Citrus Petitgrain Oils of Israel

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Mandarin (*Citrus reticulata* Blanco or *Citrus nobilis* Andrews) and orange (*Citrus sinensis* (L.)) Osbeck. were introduced to Europe by the Portuguese explorers in the 12th and the 15th century respectively. Since that time there was ever increasing popularity and demand for these fruits which lead to their wide cultivation in many countries of the world.

The name "Mandarin" was given to the *C. reticulata* by the Portuguese who brought it from China and named it to reflect the country of origin. The history of the name "Orange" is quite curious. In some European languages, the word "Appelsin" (Chinese apple), is used to designate orange. While the word "orange" itself is traceable through Arabic "Naranj" to Sanskrit "Naranga",[1] the Arabs themselves use the word "Burtukhal" (Portugal) which testifies to the contribution of the Portuguese to the introduction and distribution of citrus in the Western world.

In today's food and beverage market, the citrus flavored products are highly popular. The aroma elements from the citrus fruits—cold-pressed and distilled oils, folded and deterpenated oils, essences and extracts, are widely used in the creation of natural flavors. The commercial importance of these products lead to extensive scientific study resulting in a broad knowledge base of their chemical composition.

With the exception of bitter orange leaf oil, the so-called oil of petitgrain bigarade,[2] citrus leaf oils have found only limited application in the flavor and fragrance industry. Although the chemical compositions of petitgrain oils have been studied over the years,[2-13] our knowledge in this matter falls far behind the information available on citrus fruit oils.

Since biblical times, citrus trees were grown in the Holy Land. In the state of Israel the cultivation of citrus became the corner stone for the local food industry. Cold-pressed citrus oil produced in Israel, holds a respectful position in the international aroma material trade. Yet almost no information is found in the literature with respect to the leaf oils of Israeli citrus.

There is a big demand in our industry for natural aroma chemicals used in the creations of citrus flavors. The recovery of individual components from the peel oils is usually cost prohibitive due to the high prices of citrus oils and to the low total content of the oxygenated components which are the principle carriers of citrus flavor.

Recently, Lawrence showed that a large variety of valuable natural aroma chemicals can be found in uncommon sources of essential oils.[14] This fruitful idea, enforced by the possibility of additional exploration of already existing commercial crops, provided the motivation for our study of Israeli citrus leaf oils.

Orange Petitgrain Oils

According to Braverman,[15] the numerous varieties of sweet oranges can be classified into the following three large groups; those with normal fruits - round (such as Spanish oranges or Valencias) or oval in shape (such as Jaffas or Mediterranean oranges); those with abnormal or navel fruits (Washington navel); and those with a red or red streaked pulp (Blood oranges).

Shamouti (Jaffa), Valencia and Ruby (blood orange) are three major varieties commercially grown in Israel. The composition of their leaf essential oil is seen in Table I.

The presented data indicated that all three varieties belong to the same chemical type. Every identified constituent, although in somewhat different proportion was found in each one of the investigated essential oils.

Among the three studied varieties of sweet orange, the leaf oil of Valencia is the only one, whose composition was previously investigated in detail.[6,11,13] Being rather similar to the composition of Valencia leaf oil from Florida,[6,11] the Israeli oil differs considerably from the oil of Valencia grown in Algeria.[13] Most probably, the Algerian and Israeli Valencias belong to different subvarieties and their oils, judging by their composition, would exhibit quite a different organoleptic profile.

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Mandarin Petitgrain Oils

For nearly a hundred years, classic essential oil literature refers to mandarin petitgrain oil as containing methyl-N-methyl anthranilate as a major component.[2,3] The famous phenomenon of fluorescence of mandarin leaf oil in alcohol dilutions, first observed at the end of the last century, is due to the high content of this chemical. Affectionately describing the mandarin petitgrain oil and its interesting applications in flavors and perfumes, Arctander[16] emphasizes the advantages of methyl-N-methyl anthranilate which does not discolor or form condensation products in the presence of aldehydes (in contrast to the formation of the Schiff's bases with methyl anthranilate). He blames the shortages in supply of mandarin leaf oil for the limited applications of this excellent material.

We were told by several essential oil producers from Southern Europe that their attempts to produce mandarin petitgrain oil by distillation of leaves and twigs of mandarin trees, occasionally resulted in rather strange products—essential oils without a trace of methyl-N-methyl anthranilate. Indeed, more recent studies have shown that the leaf oils of new varieties of mandarin contain mostly hydrocarbons and linalool. Thymol, or alternately terpinen-4-ol, were found in some varieties of mandarin but not in others.[6,7]

In our study we investigated the chemical composition of the essential oils obtained from leaves of seven different varieties of *C. reticulata* grown in Israel. Among those Dancy and Clementine are well known to the citrus growers and cultivated in many places around the world, while Michal, Maya and Nectarine are local Israeli developments. The varieties Balady and Yussuf Effendy are old local mandarins grown by the Arabs long before intensive agriculture was introduced to the country.

All leaf samples studied in this work were gathered by the authors from authentic trees in Israel. Essential oils were recovered in the laboratory and studied using GC/MS. Table II lists seventy-three components identified in the mandarin leaf oils studied in this work. The data presented here indicate the existence of three distinct groups with respect to leaf oil chemical composition.

Chemovarieties of Mandarin

The first group (A), which is the classic mandarin petitgrain oil, is characterized by the presence of methyl-N-methyl anthranilate (ca.60%). The variety Balady growing in both Egypt[7] and Israel belongs to this type.

The word "Balady", in Arabic, means "local, native, well known". This variety of mandarin is probably the oldest in the Middle East since it is considered to be native in two agricultural areas, Israel and Egypt, parted by 500 km of desert. In Israel, the Balady variety is practically extinct. Its cultivation was abandoned as a commercial crop in modern times because it is not a prolific plant and its fruits are not as tasty as those of new varieties. The odor of the foliage, however, is outstanding. When one is lucky enough to find

Table I. Chemical Composition of Orange Petitgrain Oil Obtained from Three Varieties of *Citrus sinensis* (L.) Osbeck. Grown in Israel

Components	Valencia	Jaffa (Shamouti)	Ruby (Blood Orange)
α-pinene	1.75	0.88	1.02
ß-pinene	1.06	1.30	1.14
sabinene	18.66	32.58	15.81
δ-3-carene	2.52	4.34	3.06
myrcene	2.79	5.63	3.64
ethyl (E)-2-butenoate*	0.10	0.08	0.11
α-phellandrene	0.05	0.08	0.06
limonene	1.70	1.25	2.96
ß-phellandrene	0.35	0.55	0.81
(Z)-ocimene	0.18	0.06	0.50
unidentified 1	3.23	1.36	3.56
γ-terpinene	7.52	7.41	10.50
p-cymene	0.10	0.18	0.15
terpinolene	1.31	0.75	1.51
unidentified 2 (isomer of 1)	2.14	1.25	3.23
3-methyl-2-butenol*	0.02		t.
methyl heptenone	t.	t.	t.
(Z)-3-hexenol	1.25	0.41	1.93
ethyl octanoate	0.11	t.	0.06
(E)-sabinene hydrate	2.14	2.43	2.81
citronellal	1.82	1.32	1.65
linalool	8.21	5.13	20.92
(Z)-sabinene hydrate	2.17	1.53	3.23
ß-elemene	4.13	2.38	4.00
terpinen-4-ol + ß-caryophyllene	7.87	3.62	6.95
ethyl benzoate*	t.	t.	t.
α-humulene	0.11	0.98	1.19
α-terpineol	0.13	0.09	0.18
valencene*	0.03	0.02	0.04
ß-selinene*	0.02	t.	0.03
α-selinene*	0.01	0.02	0.01
bicyclogermacrene	0.06	0.08	0.06
citronellol	0.12	0.06	0.09
ethyl phenylacetate*	0.09	0.08	0.11
anethole*	0.07	0.05	0.12
ethyl laurate*	0.05	0.04	0.05
geraniol	t.	t.	t.
ß-phenylethanol*	0.04	t.	0.02
ethyl myristate*	0.03	t.	0.05
ß-sinensal	1.22	0.43	2.35
ethyl palmitate	5.57	3.54	6.77
α-sinensal	0.03	0.02	0.07
ethyl stearate*	0.21	0.13	0.07
ethyl linoleate*	0.69	0.47	0.61
ethyl linolenate*	5.26	0.35	3.74
phytol*	2.04	0.91	1.07

*Newly identified in orange leaves t. = trace

Table II. Chemical Composition (%) of Mandarin Petitgrain Oil Obtained from Seven Varieties of *Citrus reticulata* Blanco Grown in Israel

	A	B			C		
Composition	Balady	Yussuf Effendy	Dancy	Maya	Clementine	Michal	Nectarine
α-thujene	-	0.78	0.65	-	0.35	0.30	-
α-pinene	1.34	1.83	1.31	-	1.70	1.28	0.98
camphene	-	-	-	-	-	t	-
ß-pinene	0.72	1.51	1.18	0.11	0.02	1.33	0.62
sabinene	**-**	**-**	**0.41**	**1.41**	**10.62**	**20.84**	**27.20**
myrcene	0.31	0.34	0.11	0.25	-	0.54	2.00
α-phellandrene	0.05	t	-	-	-	-	0.01
ethyl-2-butenoate*	-	-	-	0.04	-	-	-
α-terpinene	0.15	0.11	0.21	0.07	0.72	0.21	0.26
limonene	4.91	1.00	0.39	0.23	0.68	0.73	2.88
ß-phellandrene*	0.03	-	-	0.06	1.94	0.18	-
(Z)-ß-ocimene	0.04	-	0.10	2.31	-	-	4.16
γ-terpinene	12.60	4.57	3.11	2.12	0.73	-	-
(Z)-3-hexenyl formate*	0.11	-	-	-	-	-	-
p-cymene	3.10	6.54	4.09	1.43	0.93	t	0.32
terpinolene	0.53	0.34	-	-	-	-	0.32
(Z)-2-pentenol*	t	-	-	-	-	-	-
(Z)-3-hexenol*	0.06	0.13	0.05	0.33	-	t	0.20
ethyl octanoate*	0.01	t	-	0.02	-	0.02	0.04
(E)-sabinene hydrate*	0.01	-	-	2.79	-	0.07	2.54
ethyl nonanoate*	0.01	-	-	-	-	-	-
(Z)-linalool oxide* (furanoid)	-	0.06	0.44	-	0.49	0.32	-
(E)-linalool oxide* (furanoid)	-	-	0.21	-	-	0.29	-
α-copaene	-	-	-	0.02	0.04	0.17	0.02
decanal	-	-	-	0.03	-	-	-
benzaldehyde*	-	-	-	0.02	-	-	t
citronellal	-	-	-	-	-	-	0.25
linalool	**0.11**	**45.12**	**50.73**	**55.10**	**25.17**	**30.34**	**24.80**
(Z)-sabinene hydrate*	-	-	-	-	0.04	0.21	-
(E)-ß-bergamotene*	-	-	-	0.02	-	-	0.03
ß-elemene*	-	-	0.10	0.04	-	-	1.28
terpinen-4-ol	**1.63**	**-**	**-**	**-**	**6.11**	**4.05**	**2.21**
ß-caryophyllene	0.14	5.44	0.24	2.00	0.16	0.09	0.30
valencene*	0.05	-	-	-	-	-	-
thymol methyl ether	-	-	4.63	-	-	-	-
terpinen-1-ol*	0.01	t	t	-	0.02	0.02	t
citronellyl formate*	-	-	-	-	2.56	0.65	t
ethyl decanoate*	0.03	t	-	-	0.10	0.14	t
(E)-ß-farnesene	-	-	t	t	0.61	0.82	0.02
α-humulene	0.08	0.51	0.25	0.11	0.16	0.55	t
sabinol*	-	-	t	-	t	t	-
α-terpineol	0.24	0.33	0.58	1.30	0.64	1.12	1.28
viridiflorene*	t	0.31	0.18	-	t	-	-
α-muurolene*	-	t	t	0.02	t	0.32	-
bicyclogermacrene*	-	-	-	0.06	-	0.54	0.03
(E,E)-a-farnesene	-	0.71	0.50	1.00	-	t	0.07

Table II (con't). Chemical Composition (%) of Mandarin Petitgrain Oil Obtained from Seven Varieties of *Citrus reticulata* Blanco Grown in Israel

	A	B			C		
Composition	Balady	Yussuf Effendy	Dancy	Maya	Clementine	Michal	Nectarine
citronellol	-	-	-	t	2.60	t	0.06
γ-cadinene*	-	0.06	0.02	0.06	0.08	0.47	0.06
methyl salicilate*	1.00	-	-	-	-	-	t
ethyl phenylacetate*	0.06	-	-	0.02	-	-	0.06
anethole*	-	-	0.02	0.01	0.02	t	0.03
geraniol	-	0.02	t	0.03	0.04	0.05	0.10
ethyl laurate*	-	0.02	t	0.03	t	t	0.06
para-cymen-8-ol*	0.10	0.05	t	t	0.02	0.04	t
ß-phenylethanol*	-	t	0.02	0.03	-	t	0.03
myrtenol*	-	t	t	t	t	0.12	t
(Z)-carveol*	0.04	t	0.01	-	0.03	0.06	-
humulene oxide*	-	0.03	t	-	-	0.07	-
caryophyllene oxide*	t	0.31	0.33	-	2.10	0.41	-
nerolidol	-	0.04	t	0.04	0.02	0.03	0.02
ethyl myristate*	0.18	0.11	0.14	0.05	0.88	0.41	0.06
methyl-N-methyl anthranilate	**65.71**	-	-	-	-	-	-
thymol	**0.12**	**14.43**	**11.70**	**8.21**	-	-	-
(E)-carveol*	0.04	-	-	-	t	t	-
ethyl pentadecanoate*	0.03	-	-	-	-	0.06	-
ß-sinensal*	-	-	0.41	2.98	2.11	1.52	1.60
ethyl palmitate*	1.83	2.31	2.79	6.08	7.22	4.84	3.36
ethyl heptadecanoate*	0.04	0.09	0.15	0.07	t	0.31	0.08
a-sinensal*	-	0.93	0.24	0.72	t	0.17	0.48
ethyl stearate*	0.06	0.09	0.25	0.87	t	0.53	0.16
ethyl linoleate*	0.74	0.78	0.39	1.06	0.83	1.78	0.60
ethyl linolenate*	2.64	2.86	0.68	6.88	3.63	4.89	3.33
phytol*	0.14	0.19	0.12	1.29	0.09	0.88	0.74

*Newly identified in mandarin leaves t = trace

a Balady tree somewhere in a private garden, there could be no doubt, the squeezed leaf smells like exquisite perfume!

It can be seen that the remaining six varieties fall into two groups. According to their chemical composition, varieties Yussuf Effendy, Dancy and Maya form one group (B), while Clementine, Michal and Nectarin form another group (C).

Oils of group (C) contain 10.6-27.2% of sabinene compared to the 0-1.4% in the oils of group (B). The terpinen-4-ol content is 2.2-6.1% in the oils of group (C), but not detected in group (B). The linalool content in group (C) is 24.8% to 30.3% while it is 45.1-55.1% in group (B). The important characteristic of group (B) is the high content of thymol—8.2-14.4%. These oils also contain more γ-terpinene—2.1-4.6% and p-cymene—1.4-6.5%, which are the intermediates in the biosynthesis of thymol.[17,18]

Based on the results of our investigation and the literature data, it seems that with the exception of mandarin Unshiu,[8,19] the division into three chemotypes is universal for the most of *C. reticulata* varieties grown commercially around the world.

Particular Findings

We now turn to the constituents common to all the studied leaf oils. In each analyzed sample a substantial amount of the fatty acids ethyl esters was detected. It should be mentioned in this respect that the presence of lauric, myristic and stearic acids (probably in the form of esters) was detected in the oil, extracted from aqueous distillate formed during production of bitter orange petitgrain oil, as reported by Guenther.[2]

Phytol, the presence of which was previously reported only in the Algerian lemon leaf oil,[10] was found in a noticeable concentration in every one of the orange and mandarin leaf oils studied.

Apparently for the first time, the presence of anethole was detected in the citrus oils. It was found in all the leaf oil samples with the exception of the old varieties of mandarin—Balady and Yussuf Effendy.

Sweet orange and mandarin leaf oils were found to contain the highest ever observed percentage of α- and β-sinensals. It is our opinion that these sinensals exhibit a tender and powerful orange- or mandarin-like organoleptic

profile, playing the role of the characteristic orange note congruent to that of nootkatone in the flavor of grapefruit.

Currently a very limited production of natural sinensals is based on cold-pressed citrus oils where they are present at approximately 0.05% level. Obviously they are not cheap and, therefore, cannot be widely used in the flavor creation. These very valuable and rare flavor ingredients make up 2.4% in the orange Ruby and nearly 4% of the leaf oil of mandarin Maya. Such a high content of sinensals makes Israeli citrus leaf oils a convenient and economical source of these important flavor ingredients.

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