Uruguayan Essential Oil. 12. Composition of Nova and Satsuma Mandarin Oils

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The composition of the laboratory-prepared essential oils from Uruguayan Nova and Satsuma mandarins has been studied. The volatile fraction was analyzed by HRGC and HRGC/MS (quadrupole); 79 and 73 components were identified in Nova and Satsuma mandarin oils, respectively. The linear retention indices were calculated for almost all identified components on two different stationary phases. The enantiomeric distribution of β-pinene, sabinene, limonene, linalool, and α-terpineol was studied by multidimensional gaschromatography (MDGC). Polymethoxylated flavones, present in the nonvolatile residue, were analyzed by normal-phase HPLC.

Keywords: *Citrus unshiu Marcovitch; Satsuma mandarin; Citrus reticulata Blanco; Nova mandarin; Rutaceae; essential oil; volatile fraction composition; polymethoxylated flavones; HRGC/MS; MDGC; HPLC; linear retention indices*

INTRODUCTION

***Citrus Unshiu* Marcovitch, Satsuma mandarin** almost certainly originated in Japan as a nucellar seedling from the Tsao, Chieh mandarin, imported from Wenzhow, China, probably in the mid-sixth century (Saunt, 1990). Satsuma has peculiar characteristics: a high production of fruits (50/60 kg/plant); blood pulp without seeds; a very easily removable skin; and high yield of juice (Calvarano et al., 1995). Satsumas are grown principally in Japan and Spain and to a far lesser extent in other countries worldwide. Satsumas have also been introduced in China, and a very small area is devoted to them in the Central Valley, CA, and in coastal regions of Argentina, Uruguay, and South Africa (Saunt, 1990). The Satsuma cold-pressed oil or Mikan oil is generally not available outside Japan, where it is used in both the flavor and fragrance industries (Lawrence, 1987). In Uruguay, Satsuma production has increased in recent years, and the export of Satsuma fruits has increased from 8437 metric tons in 1995 to 9158 in 1996. The harvest period for Satsuma fruit in Uruguay goes from February to May.

***Citrus reticulata* Blanco cv. Nova, Nova mandarin** is a hybrid of Fina clementine (*Citrus clementine* cv. Fina) and Orlando tangelo (*Duncan grapefruit* x *Dancy tangerine*) which was officially released in Florida in 1964. The fruit is a medium-large mandarin, comparable in size to its Orlando parent, but the rind color is a more attractive reddish-orange (Saunt, 1990). Nova mandarins are cultivated in Spain, Israel, Florida, and Uruguay. In Uruguay, Nova production has increased in recent years, and the export of Nova mandarin fruits has increased from 87 metric tons in 1995 to 301 in 1996. Most of the production is exported, and Nova fruits are not industrially processed for the juice nor for the essential oil. The harvest period for Nova fruit in Uruguay goes from April to July.

There are no reports in the literature about the composition of Uruguayan Satsuma and Nova oils. Studies have been carried out on Japanese and Russian Satsuma oils: some papers deal with the volatile fraction composition (Yamanishi et al.,1968; Kita et al., 1969; Yajima et al., 1979; Sawamura et al., 1983; Namba et al.,1985; Kekelidze et al., 1985; Shin-yan Gao et al.,1986; Kekelidze et al., 1989) and the nonvolatile residue (Kumamoto et al., 1986; Chkhikvishvili et al., 1990; Chkhikvishvili et al., 1994; Nogata et al., 1994; Tsuchida et al., 1996) of the peel oil; others deal with the oil composition of the leaves and of the flowers (Kharebava et al., 1986, Zheng-Kui and Ying-fang, 1992; Yoshikawa et al., 1996) and others with the juice composition (Masukawa et al., 1985; Maeda et al., 1985; Tada, 1987; Nizharade and Bandyukova, 1990; Araki et al., 1990; Ozaki et al., 1995; Moshonas and Shaw, 1997).

Following our researches on Uruguayan citrus essential oils (Dellacassa et al. 1992; Verzera et al. 1998), we report the results relative to the composition of Satsuma and Nova mandarin oils, which could provide new and interesting material for the flavor and fragrance industries.

MATERIALS AND METHODS

Research was carried out on two samples of Satsuma, *Citrus Unshiu* Marcovitch, and on two samples of Nova mandarins, *Citrus reticulata* Blanco cv. Nova. The fruits were picked from

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Table 1. Linear Retention Indices on Mega 5MS and Megawax for the Components Identified in Uruguayan Satsuma and Nova Mandarin Oils

component	Mega 5MS	Megawax	component	Mega 5MS	Megawax
α-thujene	920	1012	(*E*,*Z*)-2,4-decadienale	1291	nd
α-pinene	925	1008	(E,E)-2,4-decadienale	1296	nd
camphene	936	1043	neo-isopulegol acetate	1297	nd
sabinene	964	1105	neo-dihydro carveol acetate	1298	nd
β-pinene	964	1085	undecanal	1300	1580
myrcene	987	1152	δ-elemene	1328	1446
octanal	997	1270	α-terpenyl acetate	1340	1663
α-phellandrene	997	1146	α-cubebene	1342	nd
δ-3-carene	1002	1128	citronellyl acetate	1349	nd
α-terpinene	1009	1160	neryl acetate	1360	1705
limonene	1021	1181	α-copaene	1364	1451
(*Z*)-β-ocimene	1036	nd	geranyl acetate	1379	1738
(*E*)-β-ocimene	1045	1239	β-cubebene	1381	1664
γ-terpinene	1051	1225	β-elemene	1381	1559
cis-sabinene hydrate	1058	1447	dodecanal	1402	nd
octanol	1071	1546	(*E*)-caryophyllene	1404	nd
p-mentha-2,4(8)diene	1077	nd	decyl acetate	1408	1662
terpinolene	1079	1260	β-gurjunene	1413	nd
p-cymenene	1080	nd	α-guajene	1418	nd
trans-sabinene hydrate	1088	nd	γ-elemene	1422	nd
linalool	1094	1537	*trans*-α-bergamotene	1427	nd
nonanal	1098	1372	α-humulene	1437	1624
cis-limonene oxide	1122	1403	β-santalene	1449	nd
trans-limonene oxide	1127	1423	(*E*)-β-farnesene	1452	nd
(*E*)-myroxide	1136	1465	(*E*)-2-dodecenal	1458	nd
citronellal	1146	1457	germacrene D	1466	1664
cis-pinocamphone	1157	nd	γ-muurolene	1469	nd
terpinen-4-ol	1165	1575	bicyclogermacrene	1482	1688
α-terpineol	1179	1670	α-muurolene	1491	nd
dihydro carveol	1181	2003	α-bulnesene	1494	nd
cis-piperitol	1197	nd	(*Z*)-α-bisabolene	1495	nd
decanal	1199	1476	(*E*,*E*)-α-farnesene	1502	1730
trans-carveol	1209	1806	cubebol	1507	nd
octyl acetate	1210	1461	δ-cadinene	1511	1720
cis-carveol	1220	1837	elemol	1536	2043
nerol	1222	1830	germacrene B	1539	1778
citronellol	1222	nd	(*E*)-nerolidol	1556	nd
carvone	1229	1684	germacrene D-4-ol	1559	2012
neral	1231	1645	caryophyllene oxide	1563	nd
geraniol	1251	1783	tetradecanal	1605	nd
(*E*)-dec-2-en-1al	1254	nd	bulnesol	1675	nd
perilla aldehyde	1257	1729	β-sinensal	1685	2189
geranial	1262	1697	α-sinensal	1741	2287
perilla alcohol	1272	1965	nootkatone	1780	2434
trans-ascaridole	1290	nd			

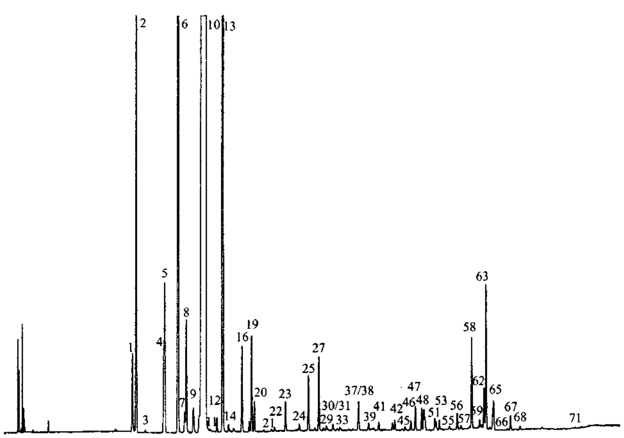

Figure 1. GC chromatogram of a Satsuma mandarin oil obtained with the SE-52 column.

April to May 1997 in "Estacion Experimental INIA-Salto Grande, Departemento de Salto" in northern Uruguay. Each sample was prepared by selecting and peeling 10 fruits (about 1 kg) from 5 kg batches (about 300 g of peels was obtained). Extraction of the essential oil was carried out in the laboratory by applying manual pressure on the rind so as to cause the breaking of the utricles and the release of the oil itself, which was collected on a watch glass, transferred to a test tube, centrifuged, and analyzed. About 2 mL of oil was obtained for each sample.

The volatile fraction of each oil was studied by HRGC and HRGC/MS; the enantiomeric ratios of β-pinene, sabinene, limonene, linalool, and α-terpineol of the volatile fraction were studied by MDGC and the polymethoxylated flavones present in the nonvolatile residue were studied by HPLC.

HRGC/MS Analysis. For the identification of volatile components, each sample was analyzed by Shimadzu QP 5000 equipped with Adams' library (Adams, 1995), on two different columns: (1) fused silica capillary column, 30 m × 0.25 mm i.d. coated with Mega 5 MS, 0.25 μm film thickness [Mega, Legnano (MI) Italy]; column temperature, 40 °C (2 min) to 240 °C at 3.0 °C/min; carrier gas He, 90 kPa; linear velocity, 42.7 cm/s at 40 °C; (2) fused silica capillary column, 30 m × 0.25 mm coated with Megawax, 0.25 μm film thickness [Mega, Legnano (MI), Italy]; column temperature, 40 °C (6 min) to 220 °C (10 min) at 2.0 °C/min; carrier gas He, 90 kPa; linear velocity, 42.8 cm/s at 40 °C. For both columns: injector temperature, 250 °C; injection mode, split; volume injected, 1 μL of a solution 1/20 in pentane of the oil. MS scan conditions: interface temperature, 250 °C; source temperature, 200 °C; E energy, 70 eV; mass scan range, 41−300 amu.

HRGC Analysis. For quantitative results of the volatile fraction, each sample was analyzed by HRGC, on a Fisons

Table 2. Composition as Single Components and as Classes of Substances of Uruguayan Satsuma Mandarin Oils[a]

		4/23/97	5/10/97			4/23/97	5/10/97
1	α-thujene	0.12	0.12	43	α-terpinyl acetate	tr	tr
2	α-pinene	0.79	0.81	44	α-cubebene[t]	tr	tr
3	camphene	tr	tr	45	citronellyl acetate	0.01	tr
4	sabinene	0.17	0.16	46	nerly acetate	0.02	0.02
5	β-pinene	0.25	0.23	47	α-copaene	0.04	0.04
6	myrcene	2.01	1.93	48	geranyl acetate	0.04	0.04
7	α-phellandrene	0.04	0.04	49	β-cubebene	0.04	0.04
8	octanal	0.19	0.20	50	β-elemene	0.04	0.02
9	α-terpinene	0.07	0.06	51	dodecanal	0.02	0.02
10	limonene	90.98	91.60	52	decyl acetate	0.02	0.01
11	(*Z*)-β-ocimene	tr	tr	53	β-caryophyllene	0.02	0.02
12	(*E*)-β-ocimene	0.03	0.02	54	γ-elemene	tr	tr
13	γ-terpinene	3.34	3.00	55	*trans*-α-bergamotene	0.01	0.01
14	*cis*-sabinene hydrate	0.01	0.01	56	α-humulene	0.03	0.03
15	octanol	tr	tr	57	β-santalene	tr	tr
16	terpinolene	0.15	0.14	58	germacrene D	0.17	0.16
17	*p*-cymenene	tr	tr	59	bicyclogermacrene	0.01	0.01
18	*trans*-sabinene hydrate	0.02	0.02	60	α-muurolene[t]	tr	tr
19	linalool	0.20	0.16	61	α-bulnesene[t]	tr	tr
20	nonanal	0.05	0.05	62	(*Z*)-α-bisabolene[t]	0.10	0.07
21	*cis*-limonene oxide	tr	tr	63	(*E*,*E*)-α-farnesene	0.29	0.25
22	*trans*-limonene oxide	0.01	0.01	64	cubebol[t]	tr	tr
23	citronellal	0.04	0.05	65	δ-cadinene	0.07	0.08
24	terpinen-4-ol	0.02	0.01	66	elemol	tr	tr
25	α-terpineol	0.10	0.09	67	germacrene B	0.03	0.03
26	*cis*-piperitol	0.01	tr	68	germacrene D-4-ol	0.01	0.01
27	decanal	0.13	0.12	69	caryophyllene oxide	tr	tr
28	octyl acetate	tr	tr	70	bulnesol[t]	tr	tr
29	trans-carveol	0.02	0.01	71	β-sinensal	tr	tr
30	nerol	tr	tr	72	α-sinensal	tr	tr
31	citronellol	0.01	0.01	73	nootkatone	tr	tr
32	*cis*-carveol	0.01	tr				
33	neral	0.01	tr				
34	carvone	tr	tr		hydrocarbons	98.83	98.89
35	geraniol	tr	tr		monoterpenes	97.95	98.11
36	(*E*)-dec-2-en-1-al	tr	tr		sesquiterpenes	0.88	0.78
37	geranial	0.02	0.02		oxygenated compounds	1.05	0.93
38	perilla aldehyde	0.05	0.05		carbonyl compounds	0.52	0.52
39	perilla alcohol	0.02	0.01		alcohols	0.45	0.33
40	trans-ascaridole	tr	tr		esters	0.09	0.07
41	undecanal	0.01	0.01		oxides	0.01	0.01
42	δ-elemene	0.03	0.02				

t = tentative identification.

Mega Series 5160 gas chromatograph equipped with a Shimadzu data processor C-R3A; fused silica capillary column, 30 m × 0.32 mm i.d. coated with SE-52, 0.40−0.45 μm film thickness [Mega, Legnano (MI), Italy]; column temperature, 45 °C (6 min) to 200 °C at 3 °C/min; injection mode, split; detector, FID; injector and detector temperature, 250 °C; carrier gas, He 95 kPa; injected volume, 1 μL of neat oil. The quantitative composition was obtained by peak area normalization, and the response factor for each component was considered to equal 1.

MDGC Analysis. Enantiomeric ratios of some monoterpene hydrocarbons (β-pinene, sabinene, limonene) and of some monoterpene alcohols (linalool, α-terpineol) were obtained by multidimensional gas chromatography, using a developmental model (Mondello et al., 1998a) set up with two GC ovens, the first one equipped with a column coated with SE−52 and the second one with a chiral column coated with a derivatizated β-cyclodextrin, a hot interface, a rotary switching valve and a system to maintain a constant flow during the transfer. With this system, a heart-cut of the relevant fractions can be made and these fraction transferred from the nonchiral column to the chiral one in the following experimental conditions: precolumn, fused silica capillary column 30 m × 0.32 mm i.d., coated with SE−52, 0.40−0.45 μm film thickness [Mega, Legnano (MI), Italy]; column temperature 45 °C (6 min), to 220 °C at 2 °C/min; analytical column, fused silica capillary column 25 m × 0.25 mm i.d., coated with a diethyl 2,3-di-*O*-(*tert* -butyldimethylsilyl-β-cyclodextrin) 30% in PS 086, 0.25 μm film thickness [Mega, Legnano (MI), Italy]; column temperature, 45° (6 min), to 180 °C, at 2 °C/min; interface temperature, 200 °C; detector FID, 250 °C (for both chromatographs).

HPLC Analysis. Polymethoxylated flavones present in the nonvolatile residue were analyzed by normal-phase HPLC, using a Waters Associates (W. A.) equipment composed of a model 519 pump; a 600 E gradient controller, a Rheodyne 9125 injector, and a photodiode array detector model 996. Peak integration and quantitative calculations were performed by Millenium 2010 (W. A.) system using a calibration curve obtained for each standard component against a coumarin standard (Dugo et al., 1994). The column was a Zorbax silica column (25 cm × 4.6 mm i.d., particle size 7 μm); mobile phase, hexane: ethyl alcohol, 95:5; flow rate 1.6 mL/min; injection volume 20 μL of a solution obtained by diluting about 50 mg of each oil and 0.1 mL of a coumarin solution of known concentration in 1 mL of hexane:ethyl acetate (75:25). Detection was by UV absorbance at 315 nm. The UV spectra of eluting peaks were monitored with the PDA detector in the region 200−400 nm.

RESULTS AND DISCUSSION

Volatile Fraction. The components identified in both oils are reported in Table 1 together with the linear retention indices calculated on Mega 5 MS and on Megawax columns.

***Citrus Unshiu* Marcovitch, Satsuma mandarin.** Figure 1 shows the SE−52 chromatogram of a Satsuma

Table 3. Composition as Single Components and as Classes of Substances of Uruguayan Nova Mandarin Oils[a]

		4/23/97	5/10/97
1	α-thujene	tr	tr
2	α-pinene	0.48	0.50
3	camphene	tr	tr
4	sabinene	0.34	0.35
5	*β*-pinene	0.14	0.14
6	myrcene	1.93	1.98
7	α-phellandrene	0.03	0.04
8	octanal	0.17	0.16
9	*δ*-3-carene	0.17	0.19
10	α-terpinene	tr	tr
11	limonene	93.13	94.22
12	(*Z*)-*β*-ocimene	0.02	0.01
13	(*E*)-*β*-ocimene	0.44	0.38
14	*γ*-terpinene	0.01	0.02
15	*cis*-sabinene hydrate	0.02	tr
16	octanol	0.04	tr
17	*p*-mentha-2,4(8)diene	tr	tr
18	terpinolene	0.03	0.03
19	*trans*-sabinene hydrate	tr	tr
20	linalool	0.88	0.67
21	nonanal	0.05	0.05
22	*cis*-limonene oxide	0.05	0.01
23	*trans*-limonene oxide	0.04	0.01
24	(*E*)-myroxide	0.02	0.01
25	citronellal	0.01	0.01
26	*cis*-pinocamphone	0.02	0.01
27	terpinen-4-ol	0.01	tr
28	α-terpineol	0.08	0.06
29	dihydro carveol	0.03	0.01
30	decanal	0.32	0.30
31	octyl acetate	tr	tr
32	*trans*-carveol	0.02	0.01
33	nerol	0.01	tr
34	citronellol	0.01	tr
35	*cis*-carveol	tr	tr
36	neral	0.03	0.01
37	carvone	0.07	0.02
38	geraniol	tr	tr
39	(*E*)-dec-2-en-1-al	0.01	0.01
40	geranial	0.06	0.04
41	perilla aldehyde	0.04	0.02
42	perilla alcohol	0.03	0.02
43	(*E*,*Z*)-2,4-decadienal	tr	tr
44	neo dihydro carveol acetate	tr	tr
46	undecanal	0.02	0.02
47	(*E*,*E*)-2,4-decadienal	0.03	0.03
48	*δ*-elemene	0.01	0.01
49	α-terpinyl acetate	tr	tr
50	citronellyl acetate	tr	tr
51	neryl acetate	0.01	tr
52	α-copaene	0.03	0.02
53	geranyl acetate	tr	tr
54	*β*-cubebene	0.01	0.01
55	*β*-elemene	0.01	0.01
56	dodecanal	0.07	0.06
57	decyl acetate	0.01	0.01
58	(*E*)-caryophyllene	0.01	0.01
59	*β*-guryunene[t]	0.01	0.01
60	α-guajene[t]	tr	tr
61	α-humulene	0.02	0.02
62	(*E*)-*β*-farnesene	0.01	tr
63	(*E*)-dodec-2-en-1-al	0.02	0.01
64	*γ*-muurolene	tr	tr
65	germacrene D	0.11	0.09
66	bicyclogermacrene	tr	tr
67	α-muurolene[t]	tr	tr
68	α-bulnesene[t]	tr	tr
69	(*E*,*E*)-α-farnesene	0.03	0.02
70	cubebol[t]	tr	tr
71	*δ*-cadinene	0.05	0.04
72	elemol	0.02	0.01
73	germacrene B	0.01	0.01
74	(*E*)-nerolidol	tr	tr
75	germacrene D-4-ol	0.01	tr
76	tetradecanal	0.01	tr
77	*β*-sinensal	0.02	0.01
78	α-sinensal	0.04	0.02
79	nootkatone	0.01	0.01
	hydrocarbons	97.03	98.11
	monoterpenes	96.72	97.86
	sesquiterpenes	0.31	0.25
	oxygenated compounds	2.29	1.61
	carbonyl compounds	1.00	0.79
	alcohols	1.16	0.78
	esters	0.02	0.01
	oxides	0.11	0.03

[a] t = tentative identification.

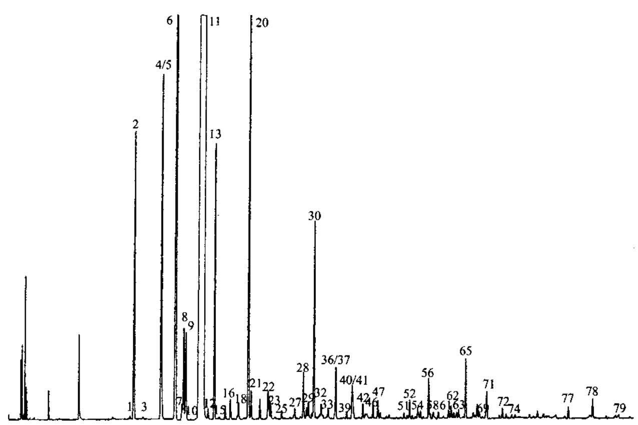

Figure 2. GC chromatogram of a Nova mandarin oil obtained with the SE-52 column.

mandarin oil; the composition as classes of substances and as single components for the two oils analyzed is reported in Table 2. Seventy-three components were identified in each oil, which constitute more than 99% of the whole volatile fraction.

The following components were identified for the first time in Satsuma peel oil: α-phellandrene, *cis*-sabinene hydrate, *p*-cymenene, *trans*-sabinene hydrate, *cis*-piperitol, neral, geranial, *trans*-ascaridole, α-cubebene, *β*-cubebene, *γ*-elemene, *trans*-α-bergamotene, bicyclogermacrene, α-muurolene, α-bulnesene, (*Z*)-α-bisabolene, cubebol, *δ*-cadinene, germacrene B, germacrene D-4-ol, bulnesol, and *β*-sinensal.

Table 4. Enantiomeric Ratios for *β*-Pinene, Sabinene, Limonene, Linalool, and α-Terpineol in Uruguayan Satsuma and Nova Oils

		satsuma oils		nova mandarin oils	
		4/23/97	5/10/97	4/23/97	5/10/97
β-pinene	1R,5R (+)	95.9	95.8	63.3	69.7
	1S,5S (−)	4.1	4.2	36.7	30.3
sabinene	1R,5R (+)	92.5	92.6	97.3	97.2
	1S,5S (−)	7.5	7.4	2.7	2.8
limonene	4S (−)	0.8	0.8	0.6	0.6
	4R (+)	99.2	99.2	99.4	99.4
linalool	3R (−)	72.9	72.6	4.0	3.7
	3S (+)	27.1	27.4	96.0	96.3
α-terpineol	8S (−)	33.2	33.1	5.6	4.5
	8R (+)	66.8	66.9	94.4	95.5

The oils were characterized by a high content of limonene (about 91%) and monoterpenes. A large number of sesquiterpenes were present, of these the main component was (*E*,*E*)-α-farnesene (0.25−0.29%).

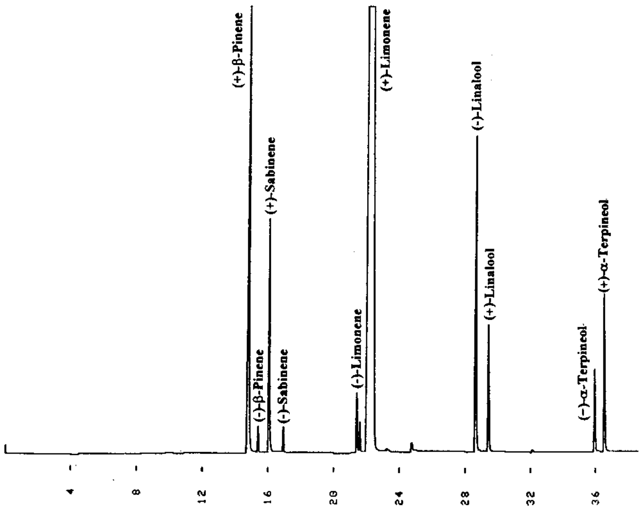

Figure 3. GC-GC chiral chromatogram of the transferred components of a Satsuma mandarin oil.

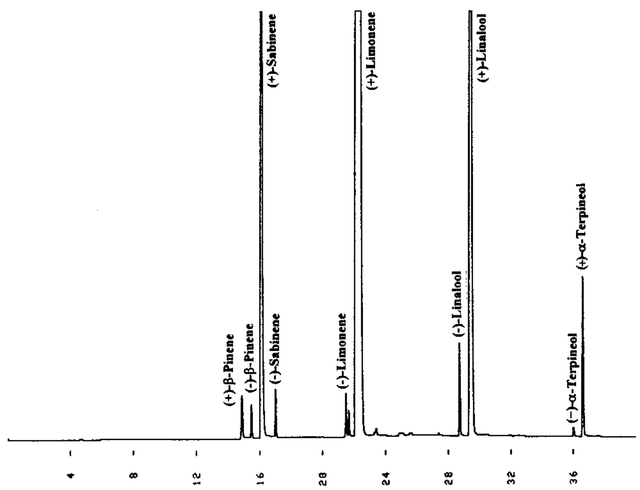

Figure 4. GC-GC chiral chromatogram of the transferred components of a Nova mandarin oil.

Table 5. Content (g/100 of oil) of Polymethoxylated Flavones of Uruguayan Satsuma and Nova Mandarin Oils

	satsuma oils		nova mandarin oils	
	4/23/97	5/10/97	4/23/97	5/10/97
tangeretin	0.17	0.16	0.14	0.12
3,3′,4′,5,6,7,8-heptamethoxy-flavone	0.30	0.31	0.40	0.36
nobiletin	0.07	0.09	0.15	0.13
tetra-*O*-methylscutellarein	tr	0.01	0.18	0.14
3,3′,4′,5,6,7-hexamethoxy-flavone	tr	tr	0.11	0.09
sinensetin	tr	tr	0.02	0.01

Among oxygenated compounds, aliphatic aldehydes constituted about 80% of the carbonyl compound fraction (0.52−0.52%); linalool (0.16−0.20%), and α-terpineol(0,09−0.10%) were the main alcohols; esters were less represented.

According to Tanaka and Swingle, Satsuma is considered a mandarin due to its appearance and size. However, the oil composition is closer to that of an orange (Dugo et al., 1994a; Cotroneo et al., 1994; Verzera et al., 1996) especially for the high content of limonene, monoterpene hydrocarbons, aliphatic aldehydes, and alcohols and for the low content of esters.

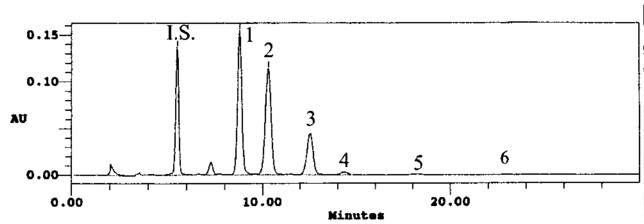

Figure 5. HPLC chromatogram of a Satsuma mandarin oil.

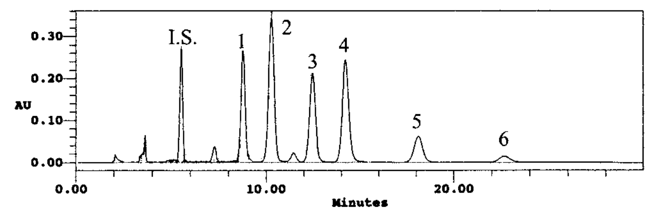

Figure 6. HPLC chromatogram of a Nova mandarin oil.

***Citrus reticulata* Blanco cv. Nova, Nova mandarin.** Figure 2 shows the SE−52 chromatograms of a Nova mandarin oil; the composition as classes of substances and as single components for the two oils analyzed is reported in Table 3. Seventy-nine components were identified in each oil, which constitute more than 99% of the whole volatile fraction of the oils.

The oils were found to be rich in monoterpene hydrocarbons (96.7−97.9%). The main component was limonene (93.1−94.2%), followed by myrcene (1.9−2.0%). The sesquiterpene fraction was rich in components, and in fact, 17 sesquiterpene hydrocarbons were identified; the main components were germacrene D (0.09−0.11%) and δ-cadinene (0.04−0.05%). Among oxygenated compounds, carbonyl compounds (0.8−1.0%) and alcohols (0.8−1.2%) had a similar content; esters were less represented (0.01−0.02%). Aliphatic aldehydes constituted most of the carbonyl compound fraction; the main component was decanal (0.30−0.32%). Among alcohols, the main component was linalool (0.67−0.88%), followed by α-terpineol (0.06−0.08%).

Looking at Table 3, minor variations in quantitative composition can be observed during the production season: the content of sesquiterpenes, carbonyl compounds, alcohols, and esters decreases, while the opposite is true of the limonene and monoterpene content.

Nova mandarin oil composition is closer to that of a Uruguayan sweet orange oil than to that of a mandarin oil. A similar finding has been previously been reported for two other Uruguayan mandarin hybrids, Ortanique and Malaquina (Dellacassa et al. 1992).

Enantiomeric Ratios. The enantiomeric ratio of β-pinene, sabinene, limonene, linalool, and α-terpineol were determined in each oil by four subsequent transfers during the same analysis. Enantiomeric ratios of the components analyzed are reported in Table 4.

Figures 3 and 4 show the chiral chromatogram of a Satsuma and a Nova oils, respectively. No information is reported in the literature about the enantiomeric ratio of the components of these oils. Comparing these results with those obtained for Italian mandarin and sweet orange oils, the enantiomeric ratios of the components analyzed were very different from those of mandarin oils and similar, especially in the case of Nova oils, to sweet orange oils (Mondello et al. 1998b).

Polymethoxylated Flavones. Figures 5 and 6 report the HPLC chromatograms of a Satsuma and a Nova oil, respectively. Table 5 reports the content (g/100 g of oil) of polymethoxylated flavones in Satsuma and Nova oils. Six polymethoxylated flavones were identified in all the oils analyzed, namely tangeretin, 3,3′,4′,5,6,7,8-heptamethoxyflavone, nobiletin, tetra-*O*-methylscutellarein, 3,3′,4′,5,6,7-hexamethoxyflavone, and sinensetin.

Regarding Satsuma oils, the main component was 3,3′,4′,5,6,7,8-heptamethoxyflavone, followed by tangeretin. In the literature, only two papers deal with the polymethoxylated flavones of Satsuma oil: Chkhikvishvili et al. (1990) identified tangeretin, 3,3′,4′,5,6,7,8-heptamethoxyflavone, nobiletin, and 3,3′,4′,5,6,7-hexamethoxyflavone, while Nogata et al. (1994) identified tangeretin and sinensetin.

Regarding Nova oils, the main component was 3,3′,4′,5,6,7,8-heptamethoxyflavone; tangeretin, nobiletin, and tetra-*O*-methylscutellarein had a similar concentration. The same components have been identified in Italian mandarin oil (Dugo et al., 1994b) but with a different quantitative composition.

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