Progress in Essential Oils

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Clementine Oil

According to Saunt (1990), there are two possible origins of clementine. One is thought to have originated from an accidental cross-pollination of Mediterranean mandarin (*Citrus delicosa* Ten.) with an ornamental sour orange known as 'Granito' (taxonomic origin unknown) in the garden of an orphanage in Misserghin Algeria, by a Father Clement Rodier (hence the name of clementine). The more accepted origin of clementine is the 'Canton' mandarin with which it has been found to be virtually identical. The main clementine cultivars grown are 'Fina,' 'Esbal,' 'Guillermina,' 'Hernandina,' 'Marisol,' 'Monreal,' 'Berkia,' 'Arrufatina,' 'Nour,' 'Nules,' 'Oroval' and 'SRA' selections (Saunt 1990). Although clementine is classified as *C. reticulata* (a type of mandarin), it also has been given the species recognition of *C. clementina* Hort. ex Jan. (Ortiz 2002). To keep the differentiation between mandarin and clementine clear, studies on the composition of clementine oil will be classified as originating from *C. clementina*.

The main constituents of clementine oil were found (Calvarano et al. 1974) to be as follows:

α-pinene (1.99%)
camphene (0.02%)
β-pinene + sabinene (2.04%)
myrcene (7.58%)
limonene (83.03%)
γ-terpinene (2.05%)
terpinolene (0.22%)
nonanal (0.03%)
citronellal (0.21%)
linalool (0.96%)
decanal (0.46%)
terpinen-4-ol (0.06%)
α-terpineol + neral (0.13%)
geranial (0.23%)

Dugo et al. (1988) determined that a clementine oil produced by hand pressing of the rind in the laboratory was found to possess the following composition:

α-pinene (0.32%)
sabinene (0.44%)
β-pinene (0.02%)
myrcene (1.63%)
octanal‡ + α-phellandrene (0.27%)
δ-3-carene (0.02%)
p-cymene + limonene‡ (95.01%)
(Z)-β-ocimene (0.01%)
(E)-β-ocimene (0.04%)
cis-sabinene hydrate (0.01%)
octanol (0.01%)
terpinolene (0.01%)
linalool (0.69%)
nonanal (0.02%)
citronellal (0.13%)
α-terpineol (0.06%)
decanal (0.31%)
nerol + citronellol (0.03%)
neral (0.01%)
geranial (0.04%)
undecanal (0.02%)
citronellyl acetate (0.01%)
neryl acetate (0.01%)
α-copaene (0.04%)
geranyl acetate (0.01%)
α-cubebene + β-elemene (0.03%)
methyl N-methyl anthranilate (0.07%)
β-caryophyllene (0.01%)
α-humulene (0.03%)
β-cubebene† (0.03%)
α-farnesene* (0.04%)
sinensal* (0.30%)

*correct isomer not identified; †incorrect identification based on GC elution order; ‡major component of mixture

Trace amounts (< 0.01%) of α-thujene, camphene, γ-terpinene and terpinen-4-ol were also found in this oil.

Kreis et al. (1991) determined the enantiomeric distribution of three monoterpene hydrocarbons in clementine oil. The results obtained were as follows:

(1R,5R)-(+)-α-pinene (100%):(1S,5S)-(-)-α-pinene (0%)

(1R,5R)-(+)-β-pinene (32%):(1S,5S)-(-)-β-pinene (68%)
(4R)-(+)-limonene (100%):(4S)-(-)-limonene (0%)

Ruberto et al. (1993) examined the composition of essential oils produced from seven synthetic *Citrus* hybrids. In this study they characterized the composition of the steam-distilled fresh rind tissue (flavedo) of the clementine used in this cross-pollination exercise. It was found to be as follows:

α-pinene (0.37%)
sabinene (0.18%)
myrcene (1.82%)
α-phellandrene (0.02%)
limonene (94.68%)
β-phellandrene (0.06%)
β-ocimene* (0.02%)
γ-terpinene (0.01%)
terpinolene (0.31%)
linalool (1.15%)
isopulegol (0.07%)
terpinen-4-ol (0.02%)
α-terpineol (0.09%)
carveol* (0.02%)
nerol (0.09%)
carvone (0.05%)
geraniol (0.04%)
geranial (0.07%)
decanal (0.27%)
undecanal (0.02%)
dodecanal (0.06%)
dodecenal* (0.02%)
1-hexen-3-ol (0.01%)
octanol (0.02%)
nonanol (0.02%)
α-terpinyl acetate (0.03%)
α-copaene (0.03%)
α-cubebene (0.02%)
β-caryophyllene (0.02%)
α-farnesene* (0.01%)
β-sinensal (0.01%)
α-sinensal (0.21%)
nootkatone (0.01%)

*correct isomer not identified

In addition, trace amounts (< 0.01%) of α-thujene, camphene, β-pinene, δ-3-carene, decanol, neryl acetate, geranyl acetate, decyl acetate and α-humulene also were found in this oil.

The same authors (Ruberto et al. 1994) analyzed the oil produced from the simultaneous distillation and extraction of the fresh rind tissue of a clementine cultivar grown in Sicily. The composition of this oil was found to be as follows:

α-pinene (0.47%)
sabinene (0.38%)
β-pinene (0.03%)
myrcene (1.83%)
α-phellandrene (0.03%)
δ-3-carene (0.02%)
α-terpinene + β-phellandrene (0.01%)
limonene (94.77%)
(E)-β-ocimene (0.02%)
γ-terpinene (0.02%)
terpinolene (0.01%)
linalool (0.82%)
citronellal (0.07%)
terpinen-4-ol (0.05%)
α-terpineol (0.12%)
carveol* (0.01%)

nerol (0.02%)
geraniol (0.04%)
geranial (0.06%)
octanal (0.37%)
decanal (0.34%)
dodecanal (0.06%)
2-dodecenal* (0.02%)
octanol (0.05%)
α-copaene (0.03%)
β-bisabolene (0.01%)
β-sinensal (0.02%)
α-sinensal (0.11%)

*correct isomer not identified

Trace amounts (< 0.01%) of α-thujene, camphene, (Z)-β-ocimene, neral, β-caryophyllene, α-humulene, 1-hexen-3-ol, nonanol, neryl acetate and nootkatone were also found in this same oil.

This oil of clementine (cv. 'Commune') listed above was also reported by Ruberto et al. (1997) in an additional paper on the use of clementine to develop other *Citrus* hybrids.

Using a fully automated HPLC-GC/MS system, Mondello et al. (1995) was able to fractionate clementine oil into a monoterpene hydrocarbon fraction and a sesquiterpene hydrocarbon fraction. The monoterpene fraction, which was 98.60% of the whole oil, contained the following hydrocarbons:

α-thujene (0.03%)
α-pinene (0.53%)
sabinene (0.50%)
β-pinene (0.08%)
myrcene (1.90%)
α-phellandrene (0.05%)
δ-3-carene (0.04%)
α-terpinene (0.03%)
limonene (96.03%)
(Z)-β-ocimene (0.01%)
(E)-β-ocimene (0.05%)
γ-terpinene (0.67%)
terpinolene (0.08%)

Trace amounts (< 0.01%) of camphene and p-cymene were also characterized.

The sesquiterpene fraction, which accounted for only 0.20% of the oil, comprised:

α-cubebene (0.3%)
α-copaene (12.9%)
β-cubebene (12.6%)
β-caryophyllene (4.0%)
α-humulene (2.2%)
(Z)-β-farnesene (9.5%)
γ-muurolene (1.1%)
germacrene D (9.3%)
valencene (1.0%)
α-muurolene (2.1%)
α-farnesene* (14.6%)
δ-cadinene (15.9%)

*correct isomer not identified

These same results also can be found in Mondello et al. (1996) and Dugo et al. (1999b).

Verzera et al. (1997) compared the chemical composition of lab-prepared pressed oils of three cultivars ('Oroval,' 'Monreal' and 'Commune') of clementine fruit harvested twice in December 1995 and once in January 1996. A summary of the results of these analyses can be seen in **T-1**. Based on these results, it shows that the oil from the 'Commune' cultivar would have the most intense aroma and flavor. Furthermore, the authors showed that the enantiomeric ratio of linalool in the three clementine oils was: (3S)-(+)-linalool (82.0–97.6%):(3R)-(-)-linalool (2.4–18.0%). In addition, Verzera et al. determined the polymethoxyflavone content of the clementine oils obtained from the three cultivars, the results of which are shown in **T-2**.

Another oil of clementine produced by simultaneous distillation and extraction of fresh rind tissue was analyzed by Ruberto et al. (1997). The constituents that were characterized in the oil were:

α-pinene (0.43%)
sabinene (0.15%)
β-pinene (0.02%)
myrcene (1.82%)
α-phellandrene (0.03%)
δ-3-carene (0.05%)
limonene (95.46%)
(E)-β-ocimene (0.03%)
γ-terpinene (0.02%)
terpinolene (0.02%)
linalool (0.53%)
citronellal (0.05%)
terpinen-4-ol (0.04%)
α-terpineol (0.07%)
carveol* (0.01%)
carvone (0.01%)
neral (0.03%)
perillaldehyde (0.07%)
α-terpinyl acetate (0.01%)
octanal (0.13%)
decanal (0.27%)
dodecanal (0.05%)
2-dodecenal* (0.01%)
octanol (0.06%)
α-copaene (0.03%)
α-cubebene (0.02%)
β-caryophyllene (0.01%)
α-humulene (0.01%)
β-farnesene* (0.02%)
β-cubebene (0.02%)
γ-cadinene (0.04%)
β-sinensal (0.01%)
α-sinensal (0.07%)
nootkatone (0.01%)

*correct isomer not identified; †incorrect identification based on GC elution order

Average comparative percentage compositions of oils produced from 'Oroval,' 'Monreal' and 'Commune' cultivars of clementine **T-1**

Compound	'Oroval'	'Monreal'	'Commune'	Compound	'Oroval'	'Monreal'	'Commune'
α-thujene	0.01	t	0.01	geranial	0.03	0.04	0.08
α-pinene	0.50	0.49	0.35	perillaldehyde	0.04	0.04	0.03
camphene	t	t	t	perillyl alcohol	0.01	0.01	0.03
sabinene	0.68	0.29	1.04	undecanal	t	t	0.01
β-pinene	0.17	0.07	0.05	(E,E)-2,4-decadienal	0.01	0.01	0.02
myrcene	1.87	1.89	1.70	α-terpinyl acetate	t	t	t
octanal	0.31	0.31	0.48	neryl acetate	t	t	t
α-phellandrene	0.03	0.02	0.03	α-copaene	0.02	0.02	0.04
δ-3-carene	0.05	0.05	0.04	geranyl acetate	t	t	0.01
α-terpinene	t	t	0.01	β-cubebene	0.02	0.02	0.04
limonene	93.85	94.50	92.36	β-elemene	0.01	0.01	0.02
(Z)-β-ocimene	0.01	0.02	0.01	dodecanal	0.05	0.05	0.10
(E)-β-ocimene	0.05	0.02	0.10	methyl N-methyl anthranilate	t	0.01	0.01
γ-terpinene	0.01	t	0.01	β-caryophyllene	0.01	0.01	0.02
cis-sabinene hydrate	0.02	t	0.05	β-gurjunene	0.02	0.01	0.03
octanol	0.01	t	0.01	*trans*-α-bergamotene	t	t	t
terpinolene	0.02	0.01	0.02	(Z)-β-farnesene	0.01	0.01	0.02
trans-sabinene hydrate	t	t	0.01	α-humulene	t	0.01	0.01
linalool	1.06	1.08	1.04	(E)-β-farnesene	0.02	0.01	0.08
nonanal	0.01	0.01	0.03	(E)-2-dodecenal	0.02	0.02	0.03
heptyl acetate	0.01	0.01	0.01	γ-muurolene	t	t	0.01
cis-limonene oxide	0.01	0.01	0.02	germacrene D	0.02	0.02	0.03
trans-limonene oxide	0.01	0.01	0.01	valencene	0.01	0.01	0.03
citronellal	0.07	0.07	0.08	bicyclogermacrene	t	t	0.01
terpinen-4-ol	t	t	0.01	(E,E)-α-farnesene	0.05	0.03	0.11
α-terpineol	0.05	0.06	0.11	β-bisabolene	t	t	t
decanal	0.25	0.24	0.46	δ-cadinene	0.03	0.03	0.05
octyl acetate	t	0.01	0.01	tridecanal	t	t	0.01
cis-carveol	t	0.01	0.04	(E)-nerolidol	0.01	0.01	0.01
nerol + citronellol	0.01	0.01	0.03	tetradecanal	t	t	0.01
neral	0.02	0.01	0.05	tetradecanol	t	t	0.01
carvone	t	t	t	β-sinensal	0.06	0.03	0.16
geraniol	t	t	t	α-sinensal	0.30	0.26	0.56
(E)-2-decenal	0.01	0.01	0.01	nootkatone	0.01	0.01	0.01

t = trace (< 0.01%)

Average polymethoxyflavone content of the oils of the 'Oroval,' 'Monreal' and 'Commune' cultivars of clementine **T-2**

Compound	'Oroval'	'Monreal'	'Commune'
tangeretin	0.10*	0.10	0.17
3,3',4',5',6,7,8-heptamethoxyflavone	0.29	0.27	0.51
nobiletin	0.09	0.09	0.09
tetra-O-methylscutellarein	0.04	0.05	0.06
3,3',4',5,6,7-hexamethoxyflavone	0.02	0.02	0.02
sinensetin	t	t	t

*g/100 g of oil; t = trace (< 0.01%)

Also, trace amounts (< 0.01%) of α-thujene, camphene, β-phellandrene, (Z)-β-ocimene and nonanal were found in this same oil.

The composition of an oil of clementine was analyzed by Gazea et al. (1998). Because of the limited sample size of fruit, instead of using a cold-pressing technique to isolate the oil, it was isolated by extraction of albedo-free peel strips with petroleum ether. The composition of the oil, which was analyzed by GC-FID and GC/MS, was found to be as follows:

α-thujene (0.04%)
α-pinene (0.56%)
camphene (0.01%)
sabinene (0.65%)
β-pinene (0.15%)
myrcene (1.66%)
α-phellandrene (0.11%)
δ-3-carene (0.03%)
α-terpinene (0.02%)
limonene (93.86%)
(Z)-β-ocimene (0.01%)
(E)-β-ocimene (0.06%)
γ-terpinene (0.81%)
terpinolene (0.02%)
linalool (0.16%)
nonanal (0.09%)
citronellal (0.04%)
terpinen-4-ol (0.02%)
α-terpineol (0.02%)
decanal (0.18%)
nerol (0.02%)
neral (0.01%)
geranial (0.03%)

Percentage composition of the oils produced from the 'Nules' and 'Commune' cultivars grown in Uruguay **T-3**

Compound	'Nules'	'Commune'	Compound	'Nules'	'Commune'
α-thujene	0.01	0.01	geranial	0.03	0.03
α-pinene	0.56	0.58	perillaldehyde	0.02	0.04
camphene	t	t	perillyl alcohol	0.01	0.01
sabinene	0.97	1.04	undecanal	0.01	t
β-pinene	0.22	0.24	(E,E)-2,4-decadienal	0.01	0.01
myrcene	2.06	2.00	α-terpinyl acetate	t	t
octanal	0.25	0.54	neryl acetate	t	t
α-phellandrene	0.03	0.03	α-copaene	0.04	0.03
δ-3-carene	0.04	0.05	geranyl acetate	t	t
α-terpinene	t	t	β-cubebene	0.04	0.03
limonene	93.64	93.12	β-elemene	0.01	0.01
(Z)-β-ocimene	0.01	t	dodecanal	0.08	0.07
(E)-β-ocimene	0.09	0.05	methyl N-methyl anthranilate	t	t
γ-terpinene	t	t	β-caryophyllene	0.01	0.01
cis-sabinene hydrate	0.03	0.03	β-gurjunene	0.02	0.01
octanol	0.02	0.06	*trans*-α-bergamotene	t	t
terpinolene	0.01	0.02	(Z)-β-farnesene	0.01	0.01
trans-sabinene hydrate	t	t	α-humulene	0.01	0.01
linalool	0.51	0.65	(E)-β-farnesene	0.02	0.02
nonanal	0.02	0.01	(E)-2-dodecenal	0.01	0.01
heptyl acetate	0.01	0.01	γ-muurolene	t	0.02
cis-limonene oxide	0.01	0.01	germacrene D	0.04	0.03
trans-limonene oxide	0.02	0.01	valencene	0.01	0.01
citronellal	0.05	0.07	bicyclogermacrene	0.01	t
terpinen-4-ol	0.01	0.01	(E,E)-α-farnesene	0.04	0.04
α-terpineol	0.06	0.06	β-bisabolene	t	t
decanal	0.38	0.40	δ-cadinene	0.05	0.04
octyl acetate	t	0.01	tridecanal	t	t
cis-carveol	0.01	0.01	(E)-nerolidol	0.01	t
nerol	0.02	0.02	tetradecanal	t	0.01
neral	0.04	0.02	tetradecanol	t	t
carvone	t	t	β-sinensal	0.06	0.05
geraniol	t	t	α-sinensal	0.25	0.24
(E)-2-decenal	0.01	0.01	nootkatone	t	0.02

t = trace (< 0.01%)

undecanal (0.01%)
nonyl acetate (0.01%)
trans-caren-3-ol† (0.01%)
α-terpinyl acetate (0.06%)
citronellyl acetate (0.03%)
neryl acetate (0.01%)
β-caryophyllene (0.01%)
trans-α-bergamotene (0.01%)
valencene (0.50%)
α-farnesene* (0.05%)
β-sinensal (0.04%)
α-sinensal (0.21%)

*correct isomer not identified; †component identity in doubt

Huang and Wu (1998) reported their results of an analysis of clementine oil produced in China. The components identified in this oil were as follows:

(Z)-3-hexenol (0.03%)
α-pinene (0.53%)
sabinene (0.66%)
myrcene (2.00%)
β-pinene (0.04%)
α-phellandrene (0.02%)
δ-3-carene (0.08%)
limonene (92.85%)
(Z)-β-ocimene (0.28%)
β-phellandrene (0.03%)
γ-terpinene (0.05%)
octanol (0.02%)
terpinolene (0.67%)
citronellal (0.09%)
decanal (0.18%)
α-terpineol (0.09%)
citronellol (0.04%)
geranial (0.02%)
perillaldehyde (0.02%)
α-copaene (0.07%)
β-elemene (0.07%)
dodecanal (0.05%)
β-caryophyllene (0.02%)
β-farnesene* (0.03%)
α-humulene (0.02%)
α-farnesene* (0.06%)
γ-muurolene (0.05%)
δ-cadinene (0.07%)
β-sinensal (0.10%)
α-sinensal (0.35%)

In addition, trace amounts (< 0.01%) of hexanol, α-thujene, camphene, (E)-β-ocimene, p-cymene, *cis*-sabinene hydrate, linalool, *trans*-sabinene hydrate, terpinen-4-ol, nerol, geraniol, neral, undecanal, thymol, neryl acetate, geranyl acetate and γ-elemene were also characterized in this same oil.

The enantiomeric distribution of six chiral constituents of clementine peel oil was determined by Mondello et al. (1998). They found the following results:

(1R,5R)-(+)-β-pinene (22.9%):(1S,5S)-(-)-β-pinene (77.1%)

Polymethoxyflavone content of the 'Nules' and 'Commune' clementine cultivar oils grown in Uruguay **T-4**

Compound	'Nules'	'Commune'
tangeretin	0.14*	0.16
3,3',4',5',6,7,8-heptamethoxyflavone	0.43	0.37
nobiletin	0.13	0.11
tetra-O-methylscutellarein	0.07	0.08
3,3',4',5,6,7-hexamethoxyflavone	0.05	0.04
sinensetin	0.01	0.01

*g/100 g of oil

Enantiomeric ratios of selected components of clementine cultivar oils **T-5**

Compound	'Nules'	'Commune'
(1R,5R)-(+)-β-pinene	58.1–61.1	60.1
(1S,5S)-(-)-β-pinene	38.9–41.9	39.9
(1R,5R)-(+)-sabinene	97.5–97.6	97.6
(1S,5S)-(-)-sabinene	2.4–2.5	2.4
(4R)-(+)-limonene	99.4	99.4
(4S)-(-)-limonene	0.6	0.6
(3R)-(-)-linalool	93.3	94.7–95.0
(3S)-(+)-linalool	6.7	5.0–5.3
(4R)-(+)-α-terpineol	97.3–97.5	97.4–97.5
(4S)-(-)-α-terpineol	2.5–2.7	2.6–2.7

(1R,5R)-(+)-sabinene (90.1%):(1S,5S)-(-)-sabinene (9.9%)

(4R)-(+)-limonene (99.3%):(4S)-(-)-limonene (0.7%)

(3S)-(+)-linalool (92.5%):(3R)-(-)-linalool (7.5%)

(4S)-(+)-terpinen-4-ol (46.4%):(4R)-(-)-terpinen-4-ol (53.6%)

(4R)-(+)-α-terpineol (86.9%):(4S)-(-)-α-terpineol (13.1%)

These same results can be found in the report by Dugo et al. (1999b).

Verzera et al. (1998) analyzed lab-produced cold-pressed oils of the 'Nules' and 'Commune' cultivars of clementine grown in Uruguay. A summary of the oil composition of these two cultivars can be seen in **T-3**. In addition, the authors examined the polymethoxyflavone contents of the oils from these two Uruguayan cultivars. The results of this HPLC study are shown in **T-4**. Furthermore, Verzera et al. examined the enantiomeric ratios of five constituents of the oils of the two Uruguayan clementine cultivars. The results of this study can be found summarized in **T-5**.

Percentage composition of clementine peel oils obtained from 16 cultivars **T-6**

Compound	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
α-pinene	0.3	0.4	0.3	0.3	0.4	0.3	0.3	0.4	0.3	0.5	0.5	0.5	0.5	0.3	0.6	–
β-pinene	t	t	t	t	t	t	t	t	t	0.1	0.1	0.1	0.1	0.1	0.2	0.1
sabinene	0.3	0.7	0.4	0.6	1.0	0.9	0.9	0.6	0.9	1.3	1.8	1.8	1.2	1.8	4.0	2.8
δ-3-carene	–	t	0.1	t	t	t	t	0.1	0.1	0.1	0.1	0.1	–	t	0.1	0.1
myrcene	1.6	1.7	1.6	1.4	1.6	1.6	1.7	1.6	1.6	1.8	1.8	1.8	1.7	1.6	2.0	1.6
limonene	95.5	95.0	95.0	94.6	94.1	94.1	94.1	93.9	93.5	92.9	92.7	92.2	91.8	91.2	90.1	89.1
β-phellandrene	0.3	0.3	0.3	0.2	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
γ-terpinene	t	t	t	–	t	t	t	0.1	t	0.1	t	0.1	t	t	t	t
(E)-β-ocimene	t	t	t	t	t	t	0.2	t	t	0.1	0.1	0.1	t	t	0.1	0.1
octanal	0.1	0.1	t	0.1	0.3	0.2	0.2	–	0.2	0.2	0.3	0.3	0.3	0.3	0.2	0.1
trans-sabinene hydrate	–	t	–	t	t	t	t	t	t	t	t	t	–	0.1	t	0.2
citronellal	t	t	–	t	t	0.1	t	t	0.1	t	t	t	t	0.1	t	0.1
α-copaene	t	t	t	t	t	t	t	0.1	t	t	t	t	t	t	t	0.1
decanal	0.2	0.2	0.1	0.1	0.2	0.3	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.5
linalool	0.8	0.6	0.8	0.8	1.2	0.9	0.8	1.0	1.5	0.8	1.0	1.1	0.8	2.3	0.7	1.9
trans-α-bergamotene	–	–	–	t	–	t	t	0.1	t	–	–	–	t	t	t	–
(E)-β-farnesene	–	–	–	t	–	t	t	–	–	–	–	–	t	t	t	0.1
α-terpineol	0.1	t	t	0.1	0.1	0.1	t	0.1	0.1	t	0.1	0.1	–	0.1	0.1	0.2
germacrene D	t	t	t	t	t	t	t	t	t	t	t	t	–	t	t	0.1
geranial	–	–	t	t	t	–	–	0.1	–	0.1	–	–	–	–	0.1	–
δ-cadinene	t	t	t	–	t	–	–	0.1	t	t	t	–	–	t	–	0.1
β-sinensal	t	0.1	t	0.1	t	0.1	0.2	–	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.3
α-sinensal	0.1	0.3	0.2	0.1	0.2	0.3	0.4	0.4	0.4	0.3	0.4	–	0.3	0.5	0.4	0.7

t = trace (< 0.1%); 1 = 'MA3' oil; 2 = 'Nules' oil; 3 = 'MA2' oil; 4 = 'Hernandina' oil; 5 = 'Tardia Villareal' oil; 6 = 'Reina' oil; 7 = 'Caffin' oil; 8 = 'MacBean' oil; 9 = 'Oroval' oil; 10 = 'Monreal' oil; 11 = 'Bruno' oil; 12 = 'Tomatera' oil; 13 = 'Commune' oil; 14 = 'Marisol' oil; 15 = 'Ragheb' oil; 16 = 'Guillerma' oil

The main constituents (those 0.1% or greater) of clementine were reported by Ruberto et al. (1999). They were determined to be as follows:

α-pinene (0.4%)
sabinene (0.2%)
myrcene (1.8%)
β-phellandrene (0.1%)
limonene (94.7%)
(E)-β-ocimene (0.1%)
linalool (1.1%)
isopulegol (0.1%)
α-terpineol (0.1%)
nerol (0.1%)
geraniol (0.1%)
decanal (0.3%)
dodecanal (0.1%)
α-sinensal (0.2%)

The composition of a cold-pressed clementine oil was reported by Dugo et al. (1999a). The components characterized in the oil were as follows:

α-thujene (0.03%)
α-pinene (0.57%)
sabinene (0.52%)
β-pinene (0.09%)
myrcene (1.86%)
octanal (0.09%)
α-phellandrene (0.09%)
δ-3-carene (0.04%)
α-terpinene (0.02%)
p-cymene + β-phellandrene + limonene* (94.62%)
(Z)-β-ocimene (0.01%)
(E)-β-ocimene (0.04%)
γ-terpinene (0.68%)
octanol (0.01%)
terpinolene (0.05%)
linalool (0.21%)
nonanal (0.01%)
cis-limonene oxide (0.01%)
trans-limonene oxide (0.01%)
citronellal (0.05%)
terpinen-4-ol (0.01%)
α-terpineol (0.02%)
decanal (0.20%)
trans-carveol (0.01%)
octyl acetate (0.01%)
neral (0.02%)
linalyl acetate (0.01%)
(E)-2-decenal† (0.01%)
geranial (0.03%)
undecanal (0.01%)

α-copaene (0.03%)
β-cubebene (0.03%)
β-elemene (0.01%)
methyl N-methylanthranilate (0.02%)
dodecanal (0.05%)
β-caryophyllene (0.01%)
α-cadinene† (0.02%)
α-humulene (0.01%)
(Z)-β-farnesene (0.02%)
(E)-2-dodecenal (0.01%)
germacrene D (0.02%)
(E,E)-α-farnesene (0.03%)
δ-cadinene (0.03%)
elemol† (0.01%)
β-sinensal (0.04%)
α-sinensal (0.20%)

*major component; †tentative identification

In addition, trace amounts (< 0.01%) of camphene, *cis*-sabinene hydrate, *trans*-sabinene hydrate, *cis*-carveol, carvone, perillyl alcohol, thymol, (E,E)-2,4-decadienal, α-terpinyl acetate, neryl acetate, geranyl acetate, decyl acetate, valencene, bicyclogermacrene, nerolidol and tetradecanal were found in this same oil.

An oil produced from cold-pressed clementine fruit grown in Japan was analyzed by Sawamura (2000). This oil was found to possess the following composition:

α-pinene (0.48%)
β-pinene (0.01%)
sabinene (0.09%)
myrcene (1.23%)
limonene (93.32%)
β-phellandrene (< 0.01%)
(E)-β-ocimene (0.05%)
p-cymene (0.02%)
octanal (0.01%)
cis-limonene oxide (0.43%)
trans-limonene oxide (0.20%)
trans-linalool oxide (furanoid) (0.01%)
citronellal (0.05%)
α-copaene (0.02%)
decanal (0.01%)
linalool (0.93%)
p-menth-1-en-9-ol (0.01%)
p-mentha-1,8-dien-9-ol (0.03%)
spathulenol (0.04%)
β-sinensal (0.04%)

Lota et al. (2001) analyzed the composition of clementine cold-pressed oils obtained from 16 cultivars ('MA3,' 'Nules,' 'MA2,' 'Hernandina,' 'Tardia Villareal,' 'Reina,' 'Caffin,' 'MacBean,' 'Oroval,' 'Monreal,' 'Bruno,' 'Tomatera,' 'Commune,' 'Marisol,' 'Ragheb' and 'Guillerma') grown in Corsica. The results of the study can be seen summarized in **T-6**.

I. Calvarano, F. Bovalo and A. Di Giacomo, *L'olio essenzialo di clementine*. Essenz. Deriv. Agrum., **44**, 117–123 (1974).

G. Dugo, A. Cotroneo, A. Trozzi, M. Barbeni and A. Di Giacomo, *On the genuineness of* Citrus *essential oils. Part XXV. The essential oil from 'Wenzhou Honey' oranges.* Flav. Fragr. J., **3**, 161–166 (1988).

J. Saunt, *Citrus Varieties of the World.* pp. 41–45, Sinclair International Ltd., Norwich, England (1990).

P. Kreis, U. Hener and A. Mosandl, *Chirale inhaltstoffe ätherischer Öle 5. Mitteilung. Enantiomerenverteilung von α-pinene, β-pinene und limonen in ätherischen Ölen und Extrakten—Citrusfruchte und citrushältige Getränke.* Dtsch. Lebensmilt. Rundsch., **87**, 8–11 (1991).

G. Ruberto, D. Biondi, M. Piattelli, P. Rapisarda and A. Starrantino, *Profiles of essential oils of new* Citrus *hybrids.* Flav. Fragr. J., **8**, 179–184 (1993).

G. Ruberto, D. Biondi, M. Piattelli, P. Rapisarda and A. Starrantino, *Essential oil of the new* Citrus *hybrid,* Citrus clementina *x* C. limon. J. Essent. Oil Res., **6**, 1–8 (1994).

L. Mondello, P. Dugo, K.D. Bartle, G. Dugo and A. Cotroneo, *Automated HPLC-HRGC: A powerful method for essential oil analysis. Part V. Identification of terpene hydrocarbons of bergamot, lemon, mandarin, sweet orange, bitter orange, grapefruit, clementine and Mexican lime oils by coupled HPLC-HRGC-MS (ITD).* Flav. Fragr. J., **10**, 33–42 (1995).

L. Mondello, G. Dugo, P. Dugo and K.D. Bartle, *On-line HPLC-HRGC in the analytical chemistry of citrus essential oils.* Perfum. Flavor., **21**(4), 25–49 (1996).

A. Verzera, L. Mondello, A. Trozzi and P. Dugo, *On the genuineness of* Citrus *essential oils. Part LII. Chemical characterization of essential oil of three cultivars of* Citrus clementine *Hort.* Flav. Fragr. J., **12**, 163–172 (1997).

G. Ruberto, A. Renda, M. Piattelli, P. Rapisarda and A. Starrantino, *Essential oil of two new pigmented* Citrus *hybrids,* Citrus clementina *x* Citrus sinensis. J. Agric. Food Chem., **45**, 467–471 (1997).

G. Ruberto, D. Biondi, P. Rapisarda, A. Renda and A. Starrantino, *Essential oil of Cami, a new* Citrus *hybrid.* J. Agric. Food Chem., **45**, 3206–3210 (1997).

F. Gazea, I. Calvarano and M. Calvarano, *Characteristics of a new* Citrus *hybrid essential oil* Citrus clementina *x* C. limon. J. Essent. Oil Res., **10**, 235–239 (1998).

A. Verzera, A. Trozzi, L. Mondello, E. Dellacassa and D. Lorenzo, *Uruguayan essential oils. Part X. Composition of the oil of* Citrus clementine *Hort.* Flav. Fragr. J., **13**, 189–195 (1998).

L. Mondello, M. Catalfamo, A.R. Proteggente, I. Bonaccorsi and G. Dugo, *Multidimensional capillary GC-GC for the analysis of real complex samples. 3. Enantiomeric distribution of monoterpene hydrocarbons and monoterpene alcohols of mandarin oils.* J. Agric. Food Chem., **46**, 54–61 (1998).

Y-H. Huang and Y-L. Wu, *Chemical components of essential oils from peels of 25* Citrus *species and cultivars.* Tianran Chanwu Yanjiu Yu Kaifa, **10**(4), 48–54 (1998).

G. Ruberto, A. Starrantino and P. Rapisarda, *Essential oils from new* Citrus *fruits.* Essenz. Deriv. Agrum., **69**, 15–26 (1999).

G. Dugo, K.D. Bartle, I. Bonaccorsi, M. Catalfamo, A. Cotroneo, P. Dugo, G. Lamonica, H. McNair, L. Mondello, P. Previti, I. Stagno d'Alcontres, A. Trozzi and A. Verzera, *Advanced analytical techniques for the analysis of* Citrus *essential oils. Part I. Volatile*

fraction: HRGC/MS analysis. Essenz. Deriv. Agrum., **69**, 79–111 (1999a).

G. Dugo, K.D. Bartle, I. Bonaccorsi, M. Catalfamo, A. Cotroneo, P. Dugo, G. Lamonica, H. McNair, L. Mondello, P. Previti, I. Stagno d'Alcontres, A. Trozzi and A. Verzera, *Advanced analytical techniques for the analysis of* Citrus *essential oils. Part 2. Volatile fraction: LC-HRGC and MDGC.* Essenz. Deriv. Agrum., **69**, 159–171 (1999b).

M. Sawamura, *Volatile components of the* Citrus *genus.* Recent Res. Develop. Agric. Food Chem., **4**, 131–164 (2000).

M-L. Lota, D. de Rocca Serra, F. Tomi and J. Casanova, *Chemical variability of peel and leaf essential oils of 15 species of mandarin.* Biochem. Syst. Ecol., **29**, 77–104 (2001).

J.M. Ortiz, *Botany: taxonomy, morphology and physiology of fruits, leaves and flowers.* In: *Citrus the Genus* Citrus. Edits., G. Dugo and A. Di Giacomo, pp. 16–35, Taylor and Francis, London (2002).

Stoechas Oil

An oil of stoechas produced from wild plants of *Lavandula stoechas* L. collected in Morocco was the subject of analysis by Lahlou et al. (2001). The results of this analysis can be seen as follows:

α-pinene (1.0%)
camphene (2.1%)
p-cymene (0.5%)
1,8-cineole (11.6%)
linalool (1.7%)
α-terpineol (0.6%)
thymol (1.9%)
camphor (15.0%)
bornyl acetate (10.4%)
fenchone (22.2%)
linalool oxide* (1.4%)
δ-terpineol (0.7%)
verbenone (1.6%)
geranyl acetate (4.0%)
sabinyl acetate* (3.9%)
δ-cadinene (1.0%)

*correct isomer not identified

An oil of *L. stoechas* produced in the laboratory from plant material harvested in Alahan-Hatay, Turkey, was analyzed by Dadalioglu and Evrendilek (2004). It was found to possess the following composition:

α-pinene (1.31%)
camphene (1.40%)
1,8-cineole (8.03%)
fenchone (55.79%)
linalool (0.29%)
camphor (18.18%)
myrtenal (0.25%)
α-fenchyl acetate (0.32%)
carvone (0.33%)
bornyl acetate (1.32%)
myrtenyl acetate (6.25%)
δ-cadinene (0.90%)
carveol* (0.73%)
γ-cadinene (0.80%)
caryophyllene oxide (0.33%)

γ-selinene† (2.54%)
aromadendrene† (0.41%)

*correct isomer not identified; †incorrect identification based on GC elution order

Bouzouita et al. (2005) used a combination of GC and GC/MS to characterize an oil of *L. stoechas* produced by water distillation in the laboratory from plant material collected from its natural habitat in Kairouan, Tunisia. The composition of this oil was found to be as follows:

α-pinene (0.4%)
camphene (0.8%)
1-octen-3-ol (0.2%)
p-cymene (0.4%)
limonene + 1,8-cineole (4.9%)
fenchone (68.2%)
linalool (0.3%)
α-fenchyl alcohol (1.9%)
camphor (11.2%)
borneol (0.6%)
terpinen-4-ol (0.2%)
p-cymen-8-ol (0.4%)
α-terpineol (0.2%)
myrtenol (0.6%)
α-fenchyl acetate (0.8%)
carvone (0.3%)
bornyl acetate (1.4%)
myrtenyl acetate (1.2%)
cyclosativene (0.2%)
α-copaene (0.2%)
allo-aromadendrene (0.2%)
δ-cadinene (0.4%)
selina-3,7(11)-diene (0.2%)
viridiflorol (1.4%)

Trace amounts of *cis*-linalool oxide (furanoid), α-campholenol and a carvone isomer also were found in this oil. Also, as the authors used diethyl ether to solubilize the oil prior to analysis they were able to find BHT (1.5%) as an artifact in their analysis.

M. Lahlou, R. Berrada, A. Agoumi and M. Hmamouchi, *The potential effectiveness of essential oils in the control of human head lice in Morocco.* Internet. J. Aromatherap., **10**, 108–123 (2001).

I. Dadalioglu and G.A. Evrendilek, *Chemical compositions and antibacterial effects of essential oils of Turkish oregano (*Origanum minutiflorum*) bay laurel (*Laurus nobilis*), Spanish lavender (*Lavandula stoechas *L.) and fennel (*Foeniculum vulgare*) on common foodborne pathogens.* J. Agric. Food Chem., **52**, 8255–8260 (2004).

N. Bouzouita, F. Kachouri, M.M. Chaabouni, R. Ben Aissa, S. Zgoulti, P. Thonart, A. Carlier, M. Murlier and G.C. Lognay, *Volatile constituents and antimicrobial activity of* Lavandula stoechas *L. oil from Tunisia.* J. Essent. Oil Res., **17**, 584–584 (2005).