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RESEARCH REPORT

Italian *Citrus* Petitgrain Oils. Part III. Composition of Sweet Orange Petitgrain Oil[1]

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Abstract

The composition of Italian sweet orange petitgrain oil was studied by LC-GC/MS (ITD), GC/MS (quadrupole) and GC systems with SE-52 and Carbowax 20 M GC columns. Industrial samples and laboratory samples from leaves of the cultivars *Valencia late*, *Biondo comune* and *Moro* were analyzed. Sweet orange oils are characterized by a higher content of monoterpene hydrocarbons of which sabinene (38-49%) was the major component, and a lower content of oxygenated compounds than other *Citrus* petitgrain oils. Industrial samples of sweet orange petitgrain oil are often contaminated by other *Citrus* petitgrain oils. Because of the low value of sweet orange petitgrain oils little attention is paid to the selection of raw material to be distilled. Laboratory isolated oils show some differences in their composition, mostly for linalool and sesquiterpene hydrocarbons content. All orange petitgrain oils were characterized by the presence of α- and β-sinensal, which are absent in other *Citrus* petitgrain oils.

Key Word Index

Citrus sinensis, Rutaceae, sweet orange leaf oil, orange cultivars, *Valencia late, Biondo comune, Moro*, essential oil composition, sabinene.

Introduction

In some previous papers the composition of Italian industrial bitter orange and mandarin petitgrain oils, using combined chromatographic techniques, was reported (1,2).

An on-line LC-GC/MS (ITD) (3,4) and a GC/MS (quadrupole) (5) systems were used for peak identification, while a GC system was used for quantitative analyses. The LC-GC/MS (ITD) system was equipped with a SE-52 capillary column, 30 m, while for the GC/MS (quadrupole) and the GC systems, either SE-52 or Carbowax 20 M columns were used. In this paper we report the composition of sweet orange petitgrain oil, obtained using the same analytical techniques.

The composition of sweet orange petitgrain oil has been the subject of wide study (6-19). Most of the papers concerning sweet orange petitgrain oil have been reviewed by Lawrence (20). Almost all of the research has been carried out on laboratory isolated oils, as a result, only one paper is relative to

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Table I. Quantitative composition of sweet orange petitgrain oil reported in the literature

Monoterpene hydrocarbons					
Camphene	0.2-0.6 (9)	0.05-0.06 (10)	19.4-42.0 (14)	0.02 (19)	
δ-3-Carene	2.0-8.0 (8)	3.2-5.2 (9)	4.66-5.23 (10)	0.63-6.47 (12)	6.09-11.68 (13)
	2.52-4.34 (15,16)	7.38 (19)			
δ-4-Carene	0-0.22 (12)				
o-Cymene	0-0.09 (12)				
p-Cymene	0.1-0.9 (9)	0.20-0.23 (10)	1.18-3.39 (12)	0-12.31 (13)	0.3-0.5 (14)
	0.10-0.18 (15,16)	0.02 (19)			
Limonene	2.3-6.4 (8)	2.6-4.6 (9)	2.53-5.57 (10)	5.0-16.63 (12)	3.71-7.38 (13)
	3.6-11.3 (14)	1.25-2.96 (15,16)	3.8-4.6 (17)	5.95 (19)	
o-Mentha-1(7),5,8-triene	0-0.20 (12)				
Myrcene	3.9-6.1 (8)	3.3-4.9 (9)	3.76-4.57 (10)	0.36-4.18 (12)[c]	1.37-3.84 (13)
	2.79-5.63 (15,16)	4.1-4.6 (17)	3.73 (19)		
Ocimene	6.2-9.3 (8)[b]	4.73-8.88 (10)[b]			
(E)-β-Ocimene	3.2-4.3 (9)	0-5.39 (12)	0-6.36 (13)	0.88 (18)	8.31 (19)
(Z)-β-Ocimene	0-0.21 (12)	0.06-0.50 (15,16)	0.33 (18)		
α-Phellandrene	0.36-4.18 (12)[c]	0-0.84 (13)	5.5-41.6 (14)	0.05-0.08 (15,16)	0.69 (19)
β-Phellandrene	1.1-1.8 (8)	0.4-1.3 (9)	0.71-0.91 (10)	0.01-0.06 (12)	0-0.85 (13)
	0.35-0.81 (15,16)	0.34 (18)	0.33 (19)		
α-Pinene	1.6-2.6 (8)[a]	2.7-3.1 (9)	2.19-2.79 (10)	0.69-2.19 (12)	1.48-3.09 (13)
	0.88-1.75 (15,16)	0.94 (18)	0.55 (19)		
β-Pinene	4.5-5.7 (9)	1.50-1.74 (10)	1.49-2.04 (12)	1.28-2.49 (13)	1.06-1.30 (15,16)
	0-27.2 (17)	0.32 (18)	2.00 (19)		
Sabinene	52.0-58.0 (8)	42.4-51.0 (9)	41.80-50.75 (10)	9.02-36.47 (12)	16.03-29.48 (13)
	15.81-32.58 (15,16)	27.2-46.6 (17)	47.78 (19)		
α-Terpinene	0.7-1.5 (8)	0.1-2.6 (9)	0.39-0.52 (10)	0.06-0.08 (12)[d]	0.12 (19)
γ-Terpinene	1.1-2.4 (8)	2.8-3.0 (9)	0.84-1.04 (10)	0.04-2.15 (12)	0-2.13 (13)
	0.1-1.8 (14)	7.41-10.50 (15,16)	5.9-6.2 (17)	0.65 (19)	
Terpinolene	0.9-2.1 (8)	0.1-0.4 (9)	0.67-0.80 (10)	0-1.52 (12)	0-1.73 (13)
	0.75-1.51 (15,16)	1.57 (19)			
α-Thujene	1.6-2.6 (8)[a]	0.9-1.3 (9)	0-0.58 (12)	0.30 (19)	
Sesquiterpene hydrocarbons					
allo-Aromadendrene	0.20 (18)				
trans-β-Bergamotene	1.15 (18)				
Bicyclogermacrene	0.06-0.08 (15,16)				
β-Bisabolene	0.6-1.4 (14)	0.18 (18)	0.03 (19)		
β-Caryophyllene	0.4-0.7 (9)	4.18-5.95 (10)	0-0.32 (12)	0-1.81 (13)	1.3-2.7 (14)
	3.62-7.87 (15,16)[f]	0.21 (19)			
α-Copaene	4.52 (18)				
α-Cubebene	0.40 (18)				
α-Elemene	0-0.7 (14)				
β-Elemene	0.1-0.4 (9)	0-0.03 (12)	0-2.9 (14)	2.38-4.13 (15,16)	
δ-Elemene	0.63 (19)				
(E)-β-Farnesene	0.2-0.3 (9)	0.10-0.32 (12)[e]			
Germacrene B	0.12 (19)				
α-Humulene	tr-0.1 (9)	0.10-0.16 (10)	0.10-0.32 (12)[e]	0-5.10 (13)	0.11-1.19 (15,16)
	0.58 (18)	0.06 (19)			
Longifolene	0.04 (19)				
α-Selinene	0.01-0.02 (15,16)				
β-Selinene	0.1-0.3 (9)	tr-0.03 (15,16)			
Valencene	0.02-0.04 (15,16)	0.75 (18)			

Table I. Continued

Alcohols					
Borneol	0.03-0.06 (10)				
Carvacrol	2.96 (18)				
trans-Carveol	0-0.27 (12)				
cis-Carveol	0-0.32 (12)				
Citronellol	0.2-0.4 (9)	0-0.24 (10)	0.08-1.30 (12)	1.58-3.44 (12)	0.06-0.12 (15,16)
	0.64 (18)	0.53 (19)			
1,2-Dihydrolinalool	0.02 (19)				
Dihydrocarveol	0.59 (18)				
p-Cymen-8-ol	0-0.50 (12)				
Dihydroxylinalool	1.50 (18)				
Elemol	0-0.16 (12)	0.13 (18)			
Geraniol	0.1-0.2 (9)	0.04-0.06 (10)	1.98-4.84 (13)	tr (15,16)	0.10 (18)
	0.21 (19)				
Heptanol	0.76 (18)				
(E)-2-Hexenol	tr (9)				
Cinnamyl alcohol	1.97 (18)				
(Z)-3-Hexenol	tr (9)	0.41-1.93 (15,16)			
Isoborneol	0.40 (18)	0.20 (19)			
Isopulegol	tr-0.1 (9)	0.30-0.96 (12)	0.13 (19)		
10-epi-γ-Eudesmol	0.13 (18)				
Linalool	1.5-16.0 (8)	8.7-14.5 (9)	3.90-8.55 (10)	3.79-15.78 (12)	9.67-17.59 (13)
	5.4-8.6 (14)	5.13-20.92 (15,16)	7.7-12.7 (17)	1.65 (18)	4.38 (19)
Menthol	0.25 (18)				
p-Menth-1,4-dien-7-ol	0-0.38 (12)				
3-Methyl-2-butenol	0-0.02 (15, 16)				
Myrcenol	0.05 (19)				
Myrtenol	0-0.15 (12)				
Nerol	0.1-0.4 (9)	0.08-0.17 (10)	0.50-0.70 (12)	1.79-4.92 (13)	
Nerolidol	0-0.13 (12)[b]				
(Z)-Nerolidol	0.10 (18)				
Nonanol	0.19 (18)	0.37 (19)			
n-Octanol	0.27 (19)				
3-Octanol	0.17-2.83 (12)				
1-Octenol	16.97 (18)				
(Z)-2-Pentenol	tr (9)				
β-Phenylethanol	tr-0.04 (15,16)				
trans-Pinocarveol	0-0.34 (12)				
p-Isopropyl amisol	0-0.46 (12)				
cis-Piperitol	0-0.48 (12)				
trans-Piperitol	26.42 (18)				
Sabinene hydrate	0-0.61 (12)[b]				
cis-Sabinene hydrate	1.53-3.23 (15,16)	0.02 (19)			
trans-Sabinene hydrate	0-0.63 (13)	2.14-2.81 (15,16)	0.16 (19)		
Terpinen-4-ol	1.4-5.0 (8)	0.6-0.9 (9)	1.14-1.29 (10)	3.33-8.20 (12)	0-11.43 (13)
	3.62-7.87 (15,16)[f]				
α-Terpinenol	0.5-1.1 (8)[g]	0.2-0.6 (9)	0.17-0.30 (10)	0.80-1.98 (12)	0.62-2.24 (13)
	0.09-0.18 (15,16)	1.95 (18)	0.10 (19)		
β-Terpinenol	0.74 (18)				
Thymol	0.07 (19)				

Table I. Continued

Aldehydes					
Citronellal	0.2-3.6 (8) 1.70 (18)	1.1-2.9 (9) 2.83 (19)	1.60-2.13 (10)	0.77-1.82 (12)	1.32-1.82 (15,16)
Cumin aldehyde	0-0.60 (12)				
Decanal	tr-0.1 (9)	0.15 (19)			
2,6-Dimethylhept-5-enal	0-0.08 (12)				
Dodecanal	tr (9)				
Geranial	0.5-3.0 (8) 3.2-8.8 (17)[h]	1.9-2.5 (9) 1.04 (18)	1.37-2.06 (10) 2.61 (19)	1.72-3.01 (12)	0.69-7.90 (13)
Heptanal	0.06-1.18 (12)[d]				
Hexanal	0.36 (18)				
(E)-2-Hexenal	tr (9)				
Myrtenal	0-0.50 (12)				
Neral	0.5-1.1 (8)[g] 3.2-8.8 (17)[h]	1.3-2.7 (9) 2.20 (18)	0.08-0.17 (10) 1.87 (19)	1.01-1.70 (12)	0-1.92 (13)
Octanal	0.04 (19)				
Nonanal	tr (9)				
α-Sinensal	0-0.67 (12)	0.02-0.07 (15,16)	0.9-1.5 (17)[i]	2.93 (18)	0.13 (19)
β-Sinensal	0-1.30 (12)	0.43-2.35 (15,16)	0.9-1.5 (17)[i]	1.14 (18)	
Esters					
Benzyl acetate	0.15 (18)				
Bornyl acetate	0-9.00 (13)				
Buthyl propionate	0.17 (18)				
Cinnamyl formate	0.56 (18)				
Citronellyl acetate	0.84-1.34 (10)	0.26-0.70 (12)	0.06 (19)		
Citronellyl formate	0.35 (18)				
Citronellyl tiglate	0.37 (18)				
Ethyl benzoate	tr (15,16)				
(E)-Ethyl-2-butenoate	0.08-0.11 (15,16)				
Ethyl laurate	0.04-0.05 (15,16)				
Ethyl linoleate	0.47-0.69 (15,16)				
Ethyl linolenate	0.35-5.26 (15,16)				
Ethyl myristate	tr-0.05 (15,16)				
Ethyl octanoate	tr-0.11 (15,16)				
Ethyl palmitate	3.54-6.77 (15,16)				
Ethyl phenyl acetate	0.08-0.11 (15,16)				
Ethyl stearate	0.07-0.21 (15,16)				
(E,E)-Farnesyl acetate	0.19 (18)				
Fenchyl acetate	3.60 (18)				
Geranyl acetate	0.1 (9) 0.16 (19)	0.23-0.53 (10)	0.32-1.52 (12)	0-0.64 (13)	0.28 (18)
Geranyl formate	0-0.31 (12)	0.20 (18)			
Geranyl tiglate	1.42 (18)				
Linalyl acetate	tr-0.2 (9)	0.11-0.16 (10)	0.30-0.78 (12)	0-0.26 (13)	0.03 (19)
Linalyl formate	0.44 (18)				
Methyl geranate	0.08-0.35 (12)				
Methyl octanoate	0.12 (19)				
Neryl acetate	0.08-0.27 (12)	0.17 (19)			
Octenyl acetate	0-0.57 (13)				
α-Terpinyl acetate	0-0.12 (12)				

Table I. Continued

Oxides			
Caryophyllene oxide	0-0.70 (12)		
cis-Limonene oxide	0.05 (19)		
trans-Linalool oxide	0-1.14 (12)		
cis-Linalool oxide	0-1.46 (12)	0.37 (18)[l]	
trans-Rose oxide	0.20 (18)		
cis-Rose oxide	1.34 (18)		
Others			
β-Amyrin	1.5-9.9 (14)		
Anethole	0.05-0.12 (15,16)		
α-p-Dimethyl styrene	tr-0.1 (9)	0-0.03 (10)	
Camphor	0-1.44 (13)		
1,8-Cineole	0.17-0.28 (10)	0.16 (19)	
1,4-Cineole	0.71 (18)	0.48 (19)	
2-Dodecanone	0-0.32 (12)		
p-Isopropyl anisole	0-0.46 (12)		
Methylaceto-phenone	0-1.00 (12)		
3-Methylcoumarin	0.10 (18)		
6-Methyl-5-hep-ten-2-one	0.08-0.09 (10)	0.19-0.54 (12)	tr (15,16)
Perillene	0-0.16 (12)		
Phytol	10.8-12.2 (14)	0.91-2.04 (15,16)	0.22 (19)
Piperitone	0-1.04 (12)		
Methyl thymol	0.18-0.47 (10)		
Toluene	0-0.11 (12)		
2,6,6-Trimethyl, 2-vinyl-5-hydroxytetra-hydropyran	0-0.65 (12)		
2-Tridecanone	0-0.27 (12)		
Verbenone	0.50 (18)		

[a] α-Pinene + α-Thujene; [b] Correct isomer not characterized; [c] Myrcene + α-Phellandrene; [d] α-Terpinene + Heptenal; [e] (E)-β-Farnesene + α-Humulene; [f] (E)-Caryophyllene + Terpinen-4-ol; [g] α-Terpineol + Neral; [h] Neral + Geranial; [i] α-Sinensal + β-Sinensal; [l] Furanoid

Appendix to Table I.

Details on the references on the composition of sweet orange leaf oil

Industry steam-distilled oils (6). Laboratory steam-distilled oils (8,10-13,15-19). Laboratory solvent extracted oils (9,14). Qualitative data (6,7,11). Quantitative data (8-10,12-18). Biogenesis (7,8). Chemotaxonomy (9,10,12-18). *Citrus sinensis* (L.) Osbeck (all); cv. Hamlin (7,8,13,14,17); cv. Pineapple (8,10); cv. Valencia (8,11,12,15,16); cv. Washington Navel (9,12,14,17); cv. Fukuara (9,14); cv. Ordinary round, Snow (10); cv. Sanguigne, Portughese (12), cv. Agege I, Bendel, Meran, Umudike, Etinam (13); cv. Jaffa Shamuki, Ruby (15,16); cv. Glorious (17).

the qualitative composition of industrial sweet orange petitgrain oil (6). In fact, sweet orange petitgrain oils have a low commercial value so the industrial production is limited, and when it is made it is sometimes used for the adulteration of more valuable petitgrain oils, such as bitter orange leaf oil.

Because of the low commercial value of sweet orange leaf oil, little attention is paid to the selection of the leaf material to undergo distillation and to the cleaning of the stills that are sometimes also used for production of more valuable oils. As a result possible contaminations with bitter orange, lemon and

Table II. Compound identification by LC-GC/MS (ITD), by GC/MS (quadrupole) on Carbowax column and by GC/MS (quadrupole) on SE-52 column

Compounds	A	B	C	Compounds	A	B	C
hexanal		6		cis-piperitol		42	33
hexanol		22		decanal	30	26	34
tricyclene	1	1	1	trans-piperitol			35
α-thujene	2	3	2	citronellol	31	45	36
α-pinene	3	2	3	nerol	32	46	37
α-fenchene	4	4	4	methyl thymol		29	38
camphene	5	5	5	neral	33	35	39
sabinene	6	8	6	geraniol		47	40
β-pinene	7	7	7	linalyl acetate	34	28	41
6-methyl-5-hepten-2-one	8	21	8	geranial	35	40	42
myrcene	9	10	9	thymol	36		43
octanal	10		10	methyl geranate		38	44
α-phellandrene	11	11	11	citronellyl acetate	37	33	45
δ-3-carene	12	9	12	α-copaene*	38		
α-terpinene	13	12	13	neryl acetate	39	39	46
o-cymene	14		14	β-cubebene*	40		
p-cymene	15	18	15	geranyl acetate	41	44	47
limonene	16	13	16	β-elemene	42		48
β-phellandrene		14		methyl N-methyl anthranilate	44	50	49
1,8-cineole	17		17	cis-α-bergamotene	43		
(Z)-β-ocimene	18	15	18	β-caryophyllene	45	31	50
(E)-β-ocimene	19	17	19	(Z)-β-farnesene	47	34	51
γ-terpinene	20	16	20	α-humulene	46	36	52
cis-sabinene hydrate	21	24	21	β-santalene			53
cis-linalool oxide (furanoid)			22	valencene	48		
p-mentha-2,4(8)-diene		19	23	α-selinene	49		54
terpinolene	22	20	24	bicyclogermacrene		43	55
linalool	23	27	25	(E,E)-α-farnesene	50		56
nonanal	24	23	26	β-bisabolene		41	
cis-p-menth-2-en-1-ol	25	32	27	(E)-nerolidol	51	49	57
trans-p-menth-2-en-1-ol	26		28	(Z)-3-hexenyl benzoate			58
citronellal	27	25	29	caryophyllene oxide	52	48	59
terpinen-4-ol	28	30	30	β-sinensal	53	51	60
p-cymen-8-ol			31	α-sinensal	54	52	61
α-terpineol	29	37	32				

A = LC-GC/MS peak in Figure 1
B = GC/MS on Carbowax column peak in Figures 2 and 3
C = GC/MS on SE-52 column peak in Figures 4 and 5
* tentative; retention time does not correspond with that reported by Adams (22)

mandarin leaf oils, are not considered undesirable. Therefore, industrial sweet orange petitgrain oil is almost never pure and very often contains other different *Citrus* leaf oils.

Literature data (Table I) often referred to oils of different cultivars and geographic origins show qualitative and quantitative differences, sometimes rather considerable. For example, camphene ranged from 0.2% in *Washington Navel* cultivar (9) to 42.0% in *Hamlin* cultivar (14), while δ-3-carene can be found varying from 2.0% in *Hamlin* variety [in leaves harvested in December in Florida (8)] to 11.68% in *Bendel* cultivar grown in Algeria (13). Similarly, β-caryophyllene, which was not detected in Washington-navel, Valencia late, and Portuguese cultivars grown in Nigeria (12), has been found in levels up to 5.95% in the leaf oils of some cultivars grown in China (10). Some sesquiterpene hydrocarbons, such as allo-aromadendrene, trans-β-bergamotene, α-cubebene and α-copaene, have only been reported in sweet orange petitgrain grown in Mauritius (18), while longifolene was only found in Colombian sweet orange leaf oil (19). Another component, linalool, has been found to occur at a level of 1.5% in *Hamlin* cultivar oil produced from leaves harvested in September in Florida (8), while the *Ruby* cultivar grown in Israel was found to contain 20.92% (15,16). However, most studies reveal that sabinene was indeed the main component of sweet orange petitgrain oil.

In this paper, the composition of industrial sweet orange petitgrain oil and lab-prepared sweet orange leaf oil produced from the *Biondo Comune, Moro* and *Valencia Late* cultivars is reported.

Experimental

The analyses were made on: (i) 4 samples of sweet orange petitgrain oil produced in Sicily in Spring 1994. Each sample has been distilled from 450 kg of leaves. Yield was about 2‰; and (ii) 3 samples steam-distilled in our laboratory from leaves of *Biondo Comune, Moro* and *Valencia Late* cultivars.

All the samples were analyzed by LC-GC/MS (ITD), GC/MS (quadrupole) and GC using the same experimental conditions as described previously for the analysis of bitter orange (1) and mandarin (2) petitgrain oils. As for bitter orange and mandarin petitgrain oil, the LC-GC/MS (ITD) system was equipped with a SE-52 column, 30 m x 0.32 mm; for the analyses with the GC/MS (quadrupole), and for the GC analyses either a 60 m x 0.32 mm SE-52 or Carbowax 20 M column was used.

LC-GC/MS (ITD) system was equipped with ADAMS library, while GC/MS(quadrupole) system was coupled with two commercial libraries (NIST and ADAMS) and a home-made FFC (Flavour and Fragrance Components) bank, provided with Linear Retention Indices, to be used interactively with MS data for compound identification.

Results and Discussion

Figure 1 shows the total ion current chromatograms of a sweet orange petitgrain oil and its correspondent fractions obtained by LC-pre-separation. Figures 2-5 report the GC/MS (quadrupole) chromatograms obtained using a Carbowax 20 M and a SE-52 column, respectively, for both an industrial sample and a laboratory extracted sample.

Table II reports peaks identified by LC-GC/MS (ITD), by GC/MS (quadrupole) on Carbowax column and by GC/MS (quadrupole) on SE-52 column. Tables III and IV report the composition for both the industrial and the laboratory extracted samples. Data reported in Tables II and III were obtained considering results of GC analyses with SE-52 and Carbowax 20 M columns, and the identification by GC/MS (quadrupole) and LC-GC/MS (ITD).

LC-GC/MS (ITD) analysis of the LC fractions allowed a more certain identification of components present in small amounts, such as tricyclene, α-fenchene, octanal, cis-α-bergamotene, α-selinene and valencene. In addition, it showed the presence of 1,8-cineole, which partially overlapped with limonene, and of α-copaene and β-cubebene, which co-eluted with citronellyl acetate and neryl acetate, respectively, when the whole oil was run on the SE-52 column. Analyses carried out with the Carbowax 20 M column allowed the separation of the following pairs of compounds: limonene/β-phellandrene, geraniol/linalyl acetate and nerol/citronellol, which co-eluted on a SE-52 column. On the Carbowax column, citronellol separates from nerol, but it partially overlapped with geranyl acetate.

As can be seen from Tables III and IV and from Figures 1-5, 69 components were identified, representing about 99% of the whole oil. Tricyclene, α-fenchene, p-mentha-(2,4)-8-diene, cis- and trans-p-menth-2-en-1-ol, β-cubebene, cis-α-bergamotene, methyl N-methyl anthranilate, β-santalene, (Z)-β-farnesene, (E,E)-α-farnesene, (Z)-3-hexenyl benzoate have been identified in sweet orange petitgrain for the first time. Many compounds previously reported in literature for this oil were not detected.

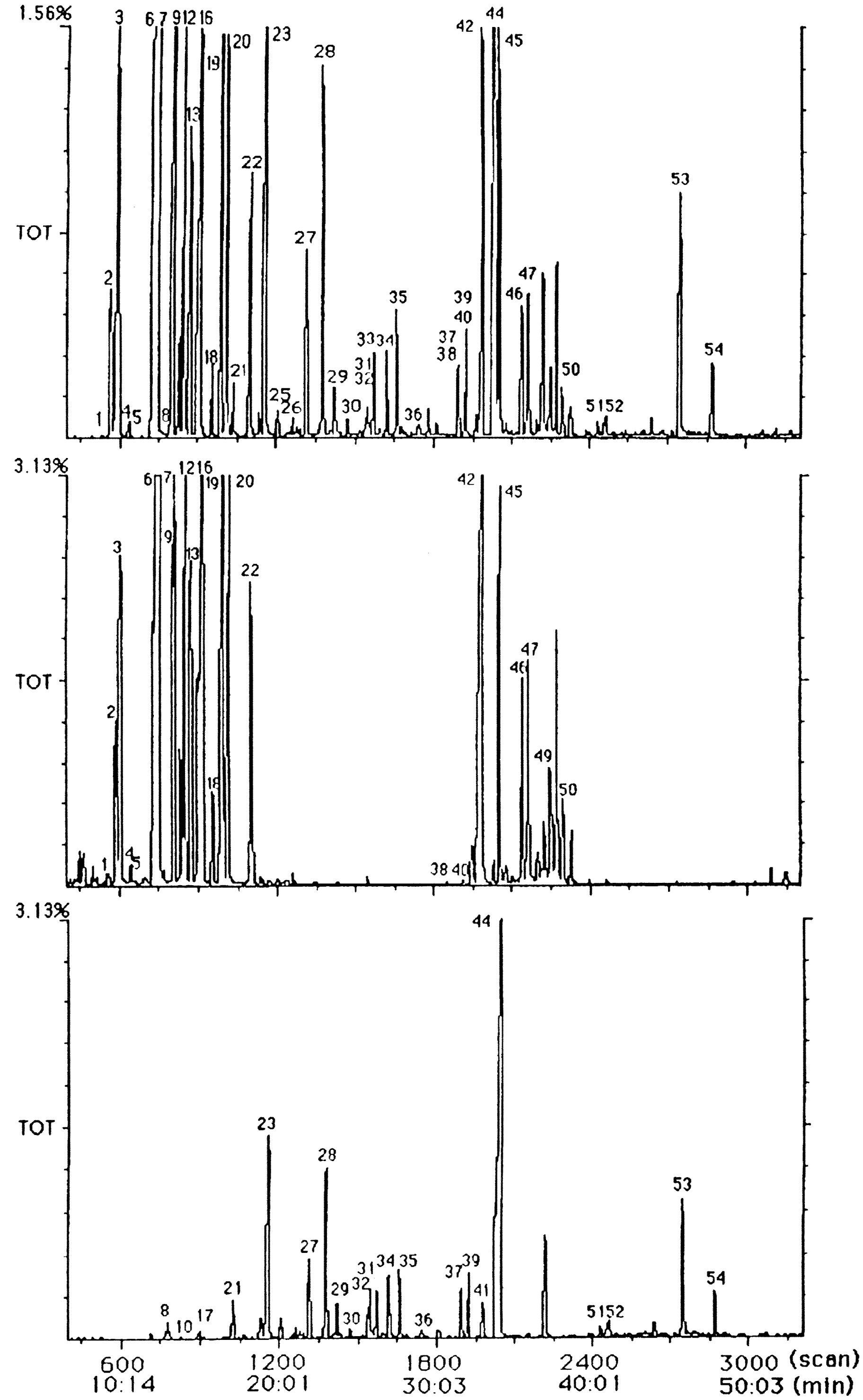

Figure 1. Total ion current chromatograms of a sweet orange petitgrain oil and of fractions from its LC-preseparation. GC column SE-52, 30 m. A = whole oil; B = hydrocarbons; C = oxygenated fraction; For peak identification, see Table II

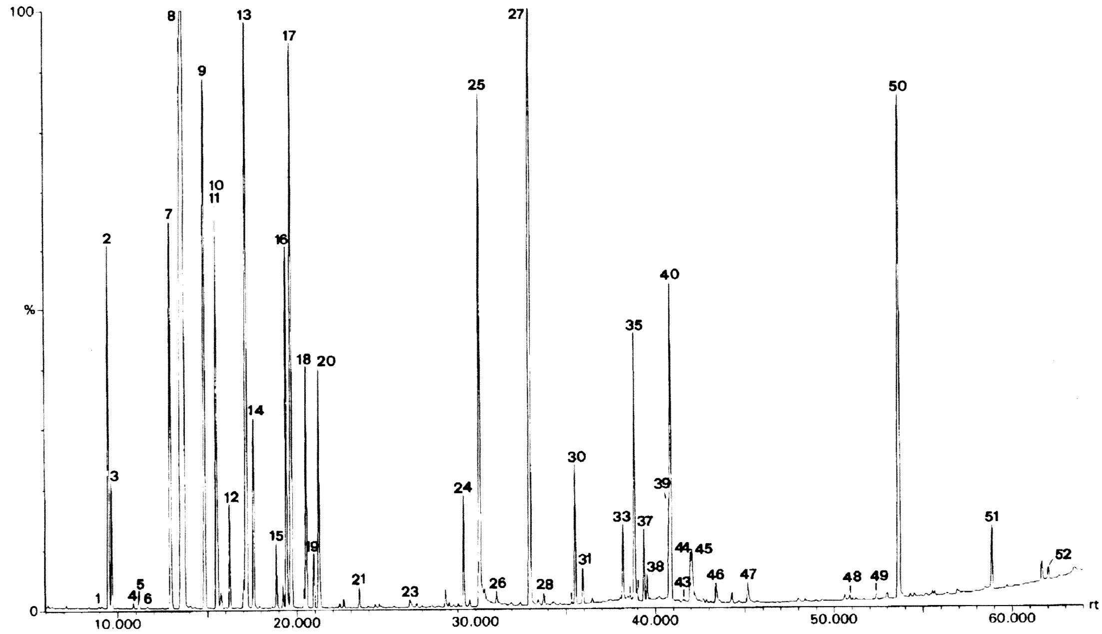

Figure 2. Total ion current chromatograms of a commercial sweet orange petitgrain oil obtained by GC/MS (quadrupole). GC column Carbowax 20 M, 60 m
For peak identification, see Table II

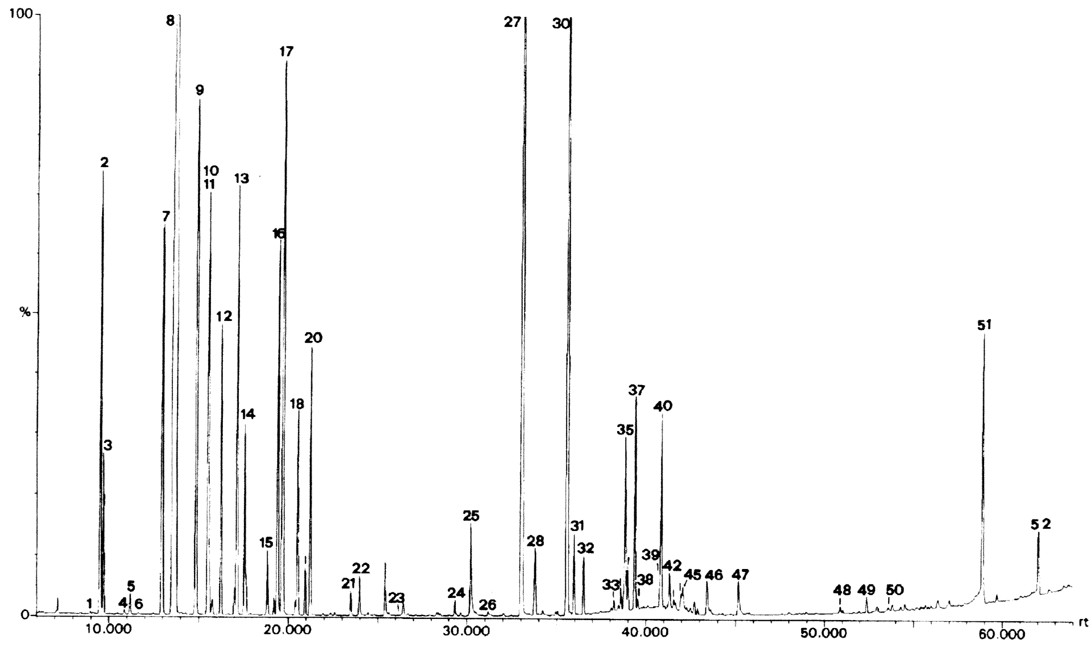

Figure 3. Total ion current chromatograms of a laboratory extracted sweet orange petitgrain oil obtained by GC/MS (quadrupole). GC column Carbowax 20 M, 60 m
For peak identification, see Table II

Table III. Quantitative composition of sweet orange petitgrain oils

Compounds*	1	2	3	4	Min	Max
hexanal	tr	tr	tr	tr	tr	tr
hexanol	tr	tr	tr	tr	tr	tr
tricyclene	tr	tr	tr	tr	tr	tr
α-thujene	0.24	0.21	0.24	0.39	0.21	0.39
α-pinene	1.15	0.99	1.25	1.51	0.99	1.51
α-fenchene	0.01	0.01	0.01	0.01	0.01	0.01
camphene	0.04	0.03	0.03	0.04	0.03	0.04
sabinene	41.93	40.82	37.64	39.26	37.64	41.93
β-pinene	2.10	1.92	1.89	2.62	1.89	2.62
6-methyl-5-hepten-2-one	0.05	0.06	0.04	0.05	0.04	0.06
myrcene	3.25	2.66	3.85	2.88	2.66	3.85
octanal	0.05	0.04	0.03	0.03	0.03	0.05
α-phellandrene	0.50	0.36	0.47	0.23	0.23	0.50
δ-3-carene	5.43	4.46	5.91	3.46	3.46	5.91
α-terpinene	0.44	0.27	0.96	0.65	0.27	0.96
o-cymene	0.03	0.05	0.04	0.05	0.03	0.05
p-cymene	0.73	1.11	0.59	2.89	0.59	2.89
limonene	8.01	6.25	8.37	5.12	5.12	8.37
β-phellandrene	0.91	0.88	1.06	0.78	0.78	1.06
1,8-cineole	0.03	0.05	-	0.03	-	0.05
(Z)-β-ocimene	0.28	0.22	0.33	0.21	0.21	0.33
(E)-β-ocimene	7.38	5.84	9.21	4.53	4.53	9.21
γ-terpinene	2.98	2.19	2.53	2.62	2.19	2.98
cis-sabinene hydrate	0.24	0.42	0.13	0.23	0.13	0.42
cis-linalool oxide (furanoid)	0.01	tr	0.01	tr	tr	0.01
p-mentha-2,4(8)-diene	0.22	0.18	0.20	0.09	0.09	0.22
terpinolene	1.44	1.13	1.52	0.98	0.98	1.52
linalool	6.66	10.71	6.64	4.34	4.34	10.71
nonanal	0.03	0.03	0.01	tr	tr	0.03
cis-p-menth-2-en-1-ol	0.04	0.04	0.11	0.09	0.04	0.11
trans-p-menth-2-en-1-ol	0.04	0.03	0.06	0.07	0.03	0.07
citronellal	3.61	4.44	2.17	0.43	0.43	4.44
terpinen-4-ol	0.55	0.64	2.59	2.36	0.55	2.59
p-cymen-8-ol	0.03	tr	0.02	0.09	tr	0.09
α-terpineol	0.30	0.21	0.28	0.21	0.21	0.30
cis-piperitol	0.01	0.02	0.03	0.07	0.01	0.07
decanal	0.06	0.05	0.07	0.02	0.02	0.07
trans-piperitol	tr	tr	0.05	0.03	tr	0.05
citronellol	0.13	0.22	0.19	0.10	0.10	0.22
nerol (a,b,c)	0.20	0.26	0.20	0.13	0.13	0.26
methyl thymol	-	tr	-	tr	-	tr
neral	1.63	2.18	0.54	0.28	0.28	2.18
geraniol	0.06	0.10	0.29	0.28	0.06	0.29
linalyl acetate	0.02	0.05	0.10	0.12	0.02	0.12
geranial	2.19	3.11	0.76	0.59	0.59	3.11
thymol	0.02	0.02	0.01	0.05	0.01	0.05
methyl geranate	0.06	0.05	0.07	0.05	0.05	0.07
citronellyl acetate	0.29	0.21	0.65	0.25	0.21	0.65
α-copaene	tr	tr	tr	0.01	tr	0.01
neryl acetate	0.35	0.29	0.34	0.38	0.29	0.38

Table III. Continued

Compounds*	1	2	3	4	Min	Max
β-cubebene	tr	tr	tr	0.10	tr	0.10
geranyl acetate	0.17	0.15	0.16	0.28	0.15	0.28
β-elemene	0.11	0.04	2.44	3.80	0.04	3.80
methyl N-methyl anthranilate	4.78	5.92	1.26	10.29	1.26	10.29
cis-α-bergamotene	tr	tr	tr	tr	tr	tr
β-caryophyllene	0.18	0.13	1.23	2.47	0.13	2.47
(Z)-β-farnesene	0.02	0.01	0.41	0.58	0.01	0.58
α-humulene	0.07	0.05	0.55	0.60	0.05	0.60
β-santalene	-	-	-	-	-	-
valencene	tr	-	tr	tr	-	tr
α-selinene	tr	-	tr	tr	-	tr
bicyclogermacrene	0.02	0.01	0.24	0.24	0.01	0.24
(E,E)-α-farnesene	0.02	0.03	0.13	0.12	0.02	0.13
β-bisabolene	-	-	0.09	-	-	0.09
(E)-nerolidol	0.02	0.01	0.05	0.05	0.01	0.05
(Z)-3-hexenyl benzoate	tr	tr	-	-	-	tr
caryophyllene oxide	0.05	0.02	0.06	0.24	0.02	0.24
β-sinensal	0.48	0.23	1.29	1.25	0.23	1.29
α-sinensal	0.10	0.04	0.32	0.24	0.04	0.32
monoterpene hydrocarbons	77.07	69.58	76.10	68.32	68.32	77.07
sesquiterpene hydrocarbons	0.42	0.27	5.09	7.92	0.27	7.92
aldehydes	8.15	10.12	5.19	2.84	2.84	10.12
alcohols	8.30	12.68	10.65	8.10	8.10	12.68
esters	5.67	6.67	2.58	11.37	2.58	11.37
others	0.14	0.13	0.11	0.32	0.11	0.32

* the compounds are listed according to the elution order on SE-52 column, 60 m

Sweet orange petitgrain oil, industrial or laboratory isolated was characterized by the presence of α- and β-sinensal, not found in other *Citrus* petitgrain oils (1,2,21), and by a higher content of sabinene, which ranged from 38% to 49% and was the main component. Oxygenated compounds represented 19% to 30% of the whole oil. The content of oxygenated compounds in sweet orange petitgrain oil was lower than in the other *Citrus* petitgrain oils (1,2,21), while monoterpene hydrocarbons were the most abundant components.

Some industrial samples contained high amounts of citronellal and β-elemene, in contrast with laboratory produced oils. This cannot be related to a contamination with different *Citrus* petitgrain oils, because they contained very small amounts of these two compounds.These differences in citronellal and β-elemene amounts could be due to the fact that industrial samples were obtained from leaves of different cultivars of sweet orange than those oils obtained in laboratory.

Differences were found even among laboratory produced oils, from leaves of different cultivars. These differences were manifested in the total alcohol content (especially linalool) and in the sesquiterpene hydrocarbons content. For example, the *Valencia* oil was found to have an increased total alcohol content and twice the linalool level of oils from other cultivars. Similarly the oil obtained from *Biondo comune* cultivar was richer in sesquiterpene hydrocarbons (2.6%), while it was about 1% in the other two oils. These differences in sesquiterpene hydrocarbons are mainly due to β-elemene and β-caryophyllene. *Moro* leaf oil contained β-santalene and did not contain any bicyclogermacrene, which was different from the leaf oils of *Valencia* and *Biondo comune*.

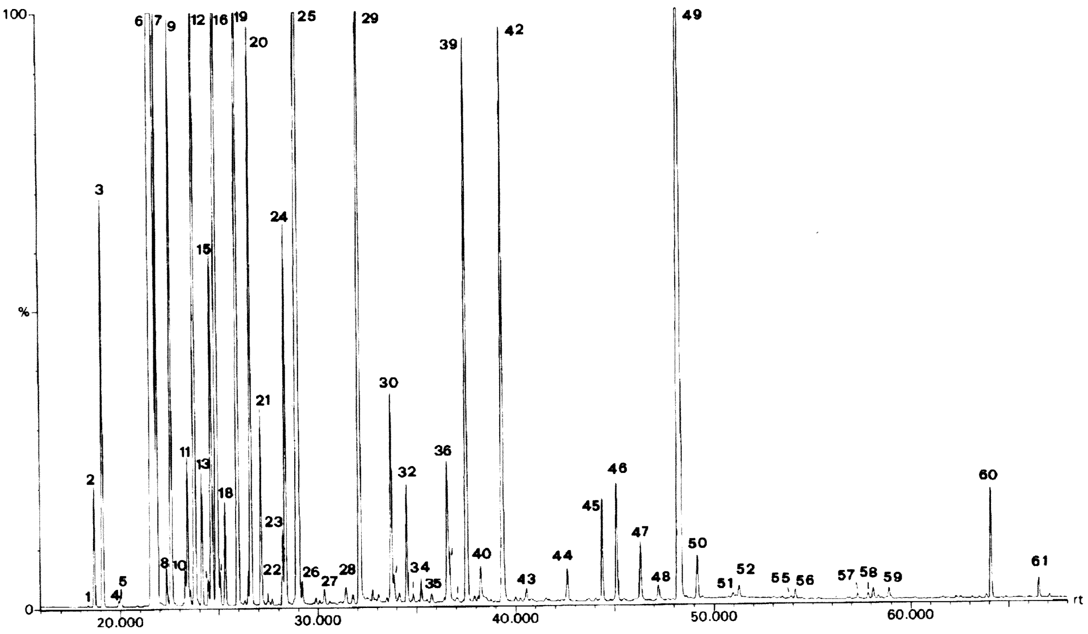

Figure 4. Total ion current chromatograms of a commercial sweet orange petitgrain oil obtained by GC/MS (quadrupole). GC column SE-52, 60 m
For peak identification, see Table II

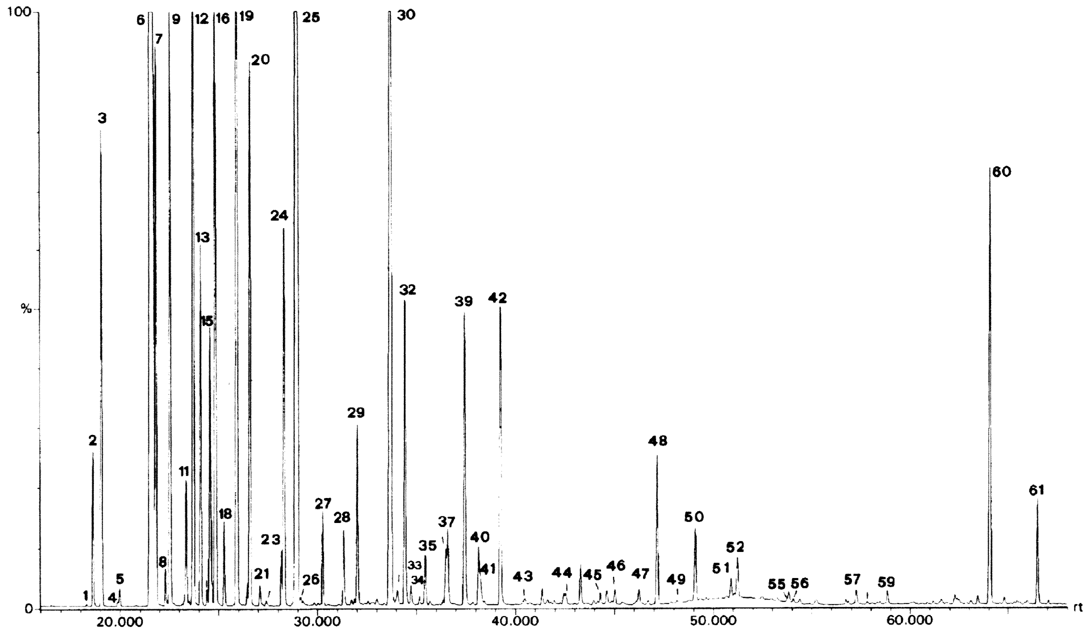

Figure 5. Total ion current chromatograms of a laboratory extracted sweet orange petitgrain oil obtained by GC/MS (quadrupole). GC column SE-52, 60 m
For peak identification, see Table II

Table IV. Quantitative composition of laboratory extracted sweet orange leaf oils

Compounds	Valencia late	Biondo comune	Moro
hexanal	tr	tr	tr
hexanol	0.09	0.09	0.011
tricyclene	tr	tr	tr
α-thujene	0.34	0.34	0.33
α-pinene	1.59	1.76	1.65
α-fenchene	0.01	0.02	0.01
camphene	0.04	0.04	0.04
sabinene	40.66	38.46	48.52
β-pinene	1.87	2.01	2.33
6-methyl-5-hepten-2-one	0.08	0.12	0.08
myrcene	3.49	4.40	3.72
octanal	tr	tr	tr
α-phellandrene	0.37	0.69	0.22
δ-3-carene	4.45	10.28	5.51
α-terpinene	1.16	0.74	0.48
o-cymene	0.03	0.06	0.08
p-cymene	0.76	0.59	1.68
limonene	2.90	3.67	4.04
β-phellandrene	0.65	0.70	0.74
1,8-cineole	-	-	-
(Z)-β-ocimene	0.22	0.33	0.19
(E)-β-ocimene	6.14	9.73	4.99
γ-terpinene	2.43	1.41	1.46
cis-sabinene hydrate	0.06	0.12	0.10
cis-linalool oxide (furanoid)	0.01	tr	tr
p-mentha-2,4(8)-diene	0.15	0.36	0.14
terpinolene	1.32	2.14	0.95
linalool	15.12	6.29	6.52
nonanal	tr	0.01	0.05
cis-p-menth-2-en-1-ol	0.25	0.16	0.19
trans-p-menth-2-en-1-ol	0.22	0.14	0.18
citronellal	0.47	0.51	0.48
terpinen-4-ol	7.33	3.75	6.14
p-cymen-8-ol	0.04	0.05	0.09
α-terpineol	0.93	0.36	0.38
cis-piperitol	0.06	0.05	0.06
decanal	0.02	0.01	0.02
trans-piperitol	0.16	0.07	0.09

Compounds	Valencia late	Biondo comune	Moro
citronellol	0.13	0.26	0.23
nerol	0.13	0.45	0.30
methyl thymol	-	-	-
neral	1.04	1.75	1.79
geraniol	0.16	0.24	0.15
linalyl acetate	0.10	0.10	0.07
geranial	1.37	2.14	2.17
thymol	0.02	0.02	tr
methyl geranate	0.04	0.04	0.10
citronellyl acetate	0.03	0.05	0.10
neryl acetate	0.04	0.11	0.15
geranyl acetate	0.04	0.16	0.15
β-elemene	0.49	1.07	0.36
methyl N-methyl anthranilate	tr	tr	tr
cis-α-bergamotene	tr	-	tr
β-caryophyllene	0.28	0.83	0.27
(Z)-β-farnesene	0.07	0.15	0.06
α-humulene	0.15	0.37	0.12
β-santalene	-	-	0.04
valencene	tr	tr	tr
α-selinene	tr	tr	tr
bicyclogermacrene	0.05	0.09	-
(E,E)-α-farnesene	0.01	0.05	-
(E)-nerolidol	0.04	0.01	0.02
(Z)-3-hexenyl benzoate	tr	0.01	tr
caryophyllene oxide	0.04	0.07	0.10
β-sinensal	1.38	1.27	1.44
α-sinensal	0.27	0.46	0.08
monoterpene hydrocarbons	68.43	77.37	77.84
sesquiterpene hydrocarbons	1.00	2.47	0.81
aldehydes	4.65	6.15	4.24
alcohols	24.52	11.94	14.41
esters	0.25	0.46	0.57
others	0.13	0.19	0.18

* the compounds are listed according to the elution order on SE-52 column, 60 m

As can be seen, it is very difficult to define the composition of the Italian sweet orange petitgrain oil, more than that of the other *Citrus* petitgrain oils, at least for two reasons:

- Little attention is paid to the selection of the leaf material to be distilled;
- The existence of numerous cultivars of sweet orange being grown in Sicily could influence the composition of oil produced industrially.

The significance of this latter reason needs further study. To this end we plan to examine the composition of sweet orange petitgrain oil produced from all of the cultivars grown in Italy.

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