiphellandrene	0.009	0.001	0.007	0.012
56	(E)-nerolidol	0.062	0.012	0.045	0.083
57	tetradecanal	0.002	0.001	0.001	0.003
58	(Z,E)-farnesol	0.004	0.003	0.001	0.012
59	α-sinensal	0.001	0.001	0.000	0.002
60	nootkatone	0.001	0.001	0.000	0.002
	hydrocarbons	97.836	0.195	97.486	98.079
	monoterpenes	97.625	0.185	97.291	97.845
	sesquiterpenes	0.211	0.032	0.167	0.260
	oxygenated compounds	1.964	0.106	1.847	2.202
	carbonyl compounds	0.459	0.078	0.349	0.629
	alcohols	0.397	0.039	0.333	0.459
	esters	1.108	0.163	0.825	1.407

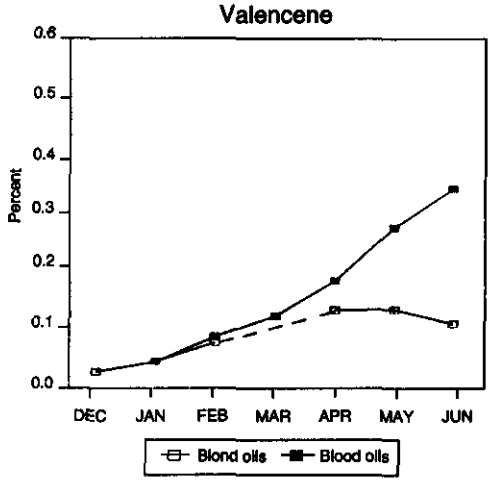

Figure 15. Variation in average content of valencene for blond and blood sweet orange oils

Table XII. Comparison of some components for different bitter orange oils

	Italy[11]	Spain[17,18]	Ivory Coast[28]	Brazil[19]
aliphatic aldehydes	0.310	0.116	0.281	0.17*
terpenic aldehydes	0.128	0.092	0.119	0.17
linalool	0.270	0.152	0.101	0.21
α-terpineol	0.042	0.567	0.081	0.07
linalyl acetate	0.894	0.284	0.070	0.37
nootkatone	0.001	0.082	0.001	-

*This result does not include octanal

linalool while it contains less of a terpenic aldehyde and α-terpineol than Brazilian oils. In both oils nootkatone is either absent or present as a trace constituent. The differences mentioned above can be seen in Table XII.

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Address correspondence to Giovanni Dugo, Dipartimento Farmaco-chimico, Facoltà di Farmacia, Università di Messina, Messina, Italy.

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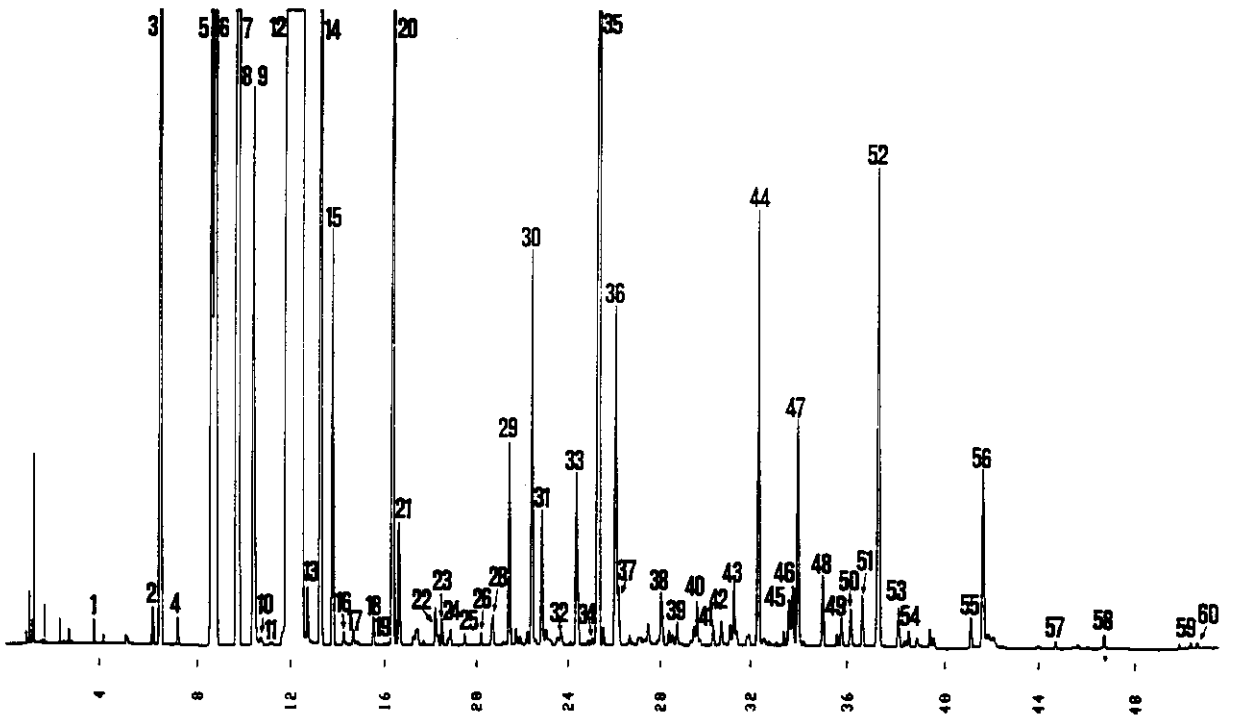

Figure 16. Gas chromatogram of a bitter orange oil. Experimental condition: see Figure 3. For identification of components, see Table XI

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