A Critical Review on the Chemical Composition of Citrus Oils

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Last year we studied over 200 publications on the chemical compositions of citrus oils. The outcome of this study has been published in "Volatile Compounds in Food".[1] In addition we investigated the chemical compositions of some important Mediterranean citrus oils.[2] Additional analyses of Israeli citrus oils will be included in this paper.

During our studies and investigations we came across several anomalies in the concentrations of the main and other important constituents of the oils. Sometimes even the identities of the constituents found may be doubted. This study is meant as a trial to clarify some of the aforementioned anomalies.

There are several thorough reviews on the chemical composition of citrus oils. In 1970 Kefford and Chandler[3] summarized the quantitative data, including terpeneless oils and individual fractions as well as total oils. In 1971 Ziegler[4] examined citrus oils and reviewed important publications on these oils. Shaw in 1979[5] reviewed the quantitative analyses of complete citrus essential oils. Lawrence[6] wrote several compilations about the chemical compositions of citrus oils.

More recently Swaine and Swaine[7] reported the quantitative compositions of the most important citrus oils. Regarding the compositional data for bitter orange oil they said "again, one marvels at the wide range of data within one aroma camp". The purpose of this publication is to analyze the wide range of quantitative data reported within one citrus oil, and to investigate its possible causes.

One should keep in mind that all cold-pressed citrus oils contain nonvolatiles, concentration of which is normally below 5%, with the exception of grapefruit and lime oils, which may contain up to 7.5% nonvolatiles.[5]

Chemical Composition of Sweet Orange Oils

Generally accepted botanical name for sweet orange is *Citrus sinensis* (L.) Osbeck (family Rutaceae). Old botanical names are *C. aurantium* L. var. dulcis ex parte, *C. aurantium* Risso ssp. sinensis, and *C. vulgaris* Risso. Within the species *C. sinensis* (L.) Osbeck there are many horticultural varieties, so called cultivars. The most common cultivar of sweet orange all over the world is Valencia (late).

Most information about cultivars of sweet orange has been gained in the United States, where orange trees are cultivated in California, Florida and Texas. One often distinguishes early-, mid- and late-season varieties. In Florida the following cultivars are found: Hamlin (early-), Pineapple (mid-), Valencia (late season), Parson Brown, Conner's seedless and Temple. The varieties found in California are: Hamlin (early-), Valencia (late season), Washington (navel), and Bahia (navel). In Texas one can find Hamlin (early-), Marss (early-), and Valencia (late season).

In Mediterranean countries the most common cultivar is Valencia (late). Early- and mid-season varieties also cultivated are: Sicily (Italy): Naveline (early), Sanguinello (mid-), Ovale (late), Tarocco and Moro. Israel: apart from the aformentioned early-, mid- and late-season varieties, mainly Valencia; a typical cultivar Shamouti is grown. (see Table I)

In South Africa Valencia (late), seedling- and navel-varieties are mostly cultivated. Little is known about the varieties cultivated in South America (Brazil), USSR and the Far East. When the cultivar is known it will be mentioned here regarding its chemical compositions of the oils. Formerly most sweet orange trees were grafted on the rootstock of *Citrus aurantium* L., ssp. amara Engler, the bitter orange tree.

Monoterpenoids

According to some published data and our own studies and investigations, the volatile part of cold-pressed sweet orange oils consists of 97.0 - 98.5 % monoterpene hydrocarbons. (See Tables I-V).

The dominant monoterpenes are:

d-limonene	94.0-97.0%
myrcene	1.5-2.0%
α-pinene	0.4-0.6%
sabinene	0.3-0.8%

Two recent publications,[7,8] however, reported that cold-pressed Californian sweet orange oils contained 57.3% and 80.1% total monoterpenes with 56.7% and 77.6% limonene respectively (see Table II). It might be possible that only Californian oils have low monoterpene content. However this appears strange, because in 1978 a USDA bulletin reported that Californian sweet orange oil contained 98.5% monoterpene hydrocarbons, of which 95.8% is limonene.

Table I. The Chemical Composition of Israeli Sweet Orange Oils (1988)

	Valencia-late	Shamouti
	peak-area percentages	
α-Thujene	0.004	0.006
α-Pinene	0.504	0.534
Camphene	0.003	0.003
Sabinene	0.295	0.804
β-Pinene	0.042	0.077
Myrcene	1.868	1.910
α-Phellandrene	0.040	0.043
δ-3-Carene	0.093	0.042
α-Terpinene	0.003	0.002
p-Cymene	tr.	tr.
Limonene	94.341	93.687
trans-β-Ocimene	0.027	0.034
Terpinolene	0.029	0.019
Total monoterpenes	**97.266**	**97.192**
Octanal	0.296	0.254
Nonanal	0.049	0.045
Decanal	0.346	0.290
(E,Z)-2,4-decadienal	0.020	0.012
(E,E)-2,4-decadienal	0.006	0.006
Undecanal	0.014	0.013
Dodecanal	0.055	0.048
Total aliph. aldehydes	**0.786**	**0.668**
Octanol	0.073	0.025
Octyl acetate	0.007	0.005
Decanol	0.005	tr.
Decyl acetate	0.027	0.035
Citronellal	0.057	0.062
Neral	0.046	0.054
Geranial	0.079	0.098
Perillaldehyde	0.013	0.023
Linalool	0.411	0.383
Terpinen-4-ol	0.005	0.002
α-Terpineol	0.048	0.034
Nerol	0.008	0.008
Geraniol	0.016	0.016
Citronellol	tr.	tr.
Neryl acetate	0.008	0.009
Geranyl acetate	0.005	0.006
α-Terpinyl acetate	0.004	0.005
Citronellyl acetate	0.001	0.004
1,8-Menthadienyl-10 acetate	0.012	tr.
Perillene	0.006	0.008
cis/trans-Limonene oxides	0.025	0.025
δ-Elemene	0.001	0.001
α-Cubebene	0.003	0.002
β-Elemene	0.021	0.018
α-Copaene	0.001	0.001
Caryophyllene	0.020	0.025
β-Copaene	0.032	0.033
β–Farnesene	0.010	0.022
α-Humulene	0.004	0.007
Germacrene D	0.011	0.019
α-Farnesene	0.097	0.255
β-Bisabolene	0.006	0.013
β-Valencene	0.006	0.001
δ-Cadinene	0.020	0.018
Nerolidol	0.009	0.007
Farnesols	0.003	0.004
β-Sinensal	0.040	0.056
α-Sinensal	0.025	0.030
Nootkatone	0.021	0.032

The variation in the concentrations of the total terpene hydrocarbons and especially in those of *d*-limonene may be due to the deterioration of the orange oil.

Recent analyses have been carried out with cold-pressed sweet orange oils from the cultivars Valencia (late) and mid-season (probably Pineapple) growing in Florida.[13-15] Detailed results are shown in Table III. The average concentration of the monoterpene hydrocarbons was 98.12%, from which *d*-limonene was 95.64%. The total amount of oxygenated products accounted for 1.4-1.5%, including octanal (estimated as 0.3%), which in 2 cases did not separate from myrcene in the GC analysis. The total concentration of 4 sesquiterpenes was 0.12%.

The gas chromatogram of the hydrocarbon fraction showed at least 9 peaks of sesquiterpenes, of which tentative identities on retention times could include β-elemene, α-

Table II. Quantitative Chemical Composition of California Cold-pressed Sweet Orange Oils

	USA-Bull. 776 (1978)	Ref.8 (1982)	Ref.7 (1988)
Ethyl butyrate	-	-	0.004
α-Pinene	0.52	0.44	0.513
β-Pinene	-	-	0.031
Sabinene	0.38	0.12	-
Myrcene	(1.73)	-	1.890
Phellandrene	0.10	-	-
d-Limonene	95.79	56.74	77.600
γ-Terpinene	-	-	0.031
p-Cymene	-	-	0.016
Total Monoterpenes	**98.52**	**57.3**	**80.085**
Hexanal	-	-	0.004
(E)-2-Hexenal	-	-	0.002
Octanal	(0.30)	-	0.196
Nonanal	0.03	-	0.032
Decanal	0.26	-	0.202
Dodecanal	0.05	-	0.026
Total Aliph. Aldehydes	**0.64**	**-**	**0.462**
Hexanol	-	-	0.002
Octanol	-	-	0.012
1-Octen-3-ol	-	tr.	-
Citronellal	0.04	-	0.052
Neral	0.04	-	0.052
Geranial	0.06	-	0.048
Total Terpene Aldehydes	**0.14**	**-**	**0.152**
Linalool	0.28	-	0.228
α-Terpineol	-	-	0.046
Geraniol	-	-	0.007
Total Terpene Alcohols	**0.28**	**-**	**0.281**
Carvone	-	5.40	0.009
β-Caryophyllene	0.02	-	0.027
β-Copaene	0.02	-	-
β-Farnesene	0.02	-	-
Valencene	0.08	-	0.007
β-Sinensal	0.05	-	-
α-Sinensal	0.02	-	-
Nootkatone	-	-	0.012

cubebene, α-copaene, γ-muurolene, α-humulene and δ-cadinene. With respect to the concentration of valencene (0.05%) the total concentration of sesquiterpene hydrocarbons could well be 0.2%. The concentration of the sesquiterpenoids α/β-sinensal and nootkatone was 0.06 - 0.08% The mid-season variety contained less oxygenated compounds, namely 1.0-1.1%, than the late-season variety 1.3-1.4%.

The chemical composition of cold-pressed sweet orange oil (cultivar Valencia-late) from Israel, Italy and Spain can well be compared with the oil from USA-Florida (see Table IV). Arras et al.[10] studied the chemical composition of Sicilian sweet orange oil from Valencia fruits, cultivated on trees with different rootstocks (see Table VI). They found that the total concentration of monoterpene hydrocarbons in the volatile part of the oils accounted for 98.1% of the oil, from which 95.3% was *d*-limonene. The total concentration of oxygenated compounds was 1.6%.

It should be noted that no oxygen-containing sesquiterpenoids were analyzed. Little attention has been paid to the concentration of δ-3-carene in orange oils. This constituent, which may be present up to 0.2%, is rather characteristic for sweet orange oil, especially Brazilian. Since sweet orange terpenes often are used to compound other citrus oils, e.g. lemon oil, the content of δ-3-carene in these oils can be an indication of reconstitution.[9]

Aliphatic Compounds

Straight chain aliphatic compounds with 1 to 16 carbon atoms have been found in sweet orange oils. Lower aliphatic aldehydes (C-1 to C-6) are important in orange juice, for its fresh, sappy and juicy organoleptic quality. Higher aliphatic aldehydes (C-8 to C-12) are character-impact constituents of sweet orange oils. Especially important components are n-octanal and n-decanal.

Table III. Quantitative Chemical Composition of USA-Florida (Valencia-late) Cold-pressed Sweet Orange Oils

	Ref.13 (1983)	Ref.14 (1986)	Ref.15 (1987)	Average
α-Pinene	0.42	0.46	0.47	0.45
Sabinene	0.24	0.27	0.28	0.26
Myrcene	(1.56)	(1.74)	1.86	1.70
Phellandrene	0.05	0.04	0.05	0.05
d-Limonene	95.17	96.08	95.66	95.65
Total Terpenes	**97.44**	**98.59**	**98.32**	**98.11**
Octanal	(0.30)	(0.30)	0.34	0.31
Nonanal	0.02	0.06	0.05	0.04
Decanal	0.28	0.24	0.26	0.26
Undecanal	0.02	-	0.02	0.02
Dodecanal	0.07	0.05	0.07	0.06
Total Aliph. Ald.	**0.69**	**0.65**	**0.74**	**0.69**
Octanol	0.03	0.03	0.05	0.04
Octyl acetate	0.01	-	0.03	0.02
Citronellal	0.05	0.05	0.05	0.05
Neral	0.07	0.08	0.09	0.08
Geranial	0.10	0.12	0.11	0.11
Perillaldehyde	0.01	-	0.01	0.01
Total Terpene Ald.	**0.23**	**0.25**	**0.26**	**0.25**
Linalool	0.25	0.23	0.29	0.26
α-Terpineol	0.03	0.02	0.05	0.03
Total Terpene Alc.	**0.28**	**0.25**	**0.34**	**0.29**
β-Caryophyllene	0.02	0.03	0.02	0.02
β-Copaene	0.02	0.02	0.02	0.02
β-Farnesene	0.02	0.02	0.02	0.02
Valencene	0.05	0.05	0.06	0.06
Total Sesquiterp.	**0.11**	**0.12**	**0.12**	**0.12**
β-Sinensal	0.03	0.04	0.04	0.04
α-Sinensal	0.02	0.02	0.02	0.02
Nootkatone	0.01	0.02	0.01	0.01

Table IV. Quantitative Chemical Composition of Valencia-late Cold-pressed Sweet Orange Oils from Different Origins

	USA-Fla (1983-1987)	Ref. 4 (1971)	Our investigations (Ref.2) Spain	Italy	Israel
α-Pinene	0.45	0.61	0.54	0.52	0.50
Sabinene	0.26	0.13	0.26	0.40	0.30
Myrcene	1.70	2.0	1.85	1.80	1.87
Phellandrene	0.05	-	0.07	0.07	0.05
d-Limonene	95.65	92.86	95.59	95.24	94.34
Terpinolene	-	0.12	0.06	0.07	0.03
Total Terpenes	**98.11**	**95.72**	**98.56**	**98.30**	**97.27**
Octanal	0.32	0.16	0.15	0.13	0.30
Nonanal	0.04	0.17	0.07	0.08	0.05
Decanal	0.26	(0.73)	0.125	0.13	0.35
Undecanal	0.01	0.22	0.005	0.005	0.015
Dodecanal	0.06	0.10	0.02	0.015	0.055
Total Aliph. Ald.	**0.69**	**-**	**0.37**	**0.36**	**0.77**
Octanol	0.04	-	0.16	0.16	0.07
Octyl acetate	0.02	-	0.005	0.01	0.01
Citronellal	0.05	0.29	0.03	0.03	0.06
Neral	0.08	0.21	0.02	0.03	0.05
Geranial	0.11	0.18	0.04	0.05	0.08
Perillaldehyde	0.01	-	0.02	0.01	0.01
Total Terpene Ald.	**0.25**	**0.68**	**0.11**	**0.12**	**0.20**
Linalool	0.26	0.62	0.39	0.35	0.41
α-Terpineol	0.03	-	0.03	0.03	0.05
Nerol	-	-	0.005	0.01	0.01
Geraniol	-	-	0.005	0.02	0.02
Total Terpene Alc.	**0.29**	**-**	**0.43**	**0.43**	**0.49**
β-Caryophyllene	0.02	0.13	O.O3	0.04	0.02
β-Copaene	0.02	-	0.02	0.02	0.03
β-Farnesene	0.02	-	0.03	0.02	0.03
Valencene	0.06	0.22	0.08	0.10	0.10
δ-Cadinene	-	0.11	0.02	0.02	0.02
Total Sesquiterp.	**0.12**	**0.45**	**0.20**	**0.20**	**0.20**
β-Sinensal	0.04	0.07	0.01	0.02	0.04
α-Sinensal	0.02	0.06	0.005	0.01	0.025
Nootkatone	0.01	-	0.005	0.01	0.02

Table V. Quantitative Chemical Composition of Italian (Sicily) Sweet Orange Oils. Valentia-late Cultivated on Different Root Stocks (10 analyses, ref.11)

α-Thujene	0.003 - 0.005%
α-Pinene	0.416 - 0.454
Camphene	trace - 0.003
Sabinene	0.374 - 0.715
β-Pinene	0.020 - 0.042
Myrcene	1.641 - 1.693
α-Phellandrene	0.050 - 0.100
δ-3-Carene	0.008 - 0.047
Limonene	94.990 -95.590
γ-Terpinene	trace - 0.009
Terpinolene	0.001 - 0.015
Octanal	0.250 - 0.350
Nonanal	0.031 - 0.061
Decanal	0.205 - 0.327
Citronellal	0.039 - 0.060
Neral	0.060 - 0.081
Geranial	0.075 - 0.104
Octanol	trace - 0.008
Linalool	0.515 - 0.745
α-Terpineol	0.045 - 0.057
Nerol + Citronellol	0.005 - 0.025
Citronellyl acetate	trace - 0.002
Neryl acetate	trace - 0.007
Geranyl acetate	0.002 - 0.011
Caryophyllene	0.010 - 0.021
α-Humulene	trace - 0.006
Valencene	0.010 - 0.087
β-Bisabolene	0.010 - 0.018

A lot of work has been carried out to quantitate the aliphatic aldehydes in orange oil. Formerly the total carbonyl-content was determined, often calculated as decanal. Nowadays individual aldehydes are quantitated by gas chromatography on fused silica capillary columns with suitable stationary phases. Up to 1980 it was assumed that decanal was the most prominent aliphatic aldehyde in orange oil, and that octanal averages approximately 70% of the decanal-value.[5] By improved methods it is now known that octanal is the dominant aldehyde and that decanal approximates 80-90% of the octanal value.[11] Octanal and decanal together have been quantitated at 0.5-1.0 % in sweet orange oil. Nonanal, undecanal and dodecanal together have been found to total 0.1-0.2%, with dodecanal being the most dominant. Some straight chain unsaturated (aliphatic) aldehydes also have been detected in sweet orange oil. (E,E)-2,4-decadienal may be the most important.

In 1970 Lifshitz et al.[10] examined the concentration of aldehydes in Floridian and Californian orange oils. They found that Florida oils contained a higher concentration (1.51%) of aldehydes than Californian oils (1.165%) (see Table VI). A more thorough investigation of the quantitation of individual and total carbonyls in cold-pressed orange oils was carried out by Wilson and Shaw.[11] From their results it is clear that the Floridian oils Valencia late (1.51%) and mid-season (1.155%) contain higher concentrations of carbonyl compounds than Californian navel oil (0.665%) (see Table VI).

In 1974 Shaw and Coleman[12] studied the chemical composition of cold-pressed orange oils produced in early - (Hamlin and Parson Brown cultivars), mid- (Pineapple cul-

Table VI. Quantitative Composition of Carbonyl Compounds in Cold-pressed Orange Oils

	Ref. 11		Ref. 12		
	Florida %	Calif. %	Valencia late %	Mid-season %	California navel %
octanal	0.54	0.35	0.393-0.505	0.342-0.374	0.150-0.172
nonanal	0.09	0.06	0.069-0.075	0.057-0.060	0.022
decanal	0.63	0.57	0.375-0.415	0.277-0.338	0.131-0.142
undecanal	0.01	0.02			
dodecanal	0.08	0.09	0.080-0.083	0.055-0.067	0.030-0.034
aliph.ald.	1.35	1.09	0.867-1.073	0.731-0.849	0.333-0.370
citronellal	-	-	0.090-0.094	0.055-0.060	0.064-0.081
neral	0.02	0.015	0.072-0.073	0.064-0.065	0.045-0.062
geranial	0.14	0.06	0.120-0.180	0.113-0.114	0.080-0.104
perillaldehyde	-	-	0.033-0.040	0.029-0.031	0.013-0.017
terp. ald.	0.16	0.075	0.315-0.387	0.261-0.270	0.202-0.264
β-sinensal	-	-	0.056-0.081	0.047-0.048	0.019-0.026
α-sinensal	-	-	0.037-0.060	0.034	0.016-0.024
nootkatone	-	-	0.024-0.051	0.015-0.035	0.043-0.045
TOTAL CARBONYLS			1.51	1.155	0.665

Table VII. The Chemical Composition of Different Cultivars of US-Florida Cold Pressed Sweet Orange Oils (13)

	early season Hamlin Parson-Brown	mid-season Pineapple	late-season Valencia
α-Pinene	0.54	0.46-0.54	0.50-0.62
Myrcene	2.08	2.02-2.05	1.78-2.18
Limonene	95.37	94.87-95.20	94.71-95.24
Decanal	0.24	0.30-0.39	0.35-0.46
Dodecanal	0.03	0.04-0.06	0.05-0.07
Citronellal	0.10	0.10-0.12	0.12-0.20
Neral	0.06	0.05-0.08	0.05-0.09
Geranial	0.12	0.14-0.17	0.12-0.17
Perillaldehyde	0.02	0.02-0.03	0.02-0.03
Linalool	0.25	0.48-0.62	0.46-0.56
β-Elemene	0.05	0.05-0.06	0.04-0.06
β-Caryophyllene	0.04	0.07	0.07-0.09
β-Farnesene	0.01	0.02	0.02
Valencene	0.04	0.09-0.12	0.07-0.15
β-Sinensal	0.07	0.07	0.07-0.13
α-Sinensal	0.02	0.02-0.04	0.02-0.06

tivar) and late season (Valencia cultivar) (see Table VII). The total concentration of oxygenated compounds in early (0.81%), mid (1.42%) and late (1.51%) season oils have been found. It is a pity that the concentrations of octanal, nonanal and undecanal were not confirmed in this investigation.

The variation in the concentrations of the oxygenated constituents in orange oils may be due to:

- the existence of different cultivars
- ecological and climatological circumstances
- technical, mainly analytical, reasons.

It may be possible that the total concentrations of aldehydes in citrus oil, determined with classical (wet) methods are too high, whereas the calculation of total peak area percentages determined with modern gas chromatography is too low. According to Lawrence[6] the difference in oxygenated constituents between early- and mid/late season may be correlated with the finding that early-season oils possess a slightly lower sensorial impact than mid- or late-season oils.

Chemical Composition of Bitter Orange Oils

The botanical name of the bitter orange is *Citrus aurantium* L. ssp. amar. Engl. (family Rutaceae). From the

Table VIII. Chemical Composition of Bitter Orange Oils According to the Published Data

	A (1988)	B (1982)	C (1979)	D (1978)	E (1967)
α-Pinene	0.36-1.25	0.36-1.25		0.36-0.45	
β-Pinene	0.03-6.15	0.03-6.15	0.9-5.5	0.03-3.83	0.86-5.50
Sabinene	0.05-1.25	0.05-1.25	-	0.05-0.77	
Myrcene	1.90-2.10	1.49-2.10		1.49-1.72	1.60-10.90
d-Limonene	48.4-96.9	48.4-96.9	74-86	87.3-96.9	73.8-86.2
γ-Terpinene	0.07-8.76	0.07-8.26		0.07-5.99	
p-Cymene	0.83	tr.-0.83		tr.-0.83	
Decanal	0.41	tr.-0.41		tr.-0.72	
Citronellol	1.10	tr.-0.55		tr.-0.55	
Linalool	12.85	tr.-12.85		tr.-1.06	
Linalyl acetate	9.72	tr.-9.72		tr.-0.26	0 - 0.99
Bornyl acetate	0.15	tr.-0.15		tr.-0.15	
α-Terpineol	0.03-3.07	0.03-3.07	0.2-0.3	0.03-0.17	
Neral	1.75	tr.-1.75		tr.-0.12	
Geranial	2.58	tr.-2.58		tr.-0.31	
Nerol	0.30	tr.-0.24		tr.-0.06	0 - 1.08
Geraniol	0.52	tr.-0.52		tr.	0 - 0.48
Camphene	0.40-0.90	-	0.4-0.9		0.27-0.89
1,8-Cineole	0.80-8.10		0.8-8.1		0.77-8.90
Octanal	1.40-2.20		1.4-2.2		0.33-2.17
Nonanal	0.10-0.40		0.1-0.4		0.12-0.40
Citronellal	0.30-0.40		0.3-0.4		0.30-0.40
Citronellyl form.	0.10-1.10		0.1-1.1		0.08-1.08
Citronellyl acetate	0.20-0.60		0.2-0.6		0 -0.61
Isopulegol	0.30-0.40		0.3-0.4		tr.-0.41
Geranyl formate	0.30-0.60		0.3-0.6		tr.-0.57
Terpinen-4-ol	0.30-0.40		0.3-0.4		
Nootkatone	0.01		0.01		

A. is according to Swaine & Swaine[7] taken from Lawrence[6]
B. is according to Lawrence[6] taken from Ortiz et al.[17], including bergamote oil
C. is according to Shaw[5] taken from Maekawa et al.[16]
D. real data from Ortiz et al.[17] without bergamot oil,
E. real data from Maekawa et al.[16]

species *C. aurantium*, also called the sour orange group, over 30 subspecies, cultivars or varieties exist.[18] The subspecies bergamot and amara are the most important and from the latter the cultivar Seville is well-known.

Relatively little quantitative data on the chemical composition of bitter orange oils have been reported.[17-22] The publications of Maekawa[17] and Ortiz et al.[18] have been cited most[5-7] (See Table VIII). Misinterpretation of these publications can lead to very confusing citations. Swaine & Swaine[7] for example recently published the chemical composition of bitter orange oil according to a review of Lawrence,[6] which was partly according to a review of Shaw[5] and partly from the publication of Ortiz et al. Shaw in his review summarized five analyses from Maekawa. Lawrence[6] published the detailed analyses of Maekawa and at the same time the summarized results of Shaw that concern the same analyses.

Some mistakes occurred in the interpretation of the same figures. The second part of Table VIII by Swaine and

Table IX. Chemical Composition of Mediterranean Bitter Orange Oils According to Our Investigations (Ref. 21)

	SPAIN 1987	ITALY 1987
α-Thujene	0.001	0.016
α-Pinene	0.447	0.592
Camphene	0.005	0.010
β-Pinene	0.295	0.900
Myrcene	1.806	2.073
α-Phellandrene	0.019	0.015
Limonene	94.338	92.430
γ-Terpinene	0.121	0.103
Terpinolene	0.099	0.094
Total Monoterpenes	**96.85**	**96.83**
Octanal	0.130	0.239
Nonanal	0.052	0.106
Decanal	0.137	0.193
(E,Z)-2,4-decadienal	0.001	0.004
(E,E)-2,4-decadienal	0.005	0.006
Undecanal	0.010	0.010
Dodecanal	0.017	0.033
Tridecanal	0.005	0.011
Tetradecanal	0.020	0.029
Total aliph. aldehydes	**0.376**	**0.531**
Octanol	0.184	0.171
Octyl acetate	0.051	0.010
Decanol	0.009	0.010
Decyl acetate	0.022	0.022
Myrtenal	0.014	0.010
Citronellal	0.009	0.016
Neral	0.021	0.055
Geranial	0.034	0.090
Perillaldehyde	0.014	0.019
Total terpene aldehydes	**0.092**	**0.190**
Linalyl acetate	0.284	0.775
Linalool	0.152	0.371
Terpinen-4-ol	0.001	0.001
α-Terpineol	0.567	0.061
Nerol	0.005	0.010
Geraniol	0.010	0.015
Citronellol	0.001	0.001
Neryl acetate	0.026	0.033
Geranyl acetate	0.133	0.094
p-Mentha-1,8-dienyl-10 acet.	0.011	0.010
Carvone	0.001	0.001
Limonene oxides	0.011	0.010
Total sesquiterpenes	**0.280**	**0.180**
α-Sinensal	0.001	0.001
β-Sinensal	0.011	0.001
Nootkatone	0.082	0.029

Table X. The Chemical Composition of Seville Bitter Orange Oil 1984 - 1990 (7 samples)

	range of peak area percentages
α-Pinene	0.287 - 0.447
Camphene	0.001 - 0.011
Sabinene	0.124 - 0.150
β-Pinene	0.295 - 0.390
Myrcene	1.596 - 1.806
α-Phellandrene	0.001 - 0.006
Limonene	91.545 - 93.70
cis-Ocimene	0.001 - 0.005
trans-Ocimene	0.160 - 0.381
γ-Terpinene	0.001 - 0.011
Terpinolene	0.001 - 0.134
Octanal	0.041 - 0.150
Nonanal	0.010 - 0.052
Decanal	0.115 - 0.200
Undecanal	0.005 - 0.011
Dodecanal	0.015 - 0.036
Octanol	0.001 - 0.037
Octyl acetate	0.010 - 0.053
Decanol	0.005 - 0.017
Decyl acetate	0.005 - 0.038
Citronellal	0.001 - 0.009
Neral	0.005 - 0.022
Geranial	0.026 - 0.067
Perillaldehyde	0.005 - 0.019
Limonene oxides	0.001 - 0.024
Camphor	0.001 - 0.005
Carvone	0.005 - 0.024
Linalool	0.099 - 0.218
Terpinen-4-ol	0.001 - 0.005
α-Terpineol	0.269 - 2.935
Nerol	0.005 - 0.042
Geraniol	0.010 - 0.232
Linalyl acetate	0.192 - 0.817
α-Terpinyl acetate	0.005 - 0.034
Neryl acetate	0.019 - 0.049
Geranyl acetate	0.129 - 0.201
Limonyl-10 acetate	0.005 - 0.020
δ-Elemene	0.024 - 0.055
β-Elemene	0.005 - 0.025
β-Caryophyllene	0.086 - 0.144
α-Bisabolene	0.005 - 0.024
α-Humulene	0.025 - 0.043
Germacrene D	0.084 - 0.140
Nerolidol	0.096 - 0.230
Farnesols	0.005 - 0.020
Nootkatone	0.046 - 0.387
α-Selinenone	0.005 - 0.022
Osthol	0.018 - 0.270
Meranzin (2 isomers)	0.090 - 0.018

Swaine, according to the review of Lawrence, taken from a publication of Ortiz, et al., not only represents bitter orange oils, but also bergamot peel oil. That is the reason for the very low concentration of d-limonene (48.42%) and the higher concentration of linalool (12.85%) and linalyl acetate (9.72%).

Monoterpenoids

In 1971 Ziegler[4] mentioned that contrary to sweet orange oil, the bitter orange oil, among its terpenes contains also β-pinene, γ-terpinene and p-cymene. Moreover he wrote that bitter orange oil amongst the aromatic compounds contains linalyl acetate and some linalool, and that the former is particularly characteristic and often missing in adulterated products. Shaw,[5] in 1979, mentioned that relatively little quantitative data on bitter orange oil has been reported, and that it appears that bitter orange oil contains higher quantities of the following compounds than sweet orange oil: myrcene and α-pinene (in one sample), nonanal, octanal, citronellyl acetate and formate, geranyl formate, linalyl acetate and 1,8-cineol.

Maekawa et al.[17] found 0.77-8.9% of 1,8-cineol in their bitter orange oils and mentioned that this was an organoleptic characteristic constituent of bitter orange oils. However, up to now, nobody else has detected this compound in bitter orange oils. The chemical composition of Spanish and Italian bitter orange oil has been studied in detail.[2] (See Table IX). The difference in the concentration of some monoterpene hydrocarbons and oxygenated compounds may be due to differences in climatological circumstances.

Seven samples of Seville bitter orange oils have been analyzed. The ranges of the concentrations of the volatile constituents are presented in Table X. As bitter orange peels

Table XI. Chemical Composition of Steam Distilled Bitter Orange Oils (Ref. 20)

	Setting Fruits	Immature Fruits	Ripening Fruits
α-Pinene	0.38	0.43	0.55
Camphene	0.01	-	-
β-Pinene	2.38	0.14	0.11
Myrcene	1.69	1.82	2.25
Limonene	46.19	95.45	92.68
Ocimene	10.01	0.28	-
α-Terpinene	0.16	0.13	-
para-Cymene	0.01	-	-
Monoterp. hydrocarbons	**60.83**	**98.35**	**95.59**
Epoxylinalool	1.30	0.93	-
Linalool	25.23	0.38	-
Linalyl acetate	4.50	0.03	0.12
α-Terpineol	2.63	0.21	0.16
Neryl acetate	1.35	0.10	0.41
Geranyl acetate	1.33	0.13	-
Monoterp. O-derivatives	**36.34**	**1.78**	**0.69**
Decanal	-	-	1.63
Total aldehydes (as C-10)	-	-	2.2

are rather acidic (pH 2.5-4) some constituents partly decompose during isolation.[21,22]

It has been long known that the oil isolated from setting bitter orange fruits, so-called petitgrains or orangettes, contain over 50% linalool and linalyle acetate, whereas the peel oil from ripe fruits contains more than 90% limonene (see Table XI). It may be concluded that during ripening the linalyl derivatives are converted into limonene.

Aliphatic Compounds

Thirty aliphatic compounds have been detected in bitter orange oil,[20,21] among which 20 saturated and unsaturated straight chain aldehydes appeared in a total concentration of 0.4-0.7%. These aliphatic aldehydes are important for the organoleptic quality of the oil. It was found that the concentration of the aldehyde increases during ripening, from 0.5-0.7%.

Chemical Composition of Lemon Oils

The botanical name for the lemon tree is *Citrus limonum* (L.) Burm. (family Rutaceae). The cultivars Eureka and Lisbon are the most important varieties. There are several quantitative analyses of the chemical composition of cold-pressed lemon oil.[1-8, 23-26] The most complete analyses have been carried out by Staroscik and Wilson (see Table XII).

Table XII. Chemical Composition of U.S. Cold-pressed Lemon Oils from California and Arizona (Ref. 25, 26)

	USA	California (coastal)			Arizona (desert-like)		
	average	early	mid	late	early	mid	late
α-Thujene	0.38	0.45	0.44	0.44	0.34	0.36	0.35
α-Pinene	1.72	2.11	2.14	2.15	1.41	1.50	1.49
Camphene	0.05	0.07	0.08	0.07	0.03	0.03	0.03
Sabinene	1.65	2.48	2.61	2.68	1.09	1.11	1.17
β-Pinene	10.13	5.62	17.29	6.58	5.38	6.07	6.44
Myrcene	1.50	1.28	.22	1.33	1.77	1.74	1.74
α-Phellandrene	0.04	0.04	0.04	0.04	0.04	0.04	0.04
δ-3-Carene	0.004	0.004	0.004	0.006	tr.	tr.	tr.
α-Terpinene	0.32	0.32	0.32	0.28	0.26	0.27	0.26
p-Cymene	0.04	0.03	0.03	0.03	0.02	0.02	0.03
Limonene	68.72	60.36	58.47	59.92	76.48	75.74	76.30
γ-Terpinene	8.55	9.78	9.74	9.39	7.80	8.03	7.90
Terpinolene	0.39	0.39	0.38	0.36	0.37	0.36	0.35
Terp. hydrocarbons	**93.53**	**92.97**	**92.76**	**93.28**	**94.99**	**95.27**	**95.10**
Heptanal	-	0.004	0.004	0.004	tr.	tr.	tr.
Octanal	0.07	0.14	0.14	0.10	0.04	0.09	0.09
Nonanal	0.12	0.21	0.27	0.21	0.06	0.06	0.06
Decanal	0.04	0.07	0.07	0.05	0.02	0.05	0.06
Dodecanal	0.02	0.03	0.03	0.02	0.007	0.01	0.02
Aliph. aldehydes	**0.25**	**0.454**	**0.514**	**0.384**	**0.127**	**0.21**	**0.23**
Methylheptenone	0.002	tr.	tr.	tr.	tr.	tr.	tr.
Octanol	0.01	0.02	0.02	0.03	0.03	0.01	0.01
Octyl acetate	0.004	0.006	0.007	0.004	tr.	0.002	0.003
Nonyl acetate	0.006	0.02	0.02	0.01	0.002	0.002	0.002
Citronellal	0.07	0.09	0.08	0.08	0.06	0.06	0.06
Neral	0.76	0.74	0.89	1.07	0.84	0.54	0.41
Geranial	1.22	1.21	1.44	1.70	1.28	0.88	0.68
Terp. aldehydes	**2.05**	**2.04**	**2.41**	**2.85**	**2.18**	**1.48**	**1.15**
Carvone	0.007	0.006	0.008	0.006	0.007	0.007	0.007
Linalool	0.14	0.13	0.15	0.21	0.20	0.12	0.09
Terpinen-4-ol	0.14	0.07	0.16	0.10	0.06	0.06	0.05
α-Terpineol	0.22	0.17	0.27	0.26	0.23	0.13	0.09
Nerol	0.04	0.02	0.04	0.04	0.05	0.02	0.02
Geraniol	0.04	0.03	0.05	0.04	0.02	0.02	0.03
Citronellyl acetate	0.02	0.03	0.02	0.01	0.01	0.03	0.04
Neryl acetate	0.50	0.51	0.57	0.60	0.32	0.51	0.55
Geranyl acetate	0.43	0.61	0.72	0.61	0.15	0.21	0.24
Terp.alc./esters	**1.53**	**1.57**	**1.98**	**1.87**	**1.04**	**1.10**	**1.07**
Caryophyllene	0.24	0.23	0.23	0.26	0.27	0.22	0.21
tr.α-Bergamotene	0.37	0.40	0.40	0.35	0.34	0.42	0.41
α-Humulene	0.02	0.02	0.02	0.02	0.02	0.02	0.02
β-Bisabolene	0.56	0.62	0.62	0.53	0.50	0.62	0.61
Sesquiterpenes	**1.19**	**1.26**	**1.27**	**1.16**	**1.13**	**1.28**	**1.25**

Table XIII. Total Monoterpenes in U.S. Cold-pressed Lemon Oils from California and Arizona (Ref. 23)

	California	Arizona
α-Pinene	1.8%	2.0%
β-Pinene	13.0	6.5
Sabinene	1.9	1.0
Myrcene	1.1	2.1
Limonene	72.2	79.8
γ-Terpinene	10.0	8.6

In 1962 Ikeda et al.[23] noticed the variation in the concentration of the individual monoterpene hydrocarbons in cold-pressed lemon oil from different areas in the USA. (see Table XIII). Ziegler[4] mentioned that lemon oil contains a certain quantity of β-pinene, and that during storage the γ-terpinene content decreases, whereas the *p*-cymene content increases.

Shaw[5] stated that the quantitative composition of lemon oil differs substantially from that of orange, grapefruit, and mandarin. He wrote that limonene is still the major hydrocarbon, but generally in lower quantity than in other oils. On the other hand, certain other hydrocarbons, especially β-pinene and γ-terpinene, are generally found in much greater quantities. However, there is a wide variation in values reported for all three of these monoterpenes, which are the main components of most lemon oils.

Nowadays if one makes a comparison of citrus oils with respect to their monoterpene hydrocarbon content, especially with regard to the concentration of limonene, one arrives at two groups; the first group with sweet orange, bitter orange, grapefruit and tangerine oils with limonene contents over 90%; and a second group with lemon, mandarin and lime, with limonene-contents of 40-80% and higher concentrations of γ-terpinene and β-pinene. It has been reported that there exists a relationship between the concentration of certain components and its optical rotation in lemon oil. Ziegler[4] mentioned that a relationship was found between optical rotation and the contents of citral and aldehydes. Staroscik and Wilson[25] found in coastal and desert lemon oils the variation in the relative amounts of β-pinene and limonene as most apparent. These two hydrocarbons are the main contributors to the optical rotation displayed in lemon oil. They wrote that the characteristically lower angular rotations of coastal lemon oils are undoubtedly due to much greater percentage of ß-pinene in those oils. The optical rotation and concentration of some important constituents according to Staroscik & Wilson are shown below:

	Coastal			Desert		
	early-	mid- Season	late-	early-	mid- Season	late-
optical rotation	+54.8	+51.0	+53.8	+74.5	+73.9	+73.8
β-pinene	15.62	17.29	16.58	5.38	6.07	6.44
limonene	60.36	58.47	59.92	76.48	75.74	76.30
citral	1.95	2.33	2.77	2.12	1.42	1.09
total aldehydes	**2.49**	**3.07**	**3.23**	**2.31**	**1.72**	**1.41**

Taking into account the optical rotation of pure *d*-limonene, + 126, and of pure δ-β-pinene, + 22, one may arrive at the following conclusions:

- the lower rotation of coastal lemon oils are due to the lower concentration of *d*-limonene and as a consequence of the higher concentration of δ-β-pinene, according to Staroscik and Wilson.
- there is a relationship between optical rotation, and between citral and total aldehyde-content, especially in mid- and late-season lemon oils in such a way that a lower optical rotation, due to a lower limonene-content, corresponds with a higher citral and aldehyde content.

According to Staroscik and Wilson[22] the monoterpene

Table XIV. Chemical Composition of Mediterranean Lemon Oils[2]

	Italy (1987)		Israel	Spain (Andalucia)		
	Sicily	Calabria	(1988)	(1987)	(1988)	(1990)(5x)
α-Thujene	0.24	0.42	0.37	0.35	0.40	0.27-0.43
α-Pinene	2.08	1.89	1.65	1.58	1.78	1.23-1.94
Camphene	0.21	0.06	0.05	0.07	0.07	0.04-0.07
Sabinene	1.70	1.50	1.52	1.29	1.77	1.21-1.93
β-Pinene	12.17	13.20	8.57	8.91	11.08	9.77-12.41
Myrcene	1.18	1.64	1.63	1.93	1.52	1.34-1.55
α-Phellandrene	0.10	0.07	0.04	0.10	0.10	0.01-0.10
δ-3-Carene	0.07	0.01	0.01	0.01	0.01	0.01
α-Terpinene	0.17	0.18	0.16	0.17	0.21	0.19-0.20
p-Cymene	0.10	0.01	0.20	0.07	0.01	0.18-0.58
Limonene	67.58	65.57	71.82	70.36	67.21	65.06-67.65
trans-Ocimene	0.01	0.28	0.14	0.59	0.59	0.10-0.60
γ-Terpinene	6.98	9.37	7.83	8.72	9.47	9.67-10.55
Terpinolene	0.39	0.38	0.34	0.46	0.50	0.41-0.46
Terpene hydrocarb.	92.33		94.31	94.42		
Octanal	0.17	0.075	0.055	0.09	0.07	0.03-0.06
Nonanal	0.09	0.09	0.11	0.12	0.16	0.08-0.13
Decanal	0.055	0.05	0.035	0.03	0.03	0.05-0.07
Undecanal	0.03	0.01	0.02	0.015	0.01	0.01-0.02
Dodecanal	0.01	0.025	0.005	0.03	0.02	0.01
Octanol	0.02	0.02	0.02	0.03	0.03	0.01-0.03
Octyl acetate	0.01	0.01	0.01	0.01	0.01	005-0.01
Nonanol	0.01	0.01	0.01	0.01	0.01	0.005
Nonyl acetate	0.01	0.01	0.01	0.01	0.01	0.01-0.02
Decyl acetate	0.01	0.01	0.01	0.01	0.01	0.005-0.01
Citronellal	0.07	0.09	0.08	0.09	0.12	0.08-0.14
Neral	1.23	0.71	0.74	0.57	0.88	0.54-1.06
Geranial	1.68	1.21	1.18	0.95	1.57	0.86-1.77
Perillaldehyde	0.05	0.05	0.02	0.04	0.02	0.02-0.03
Linalool	0.85	0.08	0.11	0.11	0.08	0.08-0.12
Terpinen-4-ol	0.03	0.03	0.03	0.02	0.03	0.06-0.10
α-Terpineol	0.18	0.15	0.17	0.17	0.10	0.41-0.84
Citronellol	0.02	0.03	0.02	0.01	0.01	0.01
Nerol	0.07	0.06	0.04	0.02	0.02	0.01-0.16
Geraniol	0.27	0.11	0.04	0.05	0.05	0.01-0.12
Citronellyl acetate	0.02	0.03	0.01	0.02	0.01	0.01-0.03
Neryl acetate	0.35	0.42	0.32	0.26	0.27	0.50-0.63
Geranyl acetate	0.23	0.55	0.20	0.26	0.25	0.47-0.70
δ-Elemene	0.01	0.01	0.02	0.01	0.01	0.01-0.03
cis-α-Bergamot.	0.02	0.03	0.03	0.04	0.04	0.03-0.04
Caryophyllene	0.13	0.20	0.24	0.20	0.18	0.20-0.28
tr.-α-Bergamot.	0.20	0.40	0.39	0.42	0.39	0.46-0.53
cis-β-Farnesene	0.02	0.03	0.03	0.04	0.02	0.04-0.06
α-Humulene	0.01	0.03	0.02	0.02	0.03	0.03-0.04
tr.β-Farnesene	0.03	0.04	0.02	0.05	0.03	0.03-0.04
Valencene	0.03	0.09	0.02	0.06	0.08	0.03-0.16
β-Bisabolene	0.31	0.64	0.66	0.66	0.65	0.68-1.00
Nootkatone	0.01	0.03	0.005	0.02	0.02	0.01-0.03

hydrocarbon fraction can vary a lot in the concentration of the individual monoterpenes, for example:

- limonene from 58-77%
- α–pinene from 2.2-1.4%
- β-pinene from 17.3- 5.4%
- sabinene from 2.7-1.1%

These fluctuations are mainly due to climatological influences.

The concentrations of the aliphatic and monoterpenoid aldehydes and the alcohols and esters are important for the organoleptic quality of cold-pressed lemon oil. As can be seen in Table X also, the concentrations of these groups of compounds will vary, depending on the growing area of the lemons.

Formacek and Kubeczka[8] showed that a selected oil of lemon, possessing a decomposed or rancid aroma note, contained:

α-pinene	1.71%
camphene	0.09
β-pinene	6.48
myrcene	0.09
limonene	54.92
p-cymene	9.66
monoterpene hydrocarbons	72.95
1-octen-3-ol	0.19
linalool	0.30
carvone	2.01

It is generally known that lemon oil deteriorates. This decomposition may be due to the acidity (of the juice) and the sensitivity of aldehydes towards oxygen. Shaw[5] wrote that terpinen-4-ol and α-terpineol levels might be expected to vary considerably in lemon oil because the strongly acidic juice can catalyze the hydration of limonene and other monoterpenes to these two alcohols if the oil comes in contact with the juice during processing. It may, however, be questioned whether limonene is so easily hydrated.

Several studies have been carried out on the deterioration of lemon flavor.[27-30] Citral, one of the significant components of lemon oil, cyclizes to give *p*-cymene and α, *p*-dimethylstyrene. Clark et al.[27] and McHale et al.[28] reported that *p*-menthadiene-8-ols and *p*-menthen-1,8-diols were major products in the early stages of the decomposition

Table XV. Chemical Composition of Italian Lemon Oils (Different GC- and NMR-C-13 Analyses)

	GC-NMR C-13 (Ref. 8)	Polar-GC	Non-polar GC (Ref. 9)
α-Thujene		a	0.4
α-Pinene	2.06	2.2	1.8
Camphene	0.06	0.1	0.1
β-Pinene	12.27	12.2	12.2
Sabinene	1.92	1.9	1.9
Myrcene	1.39	1.5	a
α-Terpinene	0.10	0.2	
(+ *p*-Cymene)			0.5
Limonene	68.36	66.5	67.0
β-Phellandrene	0.48	0.3	a
cis-β-Ocimene	0.07	-	-
γ-Terpinene	7.39	8.8	8.6
trans-β-Ocimene	0.13	-	-
p-Cymene	0.98	0.3	
Terpinolene	0.21	0.4	0.4
Nonanal	-	0.1	a
Citronellal	-	0.1	0.1
Neral	-	0.9	
(+ nerol)			1.1
Geranial		-	
(+ Bisabolene)		2.0	
(+ Geraniol)			1.8
Linalool	0.21	0.2	a
α-Terpineol	0.21	0.2	0.2
Nerol	-	0.1	
Geraniol	0.05	0.1	
Neryl acetate	-	0.7	0.5
Geranyl acetate	0.44	0.7	0.4
α-Bergamotene	-	0.4	0.4
β-Caryophyllene	-	0.3	0.2
β-Bisabolene	-	-	0.5

a= peaks not separated

Table XVI. Comparison of Mandarin and Tangerine Oils (Ref. 32)

	Italy Mandarin	US /Florida Tangerine
α-Pinene	3.93	1.00
Camphene (& unknown)	0.02	0.01
β–Pinene (& unknown)	2.16	0.44
Myrcene	1.80	2.03
α-Phellandrene	0.03	0.03
α-Terpinene	0.42	0.0
d-Limonene	67.10	91.23
γ-Terpinene	20.14	3.09
para-Cymene	1.24	0.28
Terpinolene	0.89	0.13
Octanal	0.10	0.10
Nonanal (& unknown)	0.01	0.02
Decanal	0.03	0.10
Dodecanal	0.01	0.02
(Z)-3-Hexenol	-	tr.
Heptanol	0.01	tr.
Nonanol & Caryophyllene	0.07	0.02
1,8-Cineole (tent.)	0.54	0.63
Methyl heptenone	-	tr.
Sabinene hydr.(& unkn)	0.02	0.01
Citronellal	0.01	0.04
Linalool	0.13	0.62
Decyl acetate	0.01	0.03
Neral & Terpineol	0.15	0.05
Neryl acetate	0.01	0.03
Geranyl acetate (& unkn)	0.10	0.05
Carvone & Nerol	0.01	0.03
Geraniol	tr.	tr.
trans-Carveol	tr.	0.01
Perillaldehyde	0.04	0.03
cis-Carveol	tr.	tr.
Benzyl alcohol	0.01	tr.
Thymol	0.03	0.03
N-Me,Me anthranilate	0.33	-
α-Sinensal	0.11	0.07

Table XVII. Chemical Composition of European Mandarin Oils

	Ref. 31 (1963)	Ref. 4 (1971)	Ref. 34 (1984)	Ref. 33 (1987)
α-Thujene	0.46	-	0.76 - 0.96	-
α-Pinene	2.47	1 - 4	2.12 - 2.54	3.31 - 3.47
Myrcene	1.19	1 - 4	1.69 - 1.77	1.75 - 1.91
Camphene	0.37	<1	0.02	<0.01
Sabinene	-	-	-	<0.01
β-Pinene	1.28	1 - 4	1.25 - 1.82	1.57 - 1.84
α-Terpinene	-	-	-	0.41 - 0.51
p-Cymene	8.16	4 - 10	-	0.37 - 0.45
Limonene	67.72	>10	67.92 -74.00	66.00 -72.27
γ-Terpinene	9.14	>10	16.78 -20.87	17.39 -22.70
Terpinolene	0.57	<1	0.76 - 0.94	0.89 - 1.04
Octanal	0.04	<1	0.10 - 0.23	0.05
Nonanal	-	-	0.02 - 0.03	<0.01
Decanal	0.04	<1	0.06 - 0.10	0.06 - 0.07
Undecanal	<0.01	<1	-	-
Dodecanal	0.01	<1	-	-
t.2-Nonenal	-	-	-	<0.01
t.2-Decenal	-	-	-	<0.01
t.2,c.4-Decadienal	-	-	-	<0.01
t.2,c.4-Decadienal	-	-	-	<0.01
2-Alkenal C-11/C-16	-	-	-	<0.01
Heptanol	0.02	+	-	<0.01
Octanol	0.09	+	<0.01	<0.01
Nonanol	-	-	-	<0.01
Decanol	0.04	-	-	<0.01
Decyl acetate	<0.01	-	-	-
Citronellal	-	-	0.02 - 0.04	<0.01
Neral	-	-	0.01 - 0.02	<0.01
Geranial	-	-	0.03 - 0.06	<0.01
Perillaldehyde	0.05	-	-	0.01 - 0.05
Carvone	0.03	<1	-	<0.01
cis-Sabinene hydrate	0.06	-	-	0.06 - 0.07
Linalool	0.25	<1	0.05 - 0.16	0.05 - 0.16
trans-Sabinene hydr.	0.11	-	-	<0.01
Citronellol	0.03	-	0.01 - 0.03	<0.01
Nerol	0.05	<1	-	<0.01
Geraniol	0.01	<1	-	<0.01
Terpinen-4-ol	0.11	-	0.02 - 0.06	0.05 - 0.06
α-Terpineol	1.11	<1	0.04 - 0.20	0.20 - 0.25
trans-Carveol	0.04	-	-	<0.01
cis-Carveol	0.02	-	-	<0.01
γ-isoGeraniol	-	-	-	<0.01
p-Cymen-8-ol	-	-	-	<0.01
Geranyl acetate	<0.01	<1	-	<0.01
Benzyl alcohol	0.01	-	-	-
p-Cymen-8-ol	0.03	-	-	<0.01
Thymol	0.08	-	0.01 - 0.08	0.07 - 0.08
N-Me,Me anthranilate	0.85	<1	0.31 - 0.50	0.38 - 0.43
α-Ylangene	0.01	-	-	-
β-Ylangene	-	<1	-	-
Caryophyllene	0.02	<1	0.07 - 0.11	0.06
Longifolene	0.01	-	0.09 - 0.22	-
γ-Selinene	0.01	-	-	-
α-Selinene	0.02	-	-	<0.01
α-Copaene	-	-	-	<0.01
β-Copaene	-	<1	-	-
β-Elemene	-	<1	-	-
Humulenes	-	<1	0.01	<0.01
Cadinene	-	<1	-	-
Farnesene	-	-	-	0.06-0.12
β-Bisabolene	-	-	-	<0.01

reaction.[30] Apart from the decomposition of citral (neral/geranial) the formation of other products, such as α-fenchol from β-pinene and *p*-cresol from citral, are important for the deterioration of the lemon flavor.[30]

Chemical Composition of Mandarin and Tangerine Oils

The botanical name of European mandarin is *Citrus deliciosa* Tenore; syn. *Citrus reticulata* Blanco, variety mandarin; *citrus nobilis* var. deliciosa Swingle mandarin.

The American tangerine is restricted to a class of mandarines having a deep red color characteristic of the variety Dancy. Botanical names of the tangerine are *Citrus nobilis* var. deliciosa Swingle, vareity tangerine, or *Citrus reticulata* Blanco var. tangerine.

Although the botanical origin of the mandarin and tangerine may be quite similar, the chemical compositions of their essential oils are quite different (see table XVI).

In 1963 Kugler and Kovats [31] made a thorough quantitative analysis of Mandarin peel oil (see Table XVII). They quantitated 46 components, from which thymol and N-

Table XVIII. Chemical Composition of Italian (Sicily) and Spanish (Andalucia) Mandarin Oils

	Italy	Spain
α-Thujene	0.68	0.57
α-Pinene	2.39	1.75
Camphene	0.02	0.02
Sabinene	0.22	0.21
β-Pinene	1.67	1.15
Myrcene	1.86	1.86
α-Phellandrene	0.05	0.05
δ-3-Carene	0.01	0.01
α-Terpinene	0.08	0.05
p-Cymene	0.25	0.13
Limonene	71.61	77.14
trans-β-Ocimene	0.01	0.01
γ-Terpinene	18.54	13.74
Terpinolene	0.86	0.62
Octanal	0.17	0.22
Nonanal	0.065	0.07
Decanal	0.07	0.06
Undecanal	0.005	0.005
Dodecanal	0.01	0.01
Citronellal	0.02	0.01
Neral	0.005	0.025
Geranial	0.01	0.04
Perillaldehyde	0.005	0.01
Linalool	0.10	0.16
Terpinen-4-ol	0.055	0.05
α-Terpineol	0.16	0.20
Nerol	0.005	0.005
Geraniol	0.01	0.007
Thymol	0.02	0.11
N-Me,Me anthranilate	0.15	0.28
α-Sinensal	0.20	0.19
Caryophyllene	0.10	0.09
α-Bisabolene	0.005	0.005
α-Humulene	0.015	0.015
Valencene	0.18	0.26
β-Bisabolene	0.005	0.02

Table XIX. Chemical Composition of U.S. Tangerine Oils

α-Pinene	0.62 - 0.99%
Camphene	0.014 - 0.020
β-Pinene	0.17
Myrcene	2.30
α-Phellandrene	0.03 - 0.06
β-Phellandrene	0.39 - 0.43
δ-3-Carene	0.004
α-Terpinene	0.08 - 0.094
p-Cymene	0.35 - 0.82
Limonene	88.30 - 93.60
γ-Terpinene	1.74 - 3.75
Linalool	0.87
α-Terpineol	0.06
Hexanal	<0.01
Octanal	0.23 - 0.50
Nonanal	0.06 - 0.08
Decanal	0.16 - 0.24
(E,E)-2,4,-Decadienal	0.05
Dodecanal	0.043 - 0.135
Tetradecanal	0.05
Citronellal	0.08 - 0.13
Neral	0.01- 0.06
Geranial	0.015 - 0.07
Perillaldehyde	0.05 - 0.10
α-Sinensal	0.18 - 0.26
N-Methyl methyl anthranilate	0.072
Thymol	0.022 - 0.04
Thymyl methyl ether	0.09

methyl methyl anthranilate were noted as importnt for the mandarin flavor. According to their analysis the main hydrocarbons were limonene (67.72%), γ-terpinene (9.14%) and *p*-cymene (8.16%). Ziegler[4] in 1971, also mentioned that limonene, γ-terpinene (>10%) and *p*-cymene (4-10%) were the main constituents of mandarin oil (also in fresh oils). In 1979 Shaw[5] wrote that according to published data the major component in mandarin oil, *d*-limonene, varies from 65-94%. More recent analysis[2,33,34] (see Table XVIII) show that in European mandarin oils:

a. limonene content can vary between 65 and 80%;

b. γ-terpinene is present in concentrations of 10-20%;

c. p-cymene-content is below 1%.

Mandarin oils, which contain higher concentrations of *p*-cymene, are probably very deteriorated. Thirteen sesquiterpene hydrocarbons have been detected in mandarin oils. It appears strange that Kugler & Kovats[31] found longifolene in mandarin oil, this component was the most important sesquiterpene in the oil according to Dugo et al.[34] This compound, however, probably is an artefact, because in more recent studies it has not been found. The chemical composition of U.S. tangerine oil is presented in Table XIX.

The Chemical Composition of Grapefruit Oils

The botanical name for grapefruit is *Citrus paradisi* L. Some important varieties are Duncan and Marsh seedless, which give colorless oils (see Table XX). An Israeli variety affords a pink oil (see Table XXI)

Wilson & Shaw[35,36] and Myers and Lee[37] studied the chemical composition of USA grapefruit oils in detail (Table XX). From this Table it is interesting to notice the following aspects:

- the difference of the analysis by gas chromatography on a packed and capillary column,
- the influence of the nonvolatiles (7.5%) on the complete analysis,
- the anomalies in the different analyses.

The most important anomaly in the analyses is the variation in the concentration of the monoterpene hydrocarbons. A great deal of this variation can be explained by the

Table XX. Chemical Composition of USA Grapefruit Oils

	Ref. 35 1978 volatile oil	Ref. 35 1978 total oil (a,b)	Ref. 36 1980 (a,c)	Ref. 37 1988
α-Pinene	0.44	0.49	0.39	0.38
β-Pinene			0.04	0.02
Sabinene			1.04	0.42
Myrcene	1.84	2.12	3.41	1.37
Limonene	94.35	85.60	83.66	83.40
γ-Terpinene			0.12	0.01
p-Cymene			-	0.02
Monoterpene hydrocarbons	**96.63**	**88.21**	**88.66**	**85.62**
cis-Limonene oxide		-	0.09	-
trans-Limonene oxide		-	0.05	-
Octanal		0.71	0.81	0.62
Nonanal	0.10	0.04	0.14	0.07
Decanal	0.61	0.60	0.49	0.40
Dodecanal		-	0.21	0.02
Citronellal	0.16	0.14	0.13	0.09
Neral		-	0.07	0.043
Geranial	0.12	0.11	0.08	0.06
Perillaldehyde	0.04	0.2	0.04	-
Carvone		-	0.02	-
Octanol	-	-	0.04	-
Octyl acetate	-	0.09	0.05	-
Decyl acetate	0.22	0.15	-	-
Linalool	0.27	0.30	0.13	0.10
α-Terpineol	-	-	0.04	0.04
Citronellyl acetate	+	+	0.04	-
Neryl acetate	0.18	0.22	0.02	-
Geranyl acetate	+	+	0.04	-
α-Copaene	0.07	0.06	0.07	-
β-Copaene	0.10	0.01	0.02	-
β-Elemene	0.09	0.06	0.06	-
Caryophyllene	0.29	0.25	0.31	0.24
Humulene	-	0.07	-	
δ-Cadinene	0.09	0.11	0.07	-
Elemol	0.07	0.04	0.04	-
Nootkatone	n.d.	n.d.	0.03	0.1

a. corrected for 7.5% nonvolatiles
b. packed GC-column
c. capillary GC-column

Table XXI. Chemical Composition of Israeli Grapefruit Oil

	Peak area percentages	
	Normal(1988)	**Pink(1988)**
α-Thujene	0.011	0.008
α-Pinene	0.586	0.527
Camphene	0.004	0.004
Sabinene	0.385	0.407
β-Pinene	0.259	0.148
Myrcene	1.974	1.833
α-Phellandrene	0.037	0.036
δ-3-Carene	0.001	0.012
α-Terpinene	0.004	0.003
para-Cymene	0.044	0.020
Limonene	92.995	93.806
trans-β-Ocimene	0.142	0.158
γ-Terpinene	0.161	0.096
Terpinolene	0.018	0.013
Monoterpene hydrocarbons	**96.621**	**97.071**
Octanal	0.288	0.316
Nonanal	0.049	0.014
Decanal	0.273	0.251
(E,Z)-2,4-Decadienal	0.002	0.004
(E,E)-2,4-Decadienal	0.001	0.002
Undecanal	0.011	0.011
Dodecanal	0.024	0.022
Aliphatic aldehydes	**0.647**	**0.651**
Octanol	0.023	0.036
Octyl acetate	0.035	0.030
Decanol	0.002	0.001
Decyl acetate	0.105	0.092
Citronellal	0.073	0.050
Neral	0.046	0.041
Geranial	0.082	0.075
Perillaldehyde	0.015	0.014
Carvone	0.009	0.013
Linalool	0.088	0.096
Terpinen-4-ol	0.002	0.002
α-Terpineol	0.037	0.038
Nerol	0.003	0.004
Geraniol	0.005	0.003
Citronellol	0.006	0.004
Neryl acetate	0.023	0.016
Geranyl acetate	0.070	0.062
α-Terpinyl acetate	0.009	0.007
Citronellyl acetate	0.014	0.011
1,8-Menthadienyl acetate	0.006	0.005
Perillene	0.004	0.005
cis/trans-Limonene oxides	0.020	0.018
β-Elemene	0.088	0.076
Caryophyllene	0.312	0.273
trans-α-Bergamotene	0.010	0.004
β-Farnesene	0.009	0.008
α-Humulene	0.040	0.037
β-Copaene	0.063	0.056
β-Bisabolene	0.045	0.032
δ-Cadinene	0.095	0.085
β-Sinensal	0.011	0.010
α-Sinensal	0.003	0.003
Nootkatone	0.300	0.144

Table XXII. Carbonyl Compounds in Grapefruit Oils

	Wilson & Shaw (1984)		Israeli (1988)	
	1	2	Normal	Pink
Octanal	0.520	0.466	0.288	0.316
Nonanal	0.081	0.072	0.049	0.045
Decanal	0.421	0.395	0.273	0.251
Undecanal	-	-	0.011	0.011
Dodecanal	0.050	0.048	0.024	0.022
Citronellal	0.091	0.077	0.073	0.050
Neral	0.040	0.046	0.046	0.041
Geranial	0.066	0.087	0.082	0.075
Perillaldehyde	0.018	0.024	0.015	0.014
β-Sinensal	0.018	0.027	0.011	0.010
α-Sinensal	-	-	0.003	0.003
Nootkatone	0.237	0.147	0.300	0.144
Total	1.54	1.39	1.175	0.982

Table XXIII.Comparison of Volatile Compounds in Mexican and West Indian Lime Oils (Ref. 39)

	Mexican		West Indian	
	c.p.	dist.	c.p.	dist.
α-Thujene	0.55	-	0.54	-
α-Pinene	3.72	1.14	2.37	1.69
Camphene	0.18	0.75	0.17	0.37
β-Pinene	23.81	1.75	24.23	9.49
Myrcene	2.10	1.38	1.40	0.86
α-Phellandrene	-	tr.	-	tr.
p-cymene	-	0.59	-	0.21
d-Limonene	34.30	49.20	44.17	47.25
γ-Terpinene	14.00	8.42	11.88	8.86
Terpinolene	0.76	9.00	0.83	7.24
Nonane	0.04	0.04	0.02	0.02
tert.Pentanol	tr.	tr.	tr.	tr.
2-Methyl-3-butenol-2	-	tr.	tr.	tr.
cis-3-Hexenol	-	tr.	tr.	tr.
Octanol	tr.	tr.	tr.	tr.
Decanol	tr.	tr.	tr.	tr.
Decanal	0.71	-	0.48	-
Linalool	0.31	0.18	0.25	0.12
α-Fenchol	-	0.71	-	0.32
cis-β-Terpineol	-	0.81	-	0.26
trans-β-Terpineol	-	tr.	-	tr.
Terpinene-4-ol	0.53	1.75	0.32	2.39
Geraniol	tr.	tr.	tr.	tr.
Thymol	tr.	tr.	tr.	tr.
Neryl acetate	0.16	0.03	0.07	0.04
Geranyl acetate	0.36	0.10	0.16	0.56
1,4-Cineole	-	1.92	-	0.21
1,8-Cineole	0.35	0.74	0.26	0.29
α-Elemene	0.77	0.07	0.54	0.11
β-Elemene	0.53	0.07	0.33	0.05
β-Caryophyllene	1.36	0.68	0.70	0.51
α-Bergamotene	2.16	0.81	1.34	0.61
Guaiene	0.78	0.46	0.42	0.34
β-Bisabolene	5.70	2.49	3.18	2.12

presence of the non-volatiles, but still some differences remain, which cannot be explained.

Ziegler[4] mentioned that grapefruit oil differs from orange oil in the presence of γ-terpinene. Shaw[5] found that the reported values for limonene range from 86-95% and for α-pinene from 0.2-1.6%. Furthermore Shaw mentioned that the second most abundant component, as in orange oil, is myrcene, and that the levels in both oils are about the same. He also wrote that the concentration of γ-terpinene in grapefruit oils—at 0.5 - 0.8%—is significantly higher than those reported for orange oils. In the volatile part of two Israelian grapefruit oils we found 93.0 - 93.8% of limonene, 0.5 - 0.6% α-pinene, 1.8 - 2.0% myrcene and 0.1 - 0.2% of γ-terpinene (see Table XXI).

Probably more important for the organoleptic qualities of the oils are the oxygenated compounds. As for all citrus oils it also holds true for grapefruit oil that the total concentration of carbonyl compounds is important for the organoleptic quality of the oil. Wilson and Shaw[12] studied the concentration of the carbonyls in grapefruit oil. Their results are presented in Table XXII.

We compared their data with ours for Israelian oils. The total concentration of carbonyls in USA grapefruit oils (1.4 - 1.55%) is slightly higher than that in Israeli oils (1.0 - 1.2%). This difference may be due to the non-volatiles in USA oils. From the carbonyls especially the concentration of nootkatone is important for the grapefruit-character of the oil. Both Ziegler[4] and Shaw[5] mention that nootka-tone is characteristic for the oil quality. Ziegler mentioned the presence of 0.1-0.6% nootkatone, whereas Shaw found reported values of 0.3-0.8%. Recent analyses, however, showed that the concentration of this important constituent is seldom over 0.3%. More oxygenated compounds are given in Table XX. It appears strange that, for instance, one oil contains decyl acetate and the others do not. Furthermore, rather big variations exist in the concentration of linalool, perillaldehyde and nootkatone. Thorough studies have been carried out on the volatiles of grapefruit juice by Demole et al.[38] and the headspace volatiles of fresh grapefruit and its peels by Umano and Shibamoto.[39] Many new constituents have been identified in grapefruit, with p-1-menthene-8-thiol (α-terpinethiol) as one of the organoleptically most important.

The Chemical Composition of Lime Oils

Lime oil is produced in Mexico from the Key lime, with

Table XXIV. Chemical Composition of Lime Oils

	Cold-pressed		Distilled	
	Ref. 5	Ref. 40	Ref. 5	Ref. 41
α-Thujene	0.4	0.355-0.369		
α-Pinene	1.2-2.4	2.164-2.230	0.8	1.427
Camphene	0.5	0.094-0.100	0.8	0.494
β-Pinene	10.1-11.9	19.50-19.95	0.9	2.292
Myrcene	0.7-10.3	-	0.8	1.259
α-Phellandrene	0.2	0.043-0.046	-	0.363
β-Pehllandrene	0.9	-	-	-
α-Terpinene	0.8	0.162-0.166	-	2.056
p-Cymene	0.5-1.9	0.270-0.620	11.6	2.195
Limonene	47-64	45	60	48.882
γ-Terpinene	7.3-21.7	13.55	0.6	11.859
Terpinolene	0.6-1.2	0.7	0.8	7.223
Octanal	0.8	0.041-0.065	0.03	-
Nonanal	0.2	0.033-0.036	-	-
Decanal	0.1	0.198-0.290	0.09	-
Dodecanal	-	0-0.007	0.006	-
Octanol	-	-	0.01	-
Nonanol	0.1	-	0.01	-
Decanol	-	-	0.06	-
Decyl acetate	0.1	-	-	-
Citronellal	1.4	0.015-0.042	-	-
Neral	0.4-4.6	1.332-1.820	-	0.019
Geranial	5.1-6.8	2.360-2.990	-	0.039
Borneol	-	-	0.6	0.450
Fenchol	-	-	1.2	0.732
Linalool	0.009-0.2	0.153-0.164	0.1	0.089
Terpinen-1-ol	-	-	-	0.720
Terpinen-4-ol	-	0.043-0.223	1.6	0.865
α-Terpineol	0.3-1.05	0.260-0.299	5.9	6.335
β-Terpineol	-	-	0.7	0.665
γ-Terpineol	-	-	-	0.875
Nerol	-	0.023-0.036	-	-
Geraniol	-	0.030-0.072	-	-
Pinol	-	-	0.2	-
p-Cymen-8-ol	-	-	0.6	-
Neryl acetate	2.5-3.1	-	0.01	0.116
Geranyl acetate	0.55-3.1	0.254-0.275	0.3	0.091
α-Bergamotene	2.5	1.200-1.270	0.5	0.738
β-Bisabolene	2.5-4.0	-	0.9	1.263
Caryophyllene	2.5	0.935-1.164	0.3	0.530
Sesquicitronellene	-	-	0.2	-
α-Farnesene	-	-	-	1.120

the botanical name *Citrus aurantifoli·* Swingle syn. *Citrus clatifolia.* Lime oils are also produced in West India. There are two types of lime oil, cold-pressed and distilled.

The distilled oil is obtained by steam distillation of the crushed fruits (with peels). Because the fruits are rather acidic (pH 3-5), several constituents decompose during steam distillation. A comparison of the volatile compounds in cold-pressed and distilled Mexican and West Indian lime oils is presented in Table XXIII. According to Kefford and Chandler[3] and Shaw[5] the composition of cold-pressed lime oils is quite similar to that of cold-pressed lemon oil, with a few notable differences:

- the citral content of a good quality lime oil seems to be higher;
- octanal, rather than nonanal, is the main straight-chain aldehyde;
- neryl- and geranyl acetate are in much higher quantities;
- the nonvolatile portion is considerably higher (over 7% of the cold-pressed oil).

Shaw[5] also mentioned that differences between cold-pressed and distilled lime oils are pronounced. Distilled lime oil has greatly reduced quantities of citral, β-pinene, and γ-terpinene and greatly increased quantities of *p*-cymene, terpinen-4-ol and α-terpineol and it has a more terpene-like flavor than that of the cold-pressed oil. More recent publications[41-44] show that the chemical compositions of cold-pressed and distilled lime oils are more complicated.

The major constituents of lime oils have been identified and quantified by Haro et al.[41,42] The identification of trace constituents in the oils has been published recently by Chamblee et al.[43] and by Clark et al.[44] Clark mentioned that up to 1987 there was no information in the literature on the constituents responsible for the warm-spicy, dry-out note of lime peel oil, which is important in distinguishing it from lemon. These modern analyses show that the chemical composition of cold-pressed lime oil differs from that of lemon oil, and that quite big differences exist between the chemical compositions of cold-pressed and distilled lime oil (see Table XXIV).

The differences between the chemical compositions of cold-pressed and distilled lime oil are mainly due to the conversion of β-pinene to mono- and bicyclic terpene alcohols, like terpineols, α-fenchol etc. Clark et al.[44] characterized germacrene B as an important flavor impact constituent of lime peel oil. They mentioned that germacrene B has been judged to have a warm, sweet, woody-spicy, geranium-like odor and to be very important to the fresh lime peel character.

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