Characterization of Italian Citrus Petitgrain Oils

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Petitgrain oils are obtained by steam distillation of leaves, twigs and small unripe fruits of different *Citrus* species. Because of its olfactory characteristics, bitter orange petitgrain oil is considered the most valuable of these. It is produced in Italy, France, Spain and Paraguay.

Bitter orange petitgrain oils produced in Mediterranean countries show better organoleptic properties than Paraguayan oils usually obtained from a hybrid, locally called "Apepù-Jhai," with rudimentary distillation equipment.[1,2]

Lemon, mandarin and bergamot petitgrain oils are produced in very limited amounts, almost exclusively in Italy. Sweet orange petitgrain oil, only occasionally produced by industry, is considered poorer than other petitgrain oils and it is sometimes used for the adulteration of more valuable petitgrain oils.

Only carefully selected leaf material is used to produce bitter orange, lemon, mandarin and bergamot petitgrain oils. However, for the production of sweet orange petitgrain oil, due to its low commercial value, little attention is paid to the selection of the material to be distilled and to the cleaning of the equipment, which is sometimes used for more valuable oils also. So, with sweet orange petitgrain oil, possible contamination with other petitgrain oils is not considered a problem. Therefore, it is very difficult to find pure industrial sweet orange petitgrain oils because they very often contain other citrus leaf oils.

The composition of industrial citrus petitgrain oils has only scant coverage in scientific papers, [1-20] and some of these papers report only qualitative information.[1,3,5,8,13,15.] But, the composition of laboratory-extracted samples, whether from steam distillation [21-46] or from solvent extractions, [47-51] has been more widely studied. These investigations focus on the biogenesis and the ontogenesis of citrus volatile aromatic compounds, and the classification and the characterization of the different *Citrus* species. The least studied citrus petitgrain oil is bergamot.[3,7,24,26,36] Most of the papers concerning citrus petitgrain oils have been reviewed by Lawrence.[20]

In spite of the broad research already done on citrus petitgrain oils, their composition is not as well defined as that of the citrus peel oils. This is because of the difficulty of analyzing natural complex mixtures, such as petitgrain oils, and also because of the nature of the samples, which can differ by geographical origin, cultivar, extraction procedure, type utilized, age and freshness of the leaves.

As can be seen from Lawrence's review [20] and from the tables of some other papers concerning single petitgrain oils,[52-55] published data often disagree.

Compositions of Italian industrial bitter orange, lemon and mandarin petitgrain oils, and of laboratory-extracted and commercial samples of sweet orange petitgrain oil, are reported in this paper.

Analyses were carried out on the following:

- 5 samples of industrial bitter orange petitgrain oil;
- 5 samples of industrial mandarin petitgrain oil;
- 6 samples of industrial lemon petitgrain oil;
- 4 samples of industrial sweet orange petitgrain oil;
- 3 samples of sweet orange petitgrain oil steam distilled in our laboratory from leaves of "Biondo Comune," " Moro" and "Valencia Late" cultivars.

Industrial bitter orange, lemon and mandarin petitgrain oils were extracted, from carefully selected leaf material, in a Sicilian facility in the spring of 1994. The yield was about 3‰, 1.5‰ and 2‰, respectively.

All the samples were analyzed by HPLC-HRGC-MS (ITD), HRGC-MS (quadrupole) and HRGC-FID under experimental conditions elsewhere described.[52-55] The HPLC-HRGC-MS (ITD) system was equipped with an SE-52 column, 30 m x 0.32 mm i.d. For the analyses with the HRGC-MS (quadrupole) and GC-FID systems, we used either an SE-52 or a Carbowax 20 M column, 60 m x 0.32 mm i.d.

The HPLC-HRGC-MS (ITD) system was equipped

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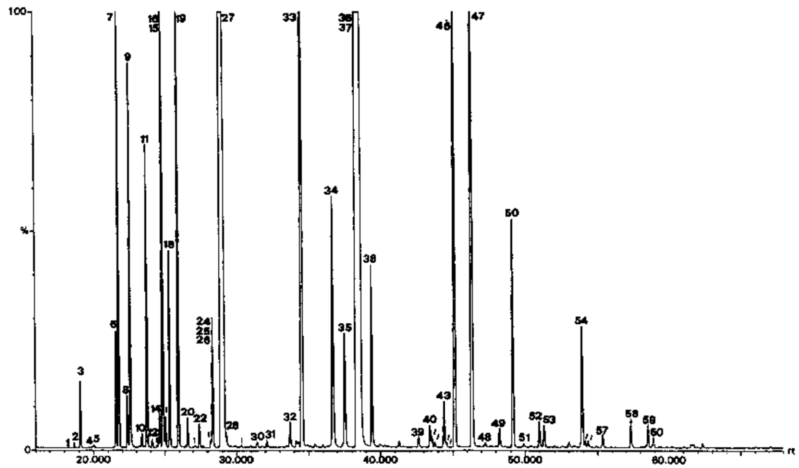

Figure 1. Total ion current chromatogram of a bitter orange petitgrain oil obtained by GC-MS (quadrupole). GC column SE-52, 60 m. For peak identification see Table II.

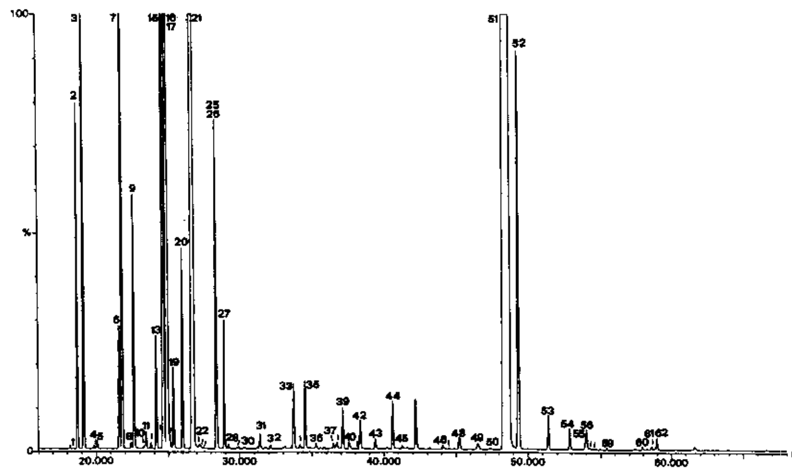

Figure 2. Total ion current chromatogram of a mandarin petitgrain oil obtained by GC-MS (quadrupole). GC column SE-52, 60 m. For peak identification see Table III.

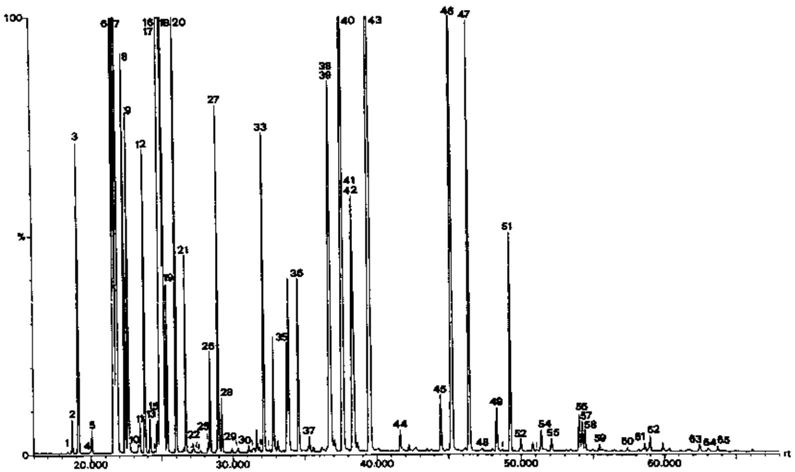

Figure 3. Total ion current chromatogram of a lemon petitgrain oil obtained by GC-MS (quadrupole). GC column SE-52, 60 m. For peak identification see Table IV.

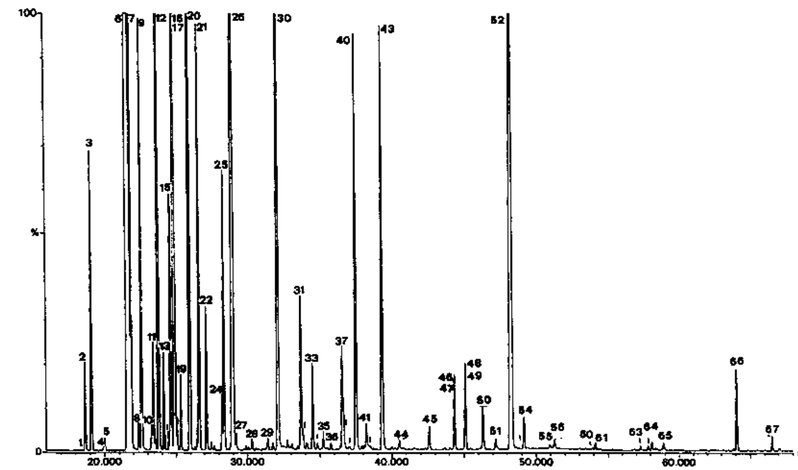

Figure 4. Total ion current chromatogram of a commercial sweet orange petitgrain oil obtained by GC-MS (quadrupole). GC column SE-52, 60 m. For peak identification see Table V.

with the Adams library,[56] while the GC-MS (quadrupole) system was coupled with two commercial libraries (NIST and Adams) and a home made Flavor and Fragrance Components (FFC) database provided with linear retention indices, to be used interactively with MS data for compound identification.[57]

Results and Discussion

The total ion current chromatograms, performed on an SE-52 column, for industrial samples of bitter orange, mandarin, lemon and sweet orange petitgrain oils, and for laboratory-extracted sweet orange petitgrain oils, are shown in Figures 1-5, respectively. The corresponding Carbowax 20 M total ion current chromatograms of the same samples are shown in Figures 6-10.

Table I shows the identification carried out with a Carbowax 20 M column. Tables II-V show the composition of bitter orange, mandarin, lemon and sweet orange petitgrain oils, respectively. These data refer to the results obtained by GC-FID with SE-52 and Carbowax 20 M columns, and to results obtained by HRGC-MS (quadrupole) and HPLC-HRGC-MS (ITD).

Bitter orange petitgrain oil: Sixty-one components were identified in bitter orange petitgrain oil, representing over 99% of the whole oil. Bitter orange petitgrain oil is

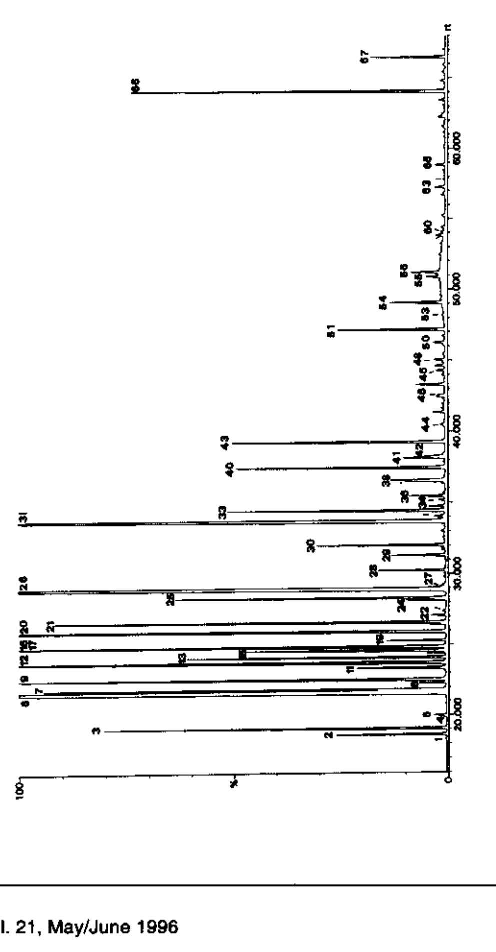

Figure 5. Total ion current chromatogram of a laboratory-extracted sweet orange petitgrain oil obtained by GC-MS (quadrupole). GC column SE-52, 60 m. For peak identification see Table V.

Table I. Components identified with Carbowax 20 M column

Bitter orange	Mandarin	Sweet orange	Lemon
1) tricyclene	1) α-pinene	1) tricyclene	1) tricyclene
2) α-pinene	2) α-thujene	2) α-pinene	2) α-pinene
3) α-thujene	3) α-fenchene	3) α-thujene	3) α-thujene
4) α-fenchene	4) camphene	4) α-fenchene	4) α-fenchene
5) camphene	5) hexanal	5) camphene	5) camphene
6) hexanal	6) β-pinene	6) hexanal	6) hexanal
7) β-pinene	7) sabinene	7) β-pinene	7) β-pinene
8) sabinene	8) δ-3-carene	8) sabinene	8) sabinene
9) δ-3-carene	9) myrcene	9) δ-3-carene	9) δ-3-carene
10) myrcene	10) α-phellandrene	10) myrcene	10) myrcene
11) α-phellandrene	11) α-terpinene	11) α-phellandrene	11) α-phellandrene
12) α-terpinene	12) limonene	12) α-terpinene	12) α-terpinene
13) limonene	13) β-phellandrene	13) limonene	13) limonene
14) β-phellandrene	14) (Z)-β-ocimene	14) β-phellandrene	14) β-phellandrene
15) (Z)-β-ocimene	15) γ-terpinene	15) (Z)-β-ocimene	15) (Z)-β-ocimene
16) γ-terpinene	16) (E)-β-ocimene	16) γ-terpinene	16) γ-terpinene
17) (E)-β-ocimene	17) p-cymene	17) (E)-β-ocimene	17) (E)-β-ocimene
18) p-cymene	18) terpinolene	18) p-cymene	18) p-cymene
19) p-mentha-(2,4)8-diene	19) octanal	19) p-mentha-(2,4)8-diene	19) p-mentha-(2,4)8-diene
20) terpinolene	20) 6-methyl-5-hepten-2-one	20) terpinolene	20) terpinolene
21) 6-methyl-5-hepten-2-one	21) hexanol	21) 6-methyl-5-hepten-2-one	21) 6-methyl-5-hepten-2-one
22) nonanal	22) (Z)-3-hexenol	22) hexanol	22) nonanal
23) p-cymenene	23) nonanal	23) nonanal	23) citronellal
24) cis-sabinene hydrate	24) p-cymenene	24) cis-sabinene hydrate	24) decanal
25) citronellal	25) 1,3,8-p-menthatriene	25) citronellal	25) linalool
26) linalool	26) cis-sabinene hydrate	26) decanal	26) linalyl acetate
27) linalyl acetate	27) citronellal	27) linalool	27) trans-α-bergamotene
28) trans-α-bergamotene	28) decanal	28) linalyl acetate	28) terpinen-4-ol
29) terpinen-4-ol	29) linalool	29) thymol methyl ether	29) (E)-caryophyllene
30) (E)-caryophyllene	30) octanol	30) terpinen-4-ol	30) cis-p-menth-2-en-1-ol
31) cis-p-menth-2-en-1-ol	31) linalyl acetate	31) (E)-caryophyllene	31) citronellyl acetate
32) citronellyl acetate	32) thymol methyl ether	32) cis-p-menth-2-en-1-ol	32) neral
33) (Z)-β-farnesene	33) terpinen-4-ol	33) citronellyl acetate	33) α-humulene
34) neral	34) (E)-caryophyllene	34) (Z)-β-farnesene	34) α-terpineol
35) α-humulene	35) cis-p-menth-2-en-1-ol	35) neral	35) neryl acetate
36) α-terpineol	36) neral	36) α-humulene	36) geranial
37) methyl geranate	37) α-humulene	37) α-terpineol	37) β-bisabolene
38) neryl acetate	38) α-terpineol	38) methyl geranate	38) bicyclogermacrene
39) geranial	39) neryl acetate	39) neryl acetate	39) geranyl acetate
40) β-bisabolene	40) geranial	40) geranial	40) citronellol
41) bicyclogermacrene	41) α-selinene	41) β-bisabolene	41) δ-cadinene
42) geranyl acetate	42) bicyclogermacrene	42) cis-piperitol	42) nerol
43) δ-cadinene	43) geranyl acetate	43) bicyclogermacrene	43) geraniol
44) nerol	44) δ-cadinene	44) geranyl acetate	44) caryophyllene oxide
45) geraniol	45) geraniol	45) citronellol	45) (E)-nerolidol
46) caryophyllene oxide	46) caryophyllene oxide	46) nerol	46) methyl N-methylanthranilate
47) (E)-nerolidol	47) methyl N-methylanthranilate	47) geraniol	47) spathulenol
48) methyl N-methylanthranilate	48) methyl N-dimethylanthranilate	48) caryophyllene oxide	48) α-bisabolol
49) spathulenol	49) spathulenol	49) (E)-nerolidol	
	50) (Z)-3-hexenyl benzoate	50) methyl N-methylanthranilate	
	51) thymol	51) β-sinensal	
	52) carvacrol	52) tricosane	
	53) methylanthranilate	53) α-sinensal	

Table II. Quantitative composition (%) of bitter orange petitgrain oil

	Compounds	Min	Max
1)	tricyclene	tr	tr
2)	α-thujene	tr	0.01
3)	α-pinene	0.03	0.30
4)	α-fenchene	tr	tr
5)	camphene	tr	0.01
6)	sabinene	0.13	0.23
7)	β-pinene	0.65	1.15
8)	6-methyl-5-hepten-2-one	0.01	0.10
9)	myrcene	0.56	1.24
10)	α-phellandrene	tr	0.03
11)	δ-3-carene	0.21	0.67
12)	α-terpinene	tr	0.02
13)	o-cymene	-	0.01
14)	p-cymene	0.03	0.08
15)	limonene	0.44	2.17
16)	β-phellandrene	0.03	0.04
17)	1,8-cineole	0.02	0.05
18)	(Z)-β-ocimene	0.20	0.44
19)	(E)-β-ocimene	0.57	1.76
20)	γ-terpinene	0.01	0.09
21)	cis-sabinene hydrate	tr	0.01
22)	cis-linalool oxide	0.03	0.09
23)	p-mentha-(2,4)8-diene	0.02	0.06
24)	terpinolene	0.08	0.22
25)	p-cymenene	0.01	0.08
26)	trans-linalool oxide	0.01	0.03
27)	linalool	21.70	32.55
28)	nonanal	0.02	0.05
29)	cis-p-menth-2-en-1-ol	tr	0.01
30)	trans-p-menth-2-en-1-ol	tr	0.02
31)	citronellal	0.01	0.04
32)	terpinen-4-ol	0.05	0.08
33)	α-terpineol	3.09	5.63
34)	nerol	0.75	0.99
35)	neral	0.21	0.43
36)	geraniol	0.71	0.95
37)	linalyl acetate	50.68	62.57
38)	geranial	0.38	0.64
39)	methyl geranate	tr	0.03
40)	linalyl n-propanoate	0.02	0.04
41)	δ-elemene	0.01	0.01
42)	α-cubebene	tr	0.01
43)	α-terpinyl acetate	0.08	0.16
44)	citronellyl acetate	tr	tr
45)	α-copaene	tr	0.01
46)	neryl acetate	1.04	1.73
47)	geranyl acetate	1.90	3.16
48)	β-elemene	tr	0.02
49)	methyl N-methyl anthranilate	tr	0.14
50)	(E)-caryophyllene	0.48	0.61
51)	trans-α-bergamotene	tr	0.01
52)	(Z)-β-farnesene	0.04	0.07
53)	α-humulene	0.04	0.06
54)	bicyclogermacrene	0.04	0.30
55)	(E,E)-α-farnesene	0.01	0.06
56)	β-bisabolene	-	0.01
57)	δ-cadinene	0.02	0.03
58)	(E)-nerolidol	0.05	0.08
59)	spathulenol	0.03	0.13
60)	caryophyllene oxide	0.02	0.07
	monoterpene hydrocarbons	3.35	8.22
	sesquiterpene hydrocarbons	0.69	1.13
	aldehydes	0.65	1.16
	alcohols	26.58	40.17
	esters	54.12	67.38
	others	0.13	0.25

Table III. Quantitative composition (%) of mandarin petitgrain oil

	Compounds	Min	Max
1)	tricyclene	tr	tr
2)	α-thujene	0.78	1.04
3)	α-pinene	1.75	2.30
4)	α-fenchene	tr	0.01
5)	camphene	0.01	0.02
6)	sabinene	0.22	0.90
7)	β-pinene	1.90	2.45
8)	6-methyl-5-hepten-2-one	tr	0.01
9)	myrcene	0.62	0.78
10)	octanal	tr	tr
11)	α-phellandrene	0.03	0.05
12)	δ-3-carene	0.01	0.10
13)	α-terpinene	0.19	0.33
14)	o-cymene	tr	tr
15)	p-cymene	2.96	4.84
16)	limonene	7.18	11.65
17)	β-phellandrene	0.03	0.05
18)	1,8-cineole	0.01	0.02
19)	(Z)-β-ocimene	0.15	0.20
20)	(E)-β-ocimene	0.42	0.72
21)	γ-terpinene	23.94	28.48
22)	cis-sabinene hydrate	0.01	0.03
23)	octanol	tr	tr
24)	cis-linalool oxide	tr	tr
25)	terpinolene	0.71	0.88
26)	p-cymenene	0.10	0.18
27)	linalool	0.27	0.64
28)	nonanal	tr	0.01
29)	1,3,8-p-menthatriene	0.01	0.02
30)	cis-p-menth-2-en-1-ol	tr	tr
31)	trans-p-menth-2-en-1-ol	0.02	0.03
32)	citronellal	0.02	0.04
33)	terpinen-4-ol	0.20	0.26
34)	p-cymen-8-ol	0.01	0.01
35)	α-terpineol	0.16	0.21
36)	decanal	0.01	0.02
37)	citronellol	tr	tr
38)	nerol	0.01	0.02
39)	thymol methyl ether	0.10	0.16
40)	neral	tr	0.03
41)	geraniol	tr	tr
42)	linalyl acetate	0.04	0.10
43)	geranial	tr	0.03
44)	thymol	0.12	0.17
45)	carvacrol	0.01	0.01
46)	methyl anthranilate	tr	0.03
47)	α-terpinyl acetate	tr	tr
48)	neryl acetate	tr	0.04
49)	geranyl acetate	tr	0.02
50)	β-elemene	tr	0.01
51)	methyl N-methylanthranilate	43.19	51.93
52)	(E)-caryophyllene	1.23	1.40
53)	α-humulene	0.10	0.13
54)	methyl N-dimethylanthranilate	tr	0.04
55)	α-selinene	tr	tr
56)	bicyclogermacrene	0.05	0.13
57)	(E,E)-α-farnesene	tr	0.03
58)	β-bisabolene	tr	0.01
59)	δ-cadinene	tr	tr
60)	(Z)-3-hexenyl benzoate	tr	0.02
61)	spathulenol	tr	0.02
62)	caryophyllene oxide	0.01	0.08
	monoterpene hydrocarbons	45.14	53.81
	sesquiterpene hydrocarbons	1.42	1.69
	aldehydes	0.04	0.13
	alcohols	0.84	1.37
	esters	43.36	52.08
	others	0.12	0.22

characterized by a very high content of oxygenated compounds ranging from 91–96%. Esters (54–67%) are the most abundant oxygenated compounds, followed by alcohols (27–40%). Aldehydes are present in low amounts, ranging from 0.6–1.2%. Linalyl acetate, the percentage of which is never less than 50%, is the major component, followed by linalool, varying from 22–33%. Limonene, (E)-β-ocimene, myrcene and β-pinene are the main components among monoterpene hydrocarbons. The fraction of sesquiterpene hydrocarbons includes 12 components, principally (E)-caryophyllene.

Components present rather narrow ranges of their percentage content, and this behavior proves the reliability of the procedure to produce and select the raw material. So, results shown in Table II can be considered representative of the composition of the Italian industrial bitter orange petitgrain oil.

Mandarin petitgrain oil: Sixty-five components were identified in mandarin petitgrain oil, representing more than 99% of the whole oil. Monoterpene hydrocarbons represent 45–54% of the whole oil, and γ-terpinene is the most abundant of this fraction, ranging from 24–28%. Sesquiterpene hydrocarbons range from 1.4–1.7% and (E)-caryophyllene is the most abundant among these components, representing about 70% of the whole sesquiterpene fraction. Methyl N-methylanthranilate, which represents 43–52% of the whole oil, is the main component. Alcohols are present in quantities varying from 0.8–1.4%. Aldehydes are present only in small amounts (0.04–0.13%).

Lack of qualitative differences among the different samples analyzed, and the rather narrow range of the percentage content of most of the components, proves, again, the appropriateness of the production procedure and of the selection of the raw materials. Some relatively large quantitative differences found for some compounds, such as p-cymene and some alcohols, may be due to different distillation conditions. The higher amount (0.96%) of linalyl acetate found in one sample may be due to the presence of about 2% of bitter orange leaves in the mandarin material distilled, whereas the higher content of sabinene (2.33%) and δ-3-carene (0.29%) in another sample may be explained by the presence of about 3-4% of sweet orange leaves. Results from those samples considered contaminated were not used in Table III.

In spite of the possibility of slight contamination, the results reported in Table III, on the whole, can be considered representative of Italian mandarin petitgrain oil produced from properly executed extraction technologies.

Lemon petitgrain oil: The sixty-six components identified in lemon petitgrain oil represent 98-99% of the whole oil. The differences, among the various samples, of the total percentage content, are due to two unidentified compounds. On the SE-52 column, one compound elutes between citronellal and terpinen-4-ol, and the other after terpinen-4-ol. These two compounds, probably monoter-

Table IV. Quantitative composition (%) of lemon petitgrain oil

	Compound	Min	Max
1)	tricyclene	tr	0.01
2)	α-thujene	0.06	0.09
3)	α-pinene	0.84	1.13
4)	α-fenchene	-	tr
5)	camphene	0.05	0.07
6)	sabinene	2.99	3.81
7	β-pinene	11.96	16.03
8)	6-methyl-5-hepten-2-one	0.67	1.61
9)	myrcene	0.79	1.60
10)	octanal	0.01	0.04
11)	α-phellandrene	0.03	0.09
12)	δ-3-carene	0.63	1.08
13)	α-terpinene	0.04	0.11
14)	o-cymene	tr	0.01
15)	p-cymene	0.04	0.51
16)	limonene	28.41	34.82
17)	β-phellandrene	2.22	2.60
18)	1,8-cineole	1.12	2.13
19)	(Z)-β-ocimene	0.30	0.44
20)	(E)-β-ocimene	1.50	2.43
21)	γ-terpinene	0.34	0.70
22)	cis-sabinene hydrate	0.02	0.06
23)	octanol	tr	0.01
24)	cis-linalool oxide	tr	0.01
25)	p-mentha-(2,4)8-diene	0.01	0.03
26)	terpinolene	0.19	0.31
27)	linalool	0.88	3.87
28)	nonanal	0.08	0.22
29)	cis-p-menth-2-en-1-ol	0.01	0.03
30)	cis-limonene oxide	0.01	0.05
31)	trans-limonene oxide	0.01	0.06
32)	isopulegol	tr	0.03
33)	citronellal	0.62	1.41
34)	iso-isopulegol	tr	tr
35)	terpinen-4-ol	0.25	0.59
36)	α-terpineol	0.53	1.00
37)	decanal	0.03	0.09
38)	citronellol	tr	tr
39)	nerol	1.90	3.14
40)	neral	6.64	10.78
41)	geraniol	0.87	6.25
42)	linalyl acetate	0.31	0.42
43)	geranial	9.87	14.07
44)	undecanal	0.02	0.08
45)	citronellyl acetate	0.13	0.23
46)	neryl acetate	3.75	6.74
47)	geranyl acetate	2.17	2.92
48)	β-elemene	tr	0.03
49)	methyl N-methylanthranilate	tr	0.39
50)	cis-α-bergamotene	tr	tr
51)	(E)-caryophyllene	0.60	1.54
52)	trans-α-bergamotene	0.03	0.20
53)	(Z)-β-farnesene	tr	0.03
54)	α-humulene	0.06	0.13
55)	geranyl propanoate	0.03	0.04
56)	bicyclogermacrene	0.06	0.23
57)	(E,E)-α-farnesene	0.03	0.14
58)	β-bisabolene	0.07	0.33
59)	δ-cadinene	0.02	0.05
60)	(E)-nerolidol	0.01	0.03
61)	spathulenol	0.01	0.09
62)	caryophyllene oxide	0.04	0.14
63)	2,3-dimethyl-3-(4-methyl-3-pentenyl)-2-norbornanol	0.02	0.06
64)	campherenol	0.01	0.02
65)	α-bisabolol	0.01	0.03
	monoterpene hydrocarbons	51.82	60.62
	sesquiterpene hydrocarbons	1.08	2.56
	aldehydes	17.70	26.66
	alcohols	6.75	14.23
	esters	7.07	9.68
	others	1.87	3.62

Table V. Quantitative composition (%) of sweet orange petitgrain oils

	Compound	Industrial		Extracted in laboratory		
				Valencia Late	Biondo Comune	Moro
1)	tricyclene	tr	tr	tr	tr	tr
2)	α-thujene	0.21	0.39	0.34	0.34	0.33
3)	α-pinene	0.99	1.51	1.59	1.76	1.65
4)	α-fenchene	0.01	0.01	0.01	0.02	0.01
5)	camphene	0.03	0.04	0.04	0.04	0.04
6)	sabinene	37.64	41.93	40.66	38.46	48.52
7)	β-pinene	1.89	2.62	1.87	2.01	2.33
8)	6-methyl-5-hepten-2-one	0.04	0.06	0.08	0.12	0.08
9)	myrcene	2.66	3.85	3.49	4.40	3.72
10)	octanal	0.03	0.05	tr	tr	tr
11)	α-phellandrene	0.23	0.50	0.37	0.69	0.22
12)	δ-3-carene	3.46	5.91	4.45	10.28	5.51
13)	α-terpinene	0.27	0.96	1.16	0.74	0.48
14)	o-cymene	0.03	0.05	0.03	0.06	0.08
15)	p-cymene	0.59	2.89	0.76	0.59	1.68
16)	limonene	5.12	8.37	2.90	3.67	4.04
17)	β-phellandrene	0.78	1.06	0.65	0.70	0.74
18)	1,8-cineole	-	0.05	-	-	-
19)	(Z)-β-ocimene	0.21	0.33	0.22	0.33	0.19
20)	(E)-β-ocimene	4.53	9.21	6.14	9.73	4.99
21)	γ-terpinene	2.19	2.98	2.43	1.41	1.46
22)	cis-sabinene hydrate	0.13	0.42	0.06	0.12	0.10
23)	cis-linalool oxide	tr	0.01	0.01	tr	tr
24)	p-mentha-(2,4)8-diene	0.09	0.22	0.15	0.36	0.14
25)	terpinolene	0.98	1.52	1.32	2.14	0.95
26)	linalool	4.34	10.71	15.12	6.29	6.52
27)	nonanal	tr	0.03	tr	0.01	0.05
28)	cis-p-menth-2-en-1-ol	0.04	0.11	0.25	0.16	0.19
29)	trans-p-menth-2-en-1-ol	0.03	0.07	0.22	0.14	0.18
30)	citronellal	0.43	4.44	0.47	0.51	0.48
31)	terpinen-4-ol	0.55	2.59	7.33	3.75	6.14
32)	p-cymen-8-ol	tr	0.09	0.04	0.05	0.09
33)	α-terpineol	0.21	0.30	0.93	0.36	0.38
34)	cis-piperitol	0.01	0.07	0.06	0.05	0.06
35)	decanal	0.02	0.07	0.02	0.01	0.02
36)	trans-piperitol	tr	0.05	0.16	0.07	0.09
37)	citronellol	0.10	0.22	0.13	0.26	0.23
38)	nerol	0.13	0.26	0.13	0.45	0.30
39)	thymol methyl ether	-	tr	-	-	-
40)	neral	0.28	2.18	1.04	1.75	1.79
41)	geraniol	0.06	0.29	0.16	0.24	0.15
42)	linalyl acetate	0.02	0.12	0.10	0.10	0.07
43)	geranial	0.59	3.11	1.37	2.14	2.17
44)	thymol	0.01	0.05	0.02	0.02	tr
45)	methyl geranate	0.05	0.07	0.04	0.04	0.10
46)	citronellyl acetate	0.21	0.65	0.03	0.05	0.10
47)	α-copaene	tr	0.01	-	-	-
48)	neryl acetate	0.29	0.38	0.04	0.11	0.15
49)	β-cubebene	tr	0.10	-	-	-
50)	geranyl acetate	0.15	0.28	0.04	0.16	0.15
51)	β-elemene	0.04	3.80	0.49	1.07	0.36
52)	methyl N-methylanthranilate	1.26	10.29	tr	-	tr
53)	cis-α-bergamotene	tr	tr	tr	tr	tr
54)	(E)-caryophyllene	0.13	2.47	0.28	0.83	0.27
55)	(Z)-β-farnesene	0.01	0.58	0.07	0.15	0.06
56)	α-humulene	0.05	0.60	0.15	0.37	0.12
57)	β-santalene	-	-	-	-	0.04
58)	valencene	-	tr	tr	tr	tr
59)	α-selinene	-	tr	tr	tr	tr
60)	bicyclogermacrene	0.01	0.24	0.05	0.09	-
61)	(E,E)-α-farnesene	0.02	0.13	0.01	0.05	-
62)	β-bisabolene	-	0.09	-	-	-
63)	(E)-nerolidol	0.01	0.05	0.04	0.01	0.02
64)	(Z)-3-hexenyl benzoate	-	tr	tr	0.01	tr
65)	caryophyllene oxide	0.02	0.24	0.04	0.07	0.10
66)	β-sinensal	0.23	1.29	1.38	1.27	1.44
67)	α-sinensal	0.04	0.32	0.27	0.46	0.08
	monoterpene hydrocarbons	68.32	77.07	68.43	77.37	77.84
	sesquiterpene hydrocarbons	0.27	7.92	1.00	2.47	0.81
	aldehydes	2.84	10.12	4.65	6.15	4.24
	alcohols	8.10	12.68	24.43	11.85	14.30
	esters	2.58	11.37	0.25	0.46	0.57
	others	0.11	0.32	0.13	0.19	0.18

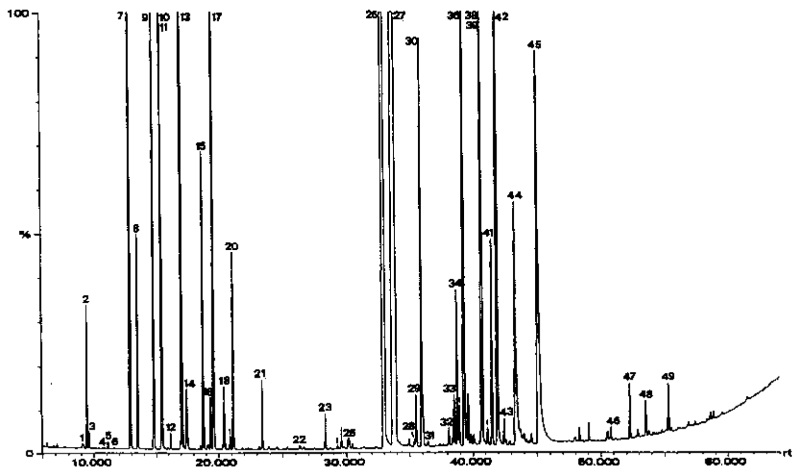

Figure 6. Total ion current chromatogram of a bitter orange petitgrain oil obtained by GC-MS (quadrupole). GC column Carbowax 20 M, 60 m. For peak identification see Table I.

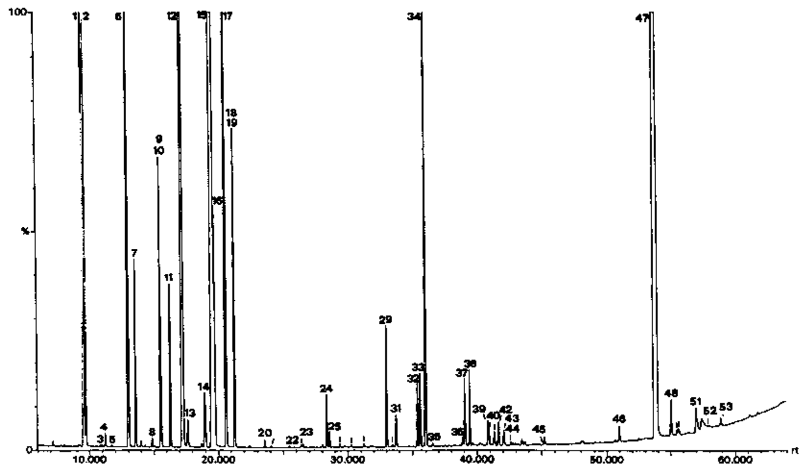

Figure 7. Total ion current chromatogram of a mandarin petitgrain oil obtained by GC-MS (quadrupole). GC column Carbowax 20 M, 60 m. For peak identification see Table I.

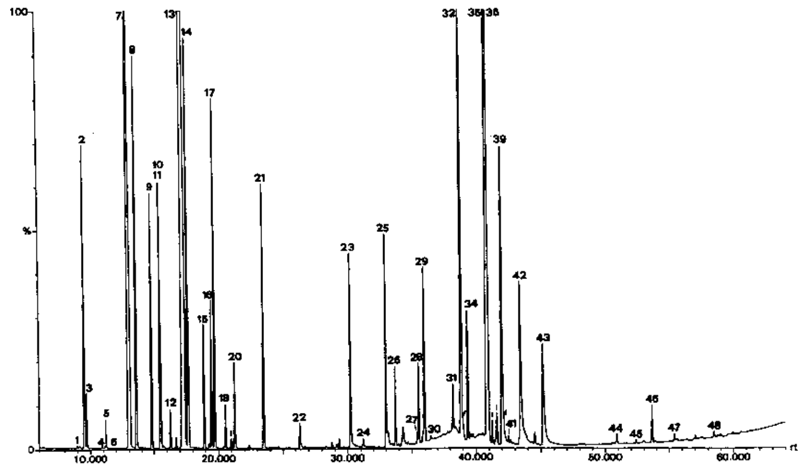

Figure 8. Total ion current chromatogram of a lemon petitgrain oil obtained by GC-MS (quadrupole). GC column Carbowax 20 M, 60 m. For peak identification see Table I.

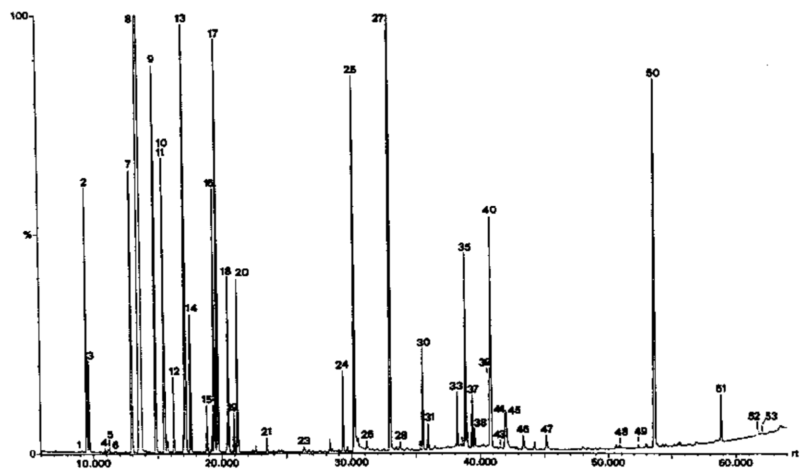

Figure 9. Total ion current chromatogram of a commercial sweet orange petitgrain oil obtained by GC-MS (quadrupole). GC column Carbowax 20 M, 60 m. For peak identification see Table I.

pene alcohols, vary considerably between samples. Monoterpene hydrocarbons range from 52–59%. The main components of this fraction are limonene (28–35%) and β-pinene (12–16%). Aldehydes (18–27%) are the class of substances that are the main contributors to the total content of oxygenated compounds; neral and geranial are the most representative components of this fraction, as they are with peel oil also. Alcohols range from 7–14%, while esters range from 7–10%. Lemon petitgrain oil is characterized by the presence of a large amount of 1,8-cineole (1.1–2.1%), which is absent in the other citrus petitgrain oils or present only as traces. Also characteristic of lemon petitgrain oil is the presence of three sesquiterpene alcohols: 2,3-dimethyl-3-(4-methyl-3-pentenyl)-2-norbornanol, campherenol and α-bisabolol, compounds which are also present in peel oil.

On the whole, of the *Citrus* species we analyzed, a lemon showed the greatest qualitative similarity between a petitgrain oil and its corresponding peel oil.

Sweet orange petitgrain oil: Sixty-seven compounds were identified in industrial sweet orange petitgrain oils, representing about 99% of the whole oil. Only 63 compounds were identified in laboratory-extracted oils. 1,8-Cineole, thymol methyl ether, α-copaene, β-cubebene, β-bisabolene and tricosane were not identified in laboratory-extracted oils, whereas hexanol and β-santalene were not identified in industrial oils. Both industrial and laboratory-extracted sweet orange petitgrain oils are characterized by a higher content of monoterpene hydrocarbons and, consequently, a lower content of oxygenated compounds than other citrus petitgrain oils. Sweet orange petitgrain oil is also characterized by the presence of α- and β-sinensal, not found in other citrus petitgrain oils, and by a higher content of sabinene, which ranges from 38–49% and always represents the main component. The ranges of the percentage content of some compounds and some classes of substances are rather wide in industrial sweet orange petitgrain oil: one could cite citronellal at 0.43–4.44%, geranial at 0.59–3.11%, β-elemene at 0.04–3.80%, total ester fraction at 2.58–11.37% and aldehyde fraction at 2.84–10.12%. This behavior shows the dishomogeneity among the various lots of leaves undergoing distillation, characteristic of the lack of care given to the production of sweet orange petitgrain oil.

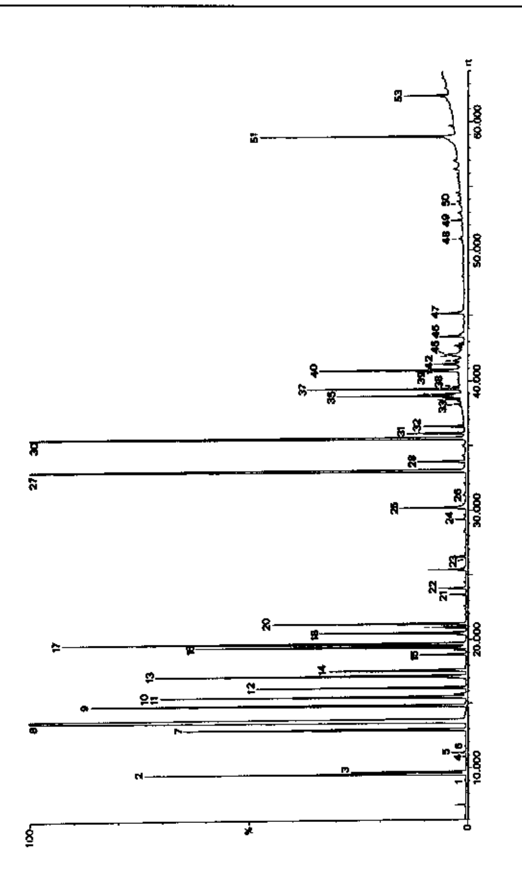

Figure 10. Total ion current chromatogram of a laboratory-extracted sweet orange petitgrain oil obtained by GC-MS (quadrupole), GC column Carbowax 20 M, 60 m. For peak identification see Table I.

Industrial sweet orange petitgrain oil, in comparison with the laboratory-extracted oil, shows a higher content of methyl N-methylanthranilate, probably because of mandarin petitgrain oil contamination. Differences between leaves of different varieties were found even among laboratory-extracted oils. The total amounts of alcohols and linalool are twice as high in the oil obtained from "Valencia" cultivar as they are in the oils from other species. The content of sesquiterpene hydrocarbons is highest in the oil obtained from "Biondo Comune" variety, while it is about 1% in the other two oils. This difference is mainly due to β-elemene and (E)-caryophyllene.

As can be seen from Table V, it is very difficult to define the composition of sweet orange petitgrain oil because of the lack of care in selecting the raw material and because of the numerous cultivars of sweet orange, which contribute differently every time to industrial distillation.

Adulteration and contamination of citrus petitgrain oils: Tables VI-IX report some compounds that, because of their relatively large content, characterize bitter orange, mandarin, lemon and sweet orange petitgrain oils, respectively. Table X shows compounds present exclusively in each petitgrain oil.

As can be seen from Tables VI-X, there are some qualitative and quantitative differences among the various petitgrain oils, and those differences tell us when those oils are being mixed or contaminated.

As can be seen from Table VI, contaminations or additions of bitter orange petitgrain oil to other petitgrain oils are easily detectable even if this kind of mixing is unlikely because of the higher commercial value of this oil. Contaminations or additions, even in very small amounts, of bitter orange petitgrain oil to the mandarin oil cause obvious increases of all the five components reported in Table VI. Contaminations or additions of bitter orange petitgrain oil to lemon and sweet orange petitgrain oils increase the amount of linalyl acetate; the presence of

Table VI. Relative percentage of some compounds characteristic of bitter orange petitgrain oil

	Bitter orange	Mandarin	Lemon	Sweet orange (laboratory-extracted oils)
linalyl acetate	50.68-62.57	0.04-0.10	0.31-0.42	0.07-0.10
linalool	21.70-32.55	0.27-0.64	0.88-3.87	6.29-15.12
α-terpineol	3.09-5.63	0.16-0.21	0.53-1.00	0.36-0.93
geranyl acetate	1.90-3.16	tr-0.02	2.17-2.92	0.04-0.16
neryl acetate	1.04-1.73	tr-0.04	3.75-6.74	0.04-0.15

Table VII. Relative percentage of some compounds characteristic of mandarin petitgrain oil

	Mandarin	Bitter orange	Lemon	Sweet orange (laboratory-extracted oils)
methyl N-methylanthranilate	43.19-51.93	tr-0.14	tr-0.39	tr
γ-terpinene	23.94-28.48	0.01-0.09	0.34-0.70	1.41-2.43
limonene	7.18-11.65	0.44-2.17	28.41-34.82	2.90-4.04
p-cymene	2.96-4.84	0.03-0.08	0.04-0.51	0.59-1.68

Table VIII. Relative percentage of some compounds characteristic of lemon petitgrain oil

	Lemon	Bitter orange	Mandarin	Sweet orange (laboratory-extracted oils)
limonene	28.41-34.82	0.44-2.17	7.18-11.65	2.90-4.04
β-pinene	11.96-16.03	0.65-1.15	1.90-2.45	1.87-2.33
geranial	9.87-14.07	0.38-0.64	tr-0.03	1.37-2.17
neral	6.64-10.78	0.21-0.43	tr-0.03	1.04-1.79
neryl acetate	3.75-6.74	1.04-1.73	tr-0.04	0.04-0.15
geranyl acetate	2.17-2.92	1.90-3.16	tr-0.02	0.04-0.16
β-phellandrene	2.22-2.60	0.03-0.04	0.03-0.05	0.65-0.74
1,8-cineole	1.12-2.13	0.02-0.05	0.01-0.02	-

Table IX. Relative percentage of some compounds characteristic of sweet orange petitgrain oil

	Sweet orange (laboratory-extracted oils)	Bitter orange	Mandarin	Lemon
sabinene	38.46-48.52	0.13-0.23	0.22-0.90	2.99-3.81
δ-3-carene	4.45-10.28	0.21-0.67	0.01-0.10	0.63-1.08
(E)-β-ocimene	4.99-9.73	0.57-1.76	0.42-0.72	1.50-2.43
terpinen-4-ol	3.75-7.33	0.05-0.08	0.20-0.26	0.25-0.59
neral	1.04-1.79	0.21-0.43	tr-0.03	6.64-10.78

Table X. Compounds present (%) exclusively in one petitgrain oil

Bitter orange	
trans-linalool oxide	0.01-0.03
linalyl n-propanoate	0.02-0.04
δ-elemene	0.01
α-cubebene*	tr-0.01
Mandarin	
1,3,8-p-menthatriene	0.01-0.02
thymol methyl ether **	0.10-0.16
carvacrol	0.01
methyl anthranilate	tr-0.03
methyl N-dimethylanthranilate	tr-0.04
Lemon	
cis-limonene oxide	0.01-0.05
trans-limonene oxide	0.01-0.06
isopulegol	tr-0.03
iso-isopulegol	tr
undecanal	0.02-0.08
geranyl propanoate	0.03-0.04
2,3-dimethyl-3-(4-methyl-3-pentenyl)-2-norbornanol	0.02-0.06
campherenol	0.01-0.02
α-bisabolol	0.01-0.03
Sweet orange (laboratory-extracted oils)	
cis-piperitol	0.05-0.06
trans-piperitol	0.07-0.16
β-santalene	0-0.04
valencene	tr
β-sinensal	1.27-1.44
α-sinensal	0.08-0.46

* tentative
** thymol methyl ether has also been found in some samples of commercial sweet orange petitgrain oil, probably because of contamination

bitter orange petitgrain oil in the sweet orange oil can be confirmed by the percentage content of geranyl and neryl acetate.

As can be seen from Table VII, the content of methyl N-methylanthranilate points out contaminations or additions of mandarin petitgrain oil to other petitgrain oils. Moreover, contaminations or additions of mandarin petitgrain oil to bitter orange petitgrain oil can be proved by the amount of γ-terpinene, p-cymene and limonene, while additions to lemon petitgrain oil can be proved by the percentage content of γ-terpinene and p-cymene. Also, the presence of mandarin petitgrain oil in other citrus petitgrain oils can be shown by trace amounts of thymol methyl ether, a compound present only in mandarin petitgrain oil (Table X).

As can be seen from Table VIII, the percentage content of 1,8-cineole positively indicates the presence of lemon petitgrain oil in the bitter orange oil. Neral, geranial, neryl and geranyl acetate, β-phellandrene and 1,8-cineole prove the presence of lemon petitgrain oil in the mandarin oil. And 1,8-cineole and neryl and geranyl acetate point to the possible presence of lemon petitgrain oil in the sweet orange oil.

Table IX and X show that the presence of sweet orange petitgrain oil in the other petitgrain oils can be proved by α- and β-sinensal, present only in this oil, and by the increase in the percentage content of sabinene, which is the main component of sweet orange petitgrain oil. Moreover, additions of sweet orange petitgrain oil to the bitter orange oil cause evident increases of (E)-β-ocimene and terpinen-4-ol, while the presence of sweet orange petitgrain oil in the mandarin oil can be proved by the percentage content of δ-3-carene and neral.

It is clear that success in using trace constituents to identify contaminations or additions depends on the initial composition of the oils that are mixed. However, the above-mentioned results enable us to differentiate among the five citrus petitgrain oils we analyzed, and these results can be a useful tool in estimating the purity of these oils.

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