Progress in Essential Oils

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Mandarin Oil

In 1986, Kekelidze et al. showed that the chemical composition of the peel oil of a Russian mandarin cultivar changed during fruit maturation. The changes in composition of the various stages of fruit maturity (from immature to fully mature fruit) are summarized as follows:

α-pinene (0.4-0.5%)
β-pinene (0.9-0.3%)
sabinene (0.1%)
myrcene (0.6-1.6%)
limonene (23.7-84.6%)
γ-terpinene (2.3-3.1%)
p-cymene (9.5-0.8%)
terpinolene (0.1%)
linalool (33.4-1.4%)
decanal (0.4-0.1%)
α-copaene (0.1%)
α-terpineol (8.9-0.1%)
β-elemene (6.5-0.4%)
β-caryophyllene (1.9-0.4%)
γ-cadinene (0.2-0.6%)
citronellol (0.1%)

In 1990, Dugo used a combination of GC and GC/MS to analyze 266 samples of mandarin oil. The constituents identified and their average amounts were found to be:

α-thujene (0.89%)
α-pinene (2.36%)
camphene (0.02%)
sabinene (0.26%)
β-pinene (1.68%)
myrcene (1.70%)
octanol + α-phellandrene (0.21%)
α-terpinene (0.44%)
p-cymene (0.33%)
limonene (69.51%)
(Z)-β-ocimene (trace)
(E)-β-ocimene (0.02%)
γ-terpinene (19.85%)
cis-sabinene hydrate (0.03%)
octanol (trace)
terpinolene (0.87%)
trans-sabinene hydrate (0.04%)
linalool (0.11%)
nonanal (0.03%)
citronellal (0.03%)
terpinen-4-ol (0.04%)
α-terpineol (0.14%)
decanal (0.09%)
nerol (0.02%)
neral (0.01%)
geraniol (trace)
geranial (0.05%)
thymol (0.05%)
undecanal (0.01%)
neryl acetate (trace)
α-copaene (trace)
geranyl acetate (trace)
α-cubebene (trace)
methyl N-methyl anthranilate (0.45%)
β-caryophyllene (0.10%)
α-humulene (0.01%)
β-cubebene† (trace)
farnesene* (0.15%)

* correct isomer not identified
† incorrect identity based on elution order

Three years later, a mandarin oil produced from C. *reticulata* var. *ponkan* was analyzed by Zhu et al. (1993) and it was found to contain:

myrcene (0.49%)
octanal (1.40%)
p-cymene (0.28%)
limonene (61.77%)
γ-terpinene (2.62%)
pentylcyclopropane† (0.45%)
linalool (17.84%)
terpinen-4-ol (1.49%)
α-terpineol (3.81%)
decanal (0.36%)
citronellol (2.24%)
neral (0.33%)
carvone (0.20%)
geraniol (0.30%)
geranial (0.74%)
carvacrol (0.37%)
cis-terpin hydrate† (0.18%)
perillaldehyde (0.53%)
cedrenol† (1.86%)

† incorrect identification based on elution order

Also in 1993, Mondello et al. reported that five polymethoxy flavones were found by HPLC in the peel oil of mandarin produced in Italy. They were:

tangeretin (0.214%)
heptamethoxyflavone (0.037%)
nobiletin (0.074%)
tetra-O-methylscutellarein (0.005%)
sinesetin (0.002%)

The following year, Controneo et al. (1994) compared the average composition of Italian mandarin oil produced between 1982 and 1986 and compared them with oils produced during the 1991/1992 season. Their results are summarized in Table I.

This same year, Dugo et al. (1994) used a normal phase HPLC to analyze the polymethoxyflavones in green, light and red mandarin oils produced by different processes. The results of this study are shown in Table II. As can be seen, the mandarin oils produced by the Pelatrice process had a higher polymethoxyflavone content than oils produced by the Torchi process.

Although linalool is not a major constituent of mandarin oil, Casabianca and Graff (1996) determined that its enantiomeric distribution was:

(3R)-(-)-linalool (4.0-6.5%) :
(3S)-(+)-linalool (93.5-96.0%)

In 1997, Verzera et al. compared the composition of Italian mandarin oils produced over the decade 1982-1992 with oils produced during the 1996/1997 season. Their results are shown in Table III.

Using capillary GC on-line coupled with isotope mass spectrometry, Faulhaber et al. (1997) examined the methyl N-methyl anthranilate content of various mandarin oils.

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Table I. Average percentage composition of mandarin oil produced in Italy over two time periods

Compound	1982/1986	1991/1992
α-thujene	0.888	0.852
α-pinene	2.363	2.277
camphene	0.018	0.018
sabinene	0.259	0.254
β-pinene	1.686	1.611
myrcene	1.702	1.728
α-phellandrene	0.062	0.079
octanal	0.143	0.125
δ-3-carene	-	0.002
α-terpinene	0.442	0.429
p-cymene	0.326	0.288
limonene	69.407	70.492
(Z)-β-ocimene	0.003	0.006
(E)-β-ocimene	0.020	0.020
γ-terpinene	19.925	19.122
cis-sabinene hydrate	0.025	0.025
octanol	0.004	0.003
terpinolene	0.874	0.854
trans-sabinene hydrate	0.046	0.041
linalool	0.115	0.112
nonanal	0.027	0.030
citronellal	0.031	0.034
terpinen-4-ol	0.040	0.041
α-terpineol	0.141	0.127
decanal	0.087	0.093
citronellol + nerol	0.020	0.020
neral	0.008	0.008
geraniol	0.004	trace
2-decenal*	trace	trace
geranial + perillaldehyde	0.047	0.052
thymol	0.053	0.050
undecanal	0.009	0.010
nonyl acetate	trace	0.004
citronellyl acetate	trace	0.004
neryl acetate	trace	0.004
geranyl acetate	trace	0.006
dodecanal	0.024	0.030
methyl N-methyl anthranilate	0.449	0.442
β-caryophyllene	0.098	0.094
α-humulene	0.010	0.010
2-dodecenal*	0.019	0.021
α-selinene	0.043	0.036
α-farnesene*	0.153	0.157
tetradecanal	-	0.005
(Z,E)-farnesol	-	0.003
α-sinensal	0.286	0.273

*correct isomer not identified

The found that its content ranged as follows:

authentic Italian oils (10)[a] 0.26-0.74%
commercial Italian oils (3): 0.45%
commercial Greek oils (2): 0.35-0.38%
commercial Brazilian oil (1): 0.45%
commercial Argentinean oil (1): 0.15%

[a] number of samples examined

In addition, the authors also measured the following isotope ratios: $\Delta^{13}C_{PDB}$ and $\Delta^{15}N_{AIR}$ for the same oils. The isotope ratios are expressed as Δ values (%) versus the standard (PDB for ^{13}C, and air for ^{15}N). The results of these isotope ratio values are shown in Table IV.

In a follow-up paper, Faulhaber et al. (1997) also measured the $\Delta^{13}C_{PDB}$ values of nine individual components and one pair of components in these same oils. The results are shown in Table V. Faulhaber et al. also measured the enantiomeric distribution of α-pinene, β-pinene and limonene using chiral GC in the same 10 authentic mandarin oils and compared these results against those obtained from a number of commercial mandarin oils. The enantiomeric distributions were found to be as follows:

(1R,5R)-(+)-α-pinene (44.2-47.9%) : (1S,5S)-(-)-α-pinene (52.1-55.8%)[a]

(1R,5R)-(+)-α-pinene (36.6-59.8%) : (1S,5S)-(-)-α-pinene (40.2-63.4%)[c]

(1R,5R)-(+)-β-pinene (97.6-99.1%) : (1S,5S)-(-)-β-pinene (0.9-24.%)[a]

(1R,5R)-(+)-β-pinene (57.1-99.2%) : (1S,5S)-(-)-β-pinene (0.8-42.9%)[c]

(4R)-(+)-limonene (97.1-98.4%) : (4S)-(-)-limonene (1.6-2.9%)[a]

(4R)-(+)-limonene (94.9-98.9%) : (4S)-(-)-limonene (1.1-5.1%)[c]

[a] = authentic oils; [c]= commercial oils

Also in 1997, Ruberto et al. determined that a peel oil of the Avana mandarin cultivar produced in Sicily contained the following constituents:

α-thujene (0.66%)
α-pinene (1.79%)
camphene (0.01%)
sabinene (0.22%)
β-pinene (1.36%)
myrcene (1.73%)
α-phellandrene (0.06%)
α-terpinene (0.40%)
β-phellandrene (0.39%)
limonene (73.58%)
(Z)-β-ocimene (trace)
(E)-β-ocimene (0.02%)
γ-terpinene (16.68%)
terpinolene (0.78%)
linalool (0.19%)
citronellal (0.04%)
terpinen-4-ol (0.20%)
α-terpineol (0.38%)
nerol (0.04%)
neral (trace)
geraniol (0.03%)
geranial (0.07%)
thymol (0.11%)
octanal (0.08%)
nonanal (0.01%)
decanal (0.11%)
octanol (0.02%)
nonanol (trace)
methyl N-methylanthranilate (0.48%)
β-caryophyllene (0.06%)
α-humulene (0.03%)
farnesene* (0.04%)
α-sinensal (0.14%)

*correct isomer not identified

Table II. The average polymethoxyflavones in mandarin oils produced by different processes

	Green Oils (Oct/Nov)		Light Oils (Dec)	Red Oils (Jan/Feb)	
Compound	**Torchi[e]**	**Pellatrice**	**Torchi**	**Torchi**	**FMC**
4'5,6,7,8-pentamethoxyflavone[a]	0.198[f]	0.234	0.202	0.229	0.226
3,3',4',5,6,7,8-heptamethoxyflavone	0.032	0.058	0.022	0.030	0.035
3',4',5,6,7,8-hexamethoxyflavone[b]	0.063	0.117	0.049	0.067	0.077
4',5,6,7-tetramethoxyflavone[c]	0.005	0.009	0.004	0.004	0.004
3',4',5,6,7-pentamethoxyflavone[d]	0.002	0.003	0.001	0.001	0.002

[a] = also known as tangeretin; [b] = also known as nobiletin; [c] = also known as tetra-O-methylscutellarein

Table III. Average percentage composition of Italian mandarin oil for the 1982/1991 and 1996/1997 time periods

Compound	1982/1992	1996/1997	Compound	1982/1992	1996/1997
α-thujene	0.876	0.939	octyl acetate	-	trace
α-pinene	2.335	2.488	citronellol + nerol	0.021	0.016
camphene	0.018	0.020	neral	0.009	0.008
heptanol	trace	trace	carvone	-	trace
sabinene + β-pinene	1.942	2.021	geraniol	0.005	trace
6-methyl-5-hepten-2-one	-	trace	2-decenal*	-	trace
myrcene	1.708	1.734	geranial	0.048	0.019
α-phellandrene	0.069	0.054	perillaldehyde	-	0.029
octanal	0.138	0.187	thymol	0.052	0.059
δ-3-carene	0.002	trace	undecanal	0.009	0.001
α-terpinene	0.438	0.450	nonyl acetate	0.004	0.009
p-cymene	0.317	0.205	citronellyl acetate	0.004	0.002
limonene	69.685	68.174	neryl acetate	0.005	0.003
(Z)-β-ocimene	0.004	0.003	α-copaene	-	0.004
(E)-β-ocimene	0.020	0.020	geranyl acetate	0.006	0.003
γ-terpinene	19.718	20.808	β-cubebene	-	0.005
cis-sabinene hydrate	0.026	0.026	dodecanal	0.026	0.020
octanol	0.004	trace	methyl N-methyl anthranilate	0.450	0.458
terpinolene	0.870	0.900	β-caryophyllene	0.097	0.100
trans-sabinene hydrate	0.045	0.047	*trans*-α-bergamotene	-	trace
linalool	0.015	0.132	α-humulene	0.010	0.008
nonanal	0.028	0.032	2-dodecenal*	0.020	0.020
p-mentha-1,3,8-triene	-	trace	germacrene D	-	0.003
trans-pinene hydrate†	-	0.002	valencene	-	0.002
cis-limonene oxide	-	trace	α-selinene	0.041	0.044
trans-limonene oxide	-	trace	α-farnesene*	0.154	0.186
camphor	-	trace	β-bisabolene	-	trace
citronellal	0.032	0.031	δ-cadinene	-	0.005
terpinen-4-ol	0.042	0.042	tetradecanal	0.006	0.005
p-cymen-8-ol	-	0.002			
α-terpineol	0.139	0.144			
decanal	0.090	0.097			

* correct isomer not identified

† probable misidentification of trans-p-menth-2-en-1-ol

Table IV. $\Delta^{13}C_{PDB}$ and $\Delta^{15}N_{AIR}$ values for methyl N-methyl anthranilate in mandarin oils of various origin

Sample Type	$\Delta^{13}C_{PDB}$	$\Delta^{15}N_{AIR}$
Italian oils[a] (0.36)	–29.54 (0.12)[b] to –31.07 (0.03)	3.62 (0.19) to 4.66
Italian oils[c] (0.20)	–29.97 (0.10) to –32.42 (0.06)	3.16 (0.08) to 4.78
Greek oils[c] (0.05)	–29.11 (0.11) to –30.37 (0.21)	7.40 (0.31) to 7.44
Brazilian oil[c]	–32.66 (0.14)	6.04 (0.25)
Argentinean oil[c]	–32.66 (0.13)	8.32 (0.26)

[a] = authentic oil;
[b] = standard deviation;
[c] = commercial oils
[d] = also known as sinesetin
[e] = process for oil isolation

Della Porta et al. (1997) performed a GC/MS analysis on an Italian mandarin oil prior to fractionation using supercritical CO_2 desorption. The composition of the original oil was as follows:

α-thujene (0.91%)
α-pinene (2.29%)
camphene (0.05%)
β-pinene (1.88%)
myrcene (1.73%)
δ-2-carene (0.02%)
α-phellandrene (0.48%)
p-cymene (4.25%)
limonene (66.41%)
(E)-β-ocimene (0.03%)
(Z)-β-ocimene (0.01%)

Table V. $\Delta^{13}C_{PDB}$ values for a number of mandarin oil constituents

Compound	I_a	I_c	G_c	B_c	A_c
α-thujene	-27.18 to -28.60	-27.37 to -29.29	-27.06 to -27.35	-30.53	-28.94
α-pinene/sabinene	-28.76 to -30.08	-28.87 to -30.56	-28.20 to -29.03	-31.30	-30.62
myrcene	-25.83 to -27.49	-26.32 to -27.94	-25.35 to -26.48	-28.55	-27.95
octanal	-28.30 to -30.90	-28.48 to -29.81	-28.25 to -29.31	-31.01	-30.22
limonene	-29.40 to -31.01	-30.10 to -30.92	-29.36 to -29.41	-32.36	-31.91
γ-terpinene	-28.93 to -30.16	-29.66 to -30.49	-28.34 to -29.10	-32.00	-30.95
terpinolene	-28.63 to -30.37	-29.06 to -30.56	-28.54 to -29.08	-31.29	-31.47
linalool	-26.39 to -28.60	-27.00 to -28.39	-26.42 to -27.10	-29.68	-29.40
methyl N-methyl anthranilate	-29.54 to -31.07	-29.97 to -32.42	-29.11 to -30.37	-32.66	-32.66
α-sinensal	-26.41 to -28.83	-26.90 to -27.99	-26.05 to -26.81	-30.35	-30.22

Table VII. Enantiomeric distribution of six chiral constituents of some commercial mandarin oils

Compound	1	2	3	4	5	6	7	8	9	10	11
(1R,5R)-(+)-β-pinene	29.3	40.3	71.1	94.2	84.0	94.6	56.8	49.6	97.0	97.8	97.4
(1S,5S)-(-)-β-pinene	70.7	59.7	28.9	5.8	16.0	5.4	43.2	50.4	3.0	2.2	2.6
(1R,5R)-(+)-sabinene	82.2	37.6	58.3	78.6	82.2	96.6	86.2	75.1	80.3	81.3	85.5
(1S,5S)-(-)-sabinene	17.8	62.4	41.7	21.4	17.8	3.4	13.8	24.9	19.7	18.7	14.5
(4R)-(+)-limonene	95.5	98.1	98.0	98.2	98.3	99.3	95.4	95.0	97.7	98.0	98.0
(4S)-(-)-limonene	4.5	1.9	2.0	1.8	1.7	0.7	4.6	5.0	2.3	2.0	2.0
(3R)-(-)-linalool	26.5	19.2	15.3	14.0	12.4	3.5	18.0	19.1	17.6	13.7	8.4
(3S)-(+)-linalool	73.5	80.8	84.7	86.0	87.6	96.5	82.0	80.9	82.1	86.3	91.6
(4R)-(-)-terpinen-4-ol	82.7	85.2	87.6	85.4	85.1	61.1	75.5	74.2	83.6	83.4	81.9
(4S)-(+)-terpinen-4-ol	17.3	14.8	12.4	14.6	14.9	38.9	24.5	25.8	16.4	16.6	18.1
(4R)-(+)-α-terpineol	56.1	25.0	24.9	53.9	46.8	75.8	63.8	53.8	32.0	30.8	42.6
(4S)-(–)-α-terpineol	43.9	75.0	75.1	46.1	53.2	24.2	36.2	46.2	68.0	69.2	57.4

γ-terpinene (19.17%)
terpinolene (1.38%)
p-mentha-1,3,8-triene (trace)
γ-terpineol (0.01%)
cis-p-menth-2-en-1-ol (trace)
linalool (0.13%)
cis-sabinene hydrate (trace)
cis-β-terpineol (trace)
isopulegol (trace)
trans-β-terpineol (trace)
terpinen-4-ol (0.04%)
α-terpineol (0.12%)
citronellol (trace)
hexanol (0.02%)
3-octanol (0.12%)
decanol (0.03%)
benzaldehyde (0.02%)
3-methylbenzaldehyde (trace)
nonanal (trace)
geranial (trace)
perillaldehyde (trace)
terpinen-4-yl acetate (0.1%)
methyl N-methylanthranilate (0.50%)
thymol (trace)
β-caryophyllene (0.08%)
α-humulene (trace)
β-selinene (trace)
α-farnesene* (0.30%)
δ-cadinene (trace)

*correct isomer not identified

After desorption using supercritical CO_2, a residue remained which contained numerous constituents, many of which could not be determined in the original oil. This residue was found to contain:

α-thujene (0.04%)
α-pinene (0.02%)
camphene (0.01%)
β-pinene (0.01%)
myrcene (0.50%)
α-phellandrene (0.15%)
p-cymene (1.18%)
limonene (2.44%)
(E)-β-ocimene (0.25%)
(Z)-β-ocimene (0.10%)
γ-terpinene (0.62%)
terpinolene (0.57%)
p-mentha-1,3,8-triene (0.03%)
γ-terpineol (0.11%)
cis-p-menth-2-en-1-ol (0.04%)
linalool (3.25%)
cis-sabinene hydrate (0.17%)
cis-β-terpineol (0.20%)
isopulegol (0.46%)
trans-β-terpineol (0.15%)
terpinen-4-ol (1.82%)
α-terpineol (11.19%)
citronellol (1.66%)
hexanol (0.04%)
3-octanol (0.36%)
octanol (0.63%)
decanol (0.81%)
dodecanol (0.45%)
tridecanol (0.05%)
heneicosanol (0.13%)
benzaldehyde (0.01%)
octanone* (0.08%)
3-methylbenzaldehyde (0.01%)
nonanal (0.12%)
cis-dihydrocarvone (0.05%)
neral (0.19%)
piperitone (0.20%)
geranial (2.30%)
perillaldehyde (1.76%)
terpinen-4-yl acetate (0.38%)
methyl N-methylanthranilate (24.05%)
citronellyl formate (0.19%)
thymyl acetate (0.24%)
neryl acetate (0.40%)
benzyl benzoate (0.36%)
thymol (4.86%)
1-decene (0.03%)
2-decene* (0.28%)
1-dodecene (0.39%)
1-hexadecene (0.13%)
heneicosane (0.06%)
docosane (0.54%)
tricosane (0.81%)
tetracosane (0.74%)
pentacosane (0.53%)
hexacosane (0.44%)
nonacosane (0.38%)
β-elemene (0.16%)
β-caryophyllene (1.86%)
α-humulene (0.17%)
β-selinene (0.39%)
α-farnesene* (2.63%)
γ-cadinene (0.15%)
germacrene B (0.19%)
spathulenol (0.05%)
globulol (0.08%)
methyl linoleate (0.27%)
methyl oleate (3.17%)
citropten (0.76%)
bergapten (0.07%)
tangeretin (10.30%)
sinesetin (0.72%)
nobiletin (2.04%)
squalene (0.30%)
stigmasterol (0.96%)

*correct isomer not identified

Omer et al. (1997) reported the results of an analysis of the peel oil of a mandarin cultivar grown in Egypt. The compounds identified in this oil were as follows:

α-pinene (3.53%)
myrcene (5.01%)
limonene (70.09%)
α-terpinene[a] (14.67%)
p-cymene (0.96%)
linalool (0.87%)
citronellol (0.51%)
terpinen-4-ol (0.67%)
neral (0.42%)
geranial (0.36%)
methyl anthranilate[b] (1.82%)

[a] misidentification of γ-terpinene
[b] misidentification of methyl N-methyl anthranilate

The following year, Caccioni et al. (1988) analyzed the cold-pressed oil of the

Avana cultivar of mandarin. They found that it contained:

α-thujene (0.64%)
α-pinene (1.78%)
camphene (0.02%)
sabinene (0.17%)
β-pinene (1.41%)
octanal (0.06%)
myrcene (1.71%)
α-phellandrene (0.07%)
δ-3-carene (trace)
α-terpinene (0.24%)
β-phellandrene (0.52%)
p-cymene (0.23%)
limonene (72.71%)
(Z)-β-ocimene (trace)
(E)-β-ocimene (0.02%)
γ-terpinene (17.17%)
octanol (0.03%)
terpinolene (0.82%)
nonanal (0.02%)
linalool (0.16%)
citronellal (0.02%)
terpinen-4-ol (0.27%)
α-terpineol (0.37%)
decanal (0.11%)
nerol (0.07%)
neral (trace)
geraniol (0.03%)
geranial (0.08%)
thymol (0.02%)
methyl N-methyl anthranilate (0.46%)
β-caryophyllene (0.06%)
α-humulene (0.02%)
(E,E)-α-farnesene (0.05%)

Mondello et al. (1998) used a multi-dimensional double oven GC-GC system to examine the enantiomeric distribution of six chiral constituents of mandarin oil. The authors compared the distribution of these six constituents in oils produced from two different mandarin cultivars as well as oils produced by the Pelatrice, Torchi and FMC processes, and some distilled oils. The results of this comparison can be seen in Table VI. In addition, the authors also examined the enantiomeric distribution of these six chiral compounds in eleven commercial samples of mandarin oil. The results are shown in Table VII. As can be seen, samples 1,2,3,5,7 and 8 appear to be adulterated based on the enantiomeric distribution of β-pinene. To assist the reader in understanding how some of these enantiomeric distribution results could arise, the authors presented the enantiomeric distribution of the same six compounds in lemon, orange, clementine and mandarin oils diluted with various amounts of these three oils (Table VIII).

In 1999, Oberhofer et al. examined the oil of mandarin produced in Italy and compared it to a commercial sample obtained in Austria. In addition, they compared the headspace of the Italian oil with that obtained after 50% of the oil had evaporated at 65°C to duplicate the aroma generated from an aroma lamp used in aromatherapy. Their results, which can be seen in Table IX, revealed that the aroma of this latter headspace was not typical of

Table VI. Enantiomeric distribution of six chiral constituents of mandarin oil produced by different processes

Compound	Pelatrice	Torchi	FMC	Distilled
(1R,5R)-(+)-β-pinene	98.3	97.7-98.4	97.4-97.6	97.1-97.7
(1S,5S)-(-)-β-pinene	1.7	1.6-2.3	2.4-2.6	2.3-3.9
(1R,5R)-(+)-sabinene	79.2	78.7-79.2	78.6-78.8	77.8-79.9
(1S,5S)-(-)-sabinene	20.8	20.8-21.3	21.2-21.4	20.1-22.2
(4R)-(+)-limonene	97.8	97.8	97.9-98.0	97.8-98.3
(4S)-(-)-limonene	2.2	2.2	2.0-2.1	1.7-2.2
(3R)-(-)-linalool	16.8	14.1-16.8	13.1-14.0	16.3-20.4
(3S)-(+)-linalool	83.2	83.2-85.9	86.9-86.9	79.6-83.7
(4R)-(-)-terpinen-4-ol	87.3	85.9-89.0	88.5-88.6	71.3-74.7
(4S)-(+)-terpinen-4-ol	12.7	11.0-14.1	11.4-11.5	25.3-28.7
(4R)-(+)-α-terpineol	25.3	23.7-24.3	28.7-28.9	26.6-38.8
(4S)-(-)-α-terpineol	74.7	75.7-76.1	71.1-71.3	61.2-73.4

Table VIII. Enantiomeric distribution of six chiral constituents of citrus oils and some blends

Compound	1	2	3	4	5	6	7
(1R,5R)-(+)-β-pinene	5.1	50.2	90.3	42.2	97.7	22.9	95.8
(1S,5S)-(-)-β-pinene	94.9	49.8	9.7	57.8	2.3	77.1	4.2
(1R,5R)-(+)-sabinene	15.1	45.6	75.0	96.8	85.8	90.1	82.5
(1S,5S)-(-)-sabinene	84.9	54.4	25.0	3.2	14.2	9.9	17.5
(4R)-(+)-limonene	98.1	97.8	98.0	99.4	98.3	99.3	98.1
(4S)-(-)-limonene	1.9	2.2	2.0	0.6	1.7	0.7	1.9
(3R)-(-)-linalool	71.5	26.9	19.3	4.9	12.4	7.5	17.1
(3S)-(+)-linalool	28.5	73.1	80.7	95.1	87.6	92.5	82.9
(4R)-(-)-terpinen-4-ol	80.3	84.3	85.6	35.1	85.0	53.6	84.9
(4S)-(+)-terpinen-4-ol	19.7	15.7	14.4	64.9	15.0	46.4	15.1
(4R)-(+)-α-terpineol	22.6	25.6	26.5	91.8	30.8	86.9	28.2
(4S)-(-)-α-terpineol	77.4	74.4	73.5	8.2	69.2	13.1	71.8

Legend:
1. lemon oil
2. mandarin oil/lemon oil (90:1)
3. mandarin/lemon oil (99:1)
4. orange oil
5. mandarin oil/orange oil (80:20)
6. clementine oil
7. mandarin oil/clementine oil (90:10)

mandarin. It was terpenic and fatty rather than the characteristic mandarin odor. In addition, based on the comparison of the quantitative data, it would appear that the original Austrian commercial sample of mandarin oil might have been adulterated.

This same year, Sawamura et al. (1999) analyzed a peel oil of mandarin produced in Japan. The constituents found in this oil were as follows:

α-pinene (1.2%)
β-pinene (0.3%)
myrcene (1.8%)
limonene (89.9%)
γ-terpinene (4.6%)
p-cymene (0.1%)
terpinolene (0.2%)
octanal (0.2%)
citronellal (0.1%)
decanal (0.1%)
linalool (0.6%)
octanol (trace)
neral (trace)
α-terpineol (0.1%)
geranial (trace)
geranyl acetate (trace)
citronellol (trace)
nerol (trace)

Using a fast HPLC procedure in which the analysis time was reduced from 20-45 min. to 7 min., Bonaccorsi et al. (1999) determined that the non-volatile oxygen heterocyclic compounds in Italian mandarin oil were as follows:

sinesetin
nobiletin
tetra-O-methylscutellarein
3,3',4',5,6,7-hexamethoxyflavone
tangeretin
imperatorin

A combination of this technique, combined with GC/MS and chiral GC, would allow the analyst to authenticate a purchased mandarin oil.

More recently, Lota et al. (2000) analyzed the cold-pressed oil composition of 41 cultivars of mandarin using a combination of analytical techniques including GC, GC/MS and ^{13}C-NMR. The compounds identified on the cultivar oils were as follows:

α-thujene (0-0.8%)
α-pinene (0.1-2.1%)
β-pinene (0-1.5%)
sabinene (0.1-1.3%)
δ-3-carene (0-trace)
myrcene (1.3-1.8%)
α-terpinene (0-0.6%)
limonene (52.2-96.2%)
β-phellandrene (0.2-0.7%)
γ-terpinene (0-36.7%)
(E)-β-ocimene (0-0.5%)
p-cymene (0-0.8%)
terpinolene (0-1.7%)
octanal (0-0.5%)
cis-limonene oxide (0-0.3%)
trans-limonene oxide (0-0.2%)
trans-sabinene hydrate (0-trace)
octyl acetate (0.03%)
citronellal (0-0.2%)
decanal (0-0.6%)
linalool (0-2.5%)

β-elemene (0-0.2%)
(E)-β-farnesene (0-0.9%)
α-terpinyl acetate (0-0.2%)
α-terpineol (0-0.4%)
germacrene D (0-0.4%)
δ-cadinene (0-0.1%)
geranyl acetate (0-0.2%)
citronellol (0-0.1%)
geraniol (0-0.1%)
methyl N-methyl anthranilate (0-1.1%)
thymol (0-0.5%)
β-sinensal (0-0.2%)
α-sinensal (0-0.7%)

It is worth noting that only two cultivar oils ("Willowleaf x Blood seedling" and "Federici") contained 0.4% and 1.1% of methyl N-methyl anthranilate, respectively.

Also, in 2000 Verzera et al used both GC and GC/MS to analyze mandarin oil produced from the "Nova" cultivar in Uruguay. Oils produced in the laboratory from fruit harvested at two different times were found to contain:

α-thujene (trace)
α-pinene (0.48-0.50%)
camphene (trace)
sabinene (0.34-0.35%)
β-pinene (0.14%)
myrcene (1.93-1.98%)
α-phellandrene (0.03-0.04%)
octanol (0.16-0.17%)
δ-3-carene (0.17-0.19%)
α-terpinene (trace)
limonene (93.1-94.2%)
(Z)-β-ocimene (0.01-0.02%)
(E)-β-ocimene (0.38-0.44%)
γ-terpinene (0.01-0.02%)
cis-sabinene hydrate (trace-0.02%)
octanol (trace-0.04%)
p-mentha-2,4(8)-diene (trace)
terpinolene (0.03%)
trans-sabinene hydrate (trace)
linalool (0.67-0.88%)
nonanal (0.05%)
cis-limonene oxide (0.01-0.05%)
trans-limonene oxide (0.01-0.04%)
(E)-myroxide (0.01-0.02%)
citronellal (0.01%)
isopinocamphone (0.01-0.02%)
terpinen-4-ol (trace-0.01%)
α-terpineol (0.060.08%)
dihydrocarveol (0.01-0.03%)
decanal (0.30-0.32%)
octyl acetate (trace)
trans-carveol (0.01-0.02%)
nerol (trace-0.01%)
citronellol (trace-0.01%)
cis-carveol (trace)
neral (0.01-0.03%)
carvone (0.02-0.07%)
geranial (trace)
(E)-2-decenal (0.01%)
geranial (0.04-0.06%)
perillaldehyde (0.02-0.04%)
perillyl alcohol (0.02-0.03%)
(E,Z)-2,4-decadienal (trace)
neodihydrocarvyl acetate (trace)
undecanal (0.02%)
(E,E)-2,4-decadienal (0.03%)
δ-elemene (0.01%)
α-terpinyl acetate (trace)
citronellyl acetate (trace)
neryl acetate (trace-0.01%)
α-copaene (0.02-0.03%)
geranyl acetate (trace)
β-cubebene (0.01%)
β-elemene (0.01%)
dodecanal (0.06-0.07%)
decyl acetate (0.01%)
β-caryophyllene (0.01%)
β-gurjunene (0.01%)
α-guiaene (trace)
α-humulene (0.02%)
(E)-β-farnesene (trace-0.01%)
(E)-2-dodecenal (0.01-0.02%)
γ-muurolene (trace)
germacrene D (0.09-0.11%)
bicyclogermacrene (trace)
α-bulnesene (trace)
(E,E)-α-farnesene (0.02-0.03%)
cubebol (trace)
δ-cadinene (0.04-0.05%)
elemol (0.01-0.02%)
germacrene B (0.01%)
(E)-nerolidol (trace)
germacrene D-4-ol (trace-0.01%)
tetradecanal (trace-0.01%)
β-sinensal (0.01-0.02%)
α-sinensal (0.02-0.04%)
nootkatone (0.01%)

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Table IX. Percentage composition of two mandarin oils and the headspace of the authentic oil under two sets of conditions

Compound	Austrian Commercial Oil	Italian Authentic Oil	Fresh Headspace	Heated Headspace
α-thujene	0.23	0.57	0.37	trace
α-pinene	1.03	1.68	1.18	trace
camphene	trace	-	-	-
sabinene	0.32	trace	trace	trace
β-pinene	0.49	1.41	1.14	trace
myrcene	1.85	1.72	2.29	trace
δ-3-carene	0.14	trace	trace	trace
α-terpinene	0.12	0.27	0.22	trace
p-cymene	0.65	1.00	2.17	trace
limonene	88.89	77.44	79.74	4.09
(E)-β-ocimene	trace	-	-	-
γ-terpinene	4.83	14.65	12.09	trace
terpinolene	0.36	0.72	0.59	trace
linalool	0.33	0.02	0.16	5.10
citronellal	-	0.02	trace	trace
decanal	0.13	0.21	trace	14.96
neral	0.16	0.09	trace	trace
geranial	trace	-	-	-
geraniol	trace	-	-	-
linalyl acetate	trace	-	-	-
geranyl acetate	0.15	0.31	trace	11.23
β-caryophyllene	trace	0.06	trace	5.73
β-bisabolene	-	0.11	trace	8.07

Table X. Comparative percentage composition of a steam distilled oil and a supercritical fluid extract (SFE) of lavandin flowers

Compound	Oil	SFE
γ-terpinene	-	0.6-1.0
limonene	1.4	0.5-1.6
linalool	46.0	32.9-33.8
terpinen-4-ol	2.1	1.7-1.8
borneol + camphor	9.2	8.2
α-terpineol	3.6	-
linalyl acetate	20.4	37.5-39.2
bornyl acetate + lavandulyl acetate	5.6	4.7-4.8
β-caryophyllene	1.0	0.8-1.0
geranyl acetate	4.3	5.6-6.2
β-farnesene*	1.1	2.2-2.6

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Lavandin Oil

In 1991, Bernreuther and Schreier used an on-line multidimensional GC/MS-chiral GC system to determine that the enantiomeric distribution of linalool in two samples of lavandin oil was

(3R)-(-)-(61.8-96.2%) :
(3S)-(+)-(3.8-38.2%).

Four years later, Bourrel et al. (1995) used GC/MS and GC to determine the composition of lavandin oil prior to using it in an antimicrobial screening test. They reported that the oil had the following composition:

α-thujene (0.4%)
camphene (0.8%)
sabinene (0.7%)
β-pinene (0.5%)
p-cymene (0.6%)
1,8-cineole (36.0%)
camphor (27.9%)
borneol (12.39%)
cryptone (1.9%
terpinen-4-ol (1.0%)
α-terpineol (0.4%)
α-terpinyl acetate (0.4%)
bornyl acetate (0.5%)
bicyclogermacrene (1.2%)
caryophyllene oxide (1.7%)
α-cadinene (0.3%)
T-cadinol (2.4%)
isoeugenyl acetate* (0.3%)

*correct isomer not identified

This reviewer does not know what was the true origin of this supposedly lavandin oil, because being devoid of linalool and linalyl acetate, it can hardly be a lavandin or even a lavender oil.

Lavandin oil produced in Shaanxi (China) was analyzed by Zhu et al. (1995) using GC/MS. The oil composition was found to be:

α-pinene (7.91%)
camphene (1.04%)

benzaldehyde (0.13%)
sabinene (0.28%)
β-pinene (0.67%)
2-octanone (1.18%)
hexyl acetate (0.10%)
linalool (5.55%)
p-menth-3-en-1-ol (0.29%)
camphor (2.39%)
isononyl acetate (33.79%)
borneol (0.89%)
β-terpineol* (0.45%)
terpinen-4-ol (0.10%)
α-terpineol (9.09%)
carvone (0.12%)
linalyl acetate (9.15%)
geranyl acetate (0.25%)
benzyl benzoate (1.94%)

Table XI. Comparative Main Component Percentage Composition of Argentinean Produced and Commercial Oils of Lavandin

Compound	Abrialis		Grosso		Super	Argentinean
1	2	3	4	5	6	
1,8-cineole	6.8	7.4-8.0	6.4	5.0-6.0	3.0	6.2
linalool	37.9	31.7-33.9	27.9	26.1-31.8	29.4	44.6
camphor	6.8	9.1-11.4	9.7	7.0-7.9	5.3	9.2
linalyl acetate	22.3	24.0-25.8	30.3	29.0-35.3	44.3	8.4
lavandulyl acetate	2.9	1.3-1.7	2.6	1.9-2.5	1.7	1.9
terpinen-4-ol	3.8	0.6-0.8	0.8	0.1-2.2	0.1	0.3
lavandulol	1.0	0.4-0.6	0.4	0.3-0.4	0.2	0.5
α-terpineol	1.3	0.5-0.6	1.1	0.4-2.6	0.2	5.5
borneol	3.1	2.5-2.6	2.8	1.8-2.4	1.7	3.1

1 = Argentinean grown, La Cumbre (Córdoba)
2 = Commercial oils
3 = Argentinean grown, El Bolsón (R. Negro)
4 = Commercial oils
5 = Commercial oil
6 = Argentinean grown, Cerrillos (Salta) selection

As can be seen from the above results, this is certainly not a typical lavandin oil. There are three possible scenarios from which such results could be obtained. First of all, a number of the constituents such as 2-octanone, p-menth-3-en-1-ol, isononyl acetate, β-terpineol and benzyl benzoate could have been identified in error; secondly, the oil used for the analysis had been subjected to adulteration; or thirdly, the oil was produced from other than lavandin flower heads. It is highly unlikely that extrinsic conditions could influence the growth of lavandin plants so that such an unusual oil composition would result.

In 1996, Ravid et al. examined the enantiomeric distribution of borneol in lavandin oil. Using chiral GC analysis on a permethylated β-cyclodextrin column, borneol, which was found in 2.1-3.0% in the oil, had the following distribution:

(1R)-(+)-borneol (96-97%) : (1S)-(-)-borneol (3-4%)

The enantiomeric distribution of linalool and linalyl acetate in French lavandin oil was determined by Casabianca and Graff (1996) to be:

(3R)-(-)-linalool (97.0-100.0%) :
(3S)-(+)-linalool (0-0.3%)

(3R)-(-)-linalyl acetate (97.5-100.0%) :
(3S)-(+)-linalyl acetate (0-2.5%)

Also in 1996, Simandi et al. found that a hydrodistilled oil of Hungarian lavandin contained as major constituents:

linalool (46.0%
α-terpineol (3.6%)
linalyl acetate (20.4%)
geranyl acetate (7.2%)

They compared this oil to a supercritical fluid CO_2 extract of lavandin and found that it contained:

linalool (31.0%)
linalyl acetate (37.5%)
geranyl acetate (7.2%)

They did not find any α-terpineol in the CO_2 extract. It should be pointed out that the increased level of linalyl acetate in the extract was the result of not hydrolyzing it, unlike what happened during hydrodistillation.

This same year, Oszagyán et al. (1996) compared the main component composition of lavender oil with a supercritical fluid CO_2 extract of lavandin flowers. A summary of the results of this study are shown in Table X. As can be seen, there are quantitative differences between the oil and extracts made using slightly different conditions. The major difference is they hydrolysis of linalyl acetate during steam distillation resulting in a lower linalyl acetate and higher linalool content of the oil compared to the extract.

More recently, Mizrahi et al. (1999) compared the composition of commercial lavandin oil produced from different cultivars with oils produced from the same cultivars grown in Argentina. A summary of their results is presented in Table IX. As can be seen, the composition of the Argentinean oils were fairly comparable to the imported commercial oils. Perhaps the only anomalous oil was that produced in Cerrillos in which the linalyl acetate content was very low and the linalool content was too high.

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Table XII. Linalool and 1,8-cineole contents of *Thymus mastichina* oils and extracts (linalool-chemotype) produced by different processes

Compound	Hydrodistilled Oil	Steam Distilled Distilled Oil	Microwave Extract	Hexane Extract	SFE CO_2
linalool	74.58	76.79	65.19	65.63	71.51
1,8-cineole	1.90	1.41	1.72	0.61	1.15

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Spanish Marjoram Oil

In 1986, Morales Valverde examined the composition of two oils obtained from *Thymus mastichina* ssp. *mastichina* and determined that they contained the following constituents:

α-pinene (2.6-3.3%)
camphene (0.1-1.4%)
β-pinene (2.7-5.3%)
sabinene (0.8-2.2%)
myrcene (0.9-1.3%)
limonene (0.1-2.4%)
1,8-cineole (60.1-66.5%)
γ-terpinene (0.2-0.6%)
p-cymene (1.0-3.4%)
camphor (0-1.0%)
linalool (6.2-14.5%)
linalyl acetate (0-1.0%)
β-caryophyllene (trace-1.0%)
terpinen-4-ol (0.1-0.9%)
α-terpineol (2.1-2.6%)
borneol (trace-1.0%)
allo-aromadendrene (0-0.9%)
thymol (trace-1.9%)

Nine years later, Tomei et al. (1995) analyzed an oil of T. *mastichina* using GC and GC/MS. The oil, which was produced from plant material collected from Andaluçia (Spain) was found to possess a typical composition, which was described as follows:

α-pinene (2.63%)
camphene (2.45%)
β-pinene (2.70%)

Table XIII. Comparative percentage composition of a hydrodistilled oil with a subcritical water extract of *Thymus mastichina*

Compound	Hydrodistilled Oil	Supercritical Water Extract
α-pinene	0.91	0.04
β-pinene	1.62	0.15
myrcene	1.85	0.08
1,8-cineole	24.81	18.87
linalool	0.76	1.36
myrcenol	0.75	0.87
terpinen-4-ol	0.39	0.71
α-terpineol	2.20	2.92
geraniol	1.31	1.77
geranyl acetate	1.34	0.76

myrcene (1.92%)
limonene (1.35%)
1,8-cineole (39.90%)
γ-terpinene (2.20%)
camphor (1.37%)
linalool (19.41%)
β-caryophyllene (0.43%)
α-terpineol (4.04%)
borneol (0.52%)
geraniol (0.71%)
thymol (0.51%)
carvacrol (trace)

Oils obtained from a linalool chemotype of *T. mastichina* produced from plant material collected over a couple of seasons in Portugal were analyzed (Vernancio et al. 1996) by GC and GC/MS and found to contain:

α-pinene (1.00-2.47%)
camphene (2.24-5.69%)
β-pinene (0.33-0.72%)
myrcene (0.24-0.59%)
p-cymene (0.28-0.76%)
1,8-cineole (1.30-11.97%)
limonene (0.23-0.68%)
linalool (60.99-77.42%)
camphor (3.50-7.61%)
borneol (3.01-4.87%)
α-terpineol (0.20-0.66%)
linalyl acetate (0.30-0.68%)

In addition, the authors compared the linalool and 1,8-cineole contents of oils and extracts of this same linalool chemotype produced by different processes. these results can be seen in Table XII.

In 1997, Soriano et al. analyzed an oil of Spanish *T. mastichina* and found that it possessed the following composition:

α-thujene (trace)
α-pinene (2.0%)
camphene (0.4%)
β-pinene (2.6%)
sabinene (2.2%)
myrcene (1.4%)
α-terpinene (0.1%)
limonene (2.1%)
1,8-cineole (42.6%)
(Z)-β-ocimene (trace)
γ-terpinene (0.1%)
(E)-β-ocimene (0.2%)
p-cymene (0.3%)
terpinolene (0.1%)
cis-linalool oxide† (0.8%)
trans-sabinene hydrate (0.4%)
trans-linalool oxide† (0.8%)
camphor (trace)
linalool (32.8%)
linalyl acetate (0.5%)
β-caryophyllene (0.4%)
terpinen-4-ol (0.3%)
cis-verbenol (0.1%)
δ-terpineol (1.1%)
α-terpineol (3.0%)
borneol (trace)

geranial (0.4%)
geranyl acetate (0.2%)
citronellol (0.1%)
geraniol (0.1%)
caryophyllene oxide (0.3%)
viridiflorol (0.35)
elemol (0.3%)
spathulenol (0.2%)
thymol (trace)
carvacrol (trace)
α-cadinol (trace)

† furanoid form

Two years later, Jiménez Carmona et al. (1999) used a continuous subcritical water extraction procedure to produce a volatile concentrate of Spanish marjoram. They compared the composition of this subcritical water extract with an oil produced from the same batch of plant material by hydrodistillation. The results of this study can be found in Table XIII.

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Moroccan Tansy Oil

Over the past decade, an oil of Moroccan tansy, Moroccan blue chamomile or Moroccan tanacetum (*Tanacetum annum* L.) has become a commercial entity. In 1997, Greche et al. examined the compositions of 71 samples of oil prepared from plants harvested from eight different locations at three different times of the year. A summary of the components found in these oils can be seen as follows:

α-thujene (0.01-0.16%)
α-pinene (0.74-1.79%)
camphene (0.29-0.91%)
sabinene (4.12-8.60%)
β-pinene (1.64-4.97%)
myrcene (1.14-13.83%)
α-phellandrene (1.38-4.75%)
α-terpinene (0.16-1.19%)
p-cymene (1.14-3.37%)
limonene (0.83-2.09%)
1,8-cineole (0.38-1.73%)
γ-terpinene (0.17-0.53%)
terpinolene (0.04-0.23%)
linalool (0.02-0.30%)
2-methylbutyl 2-methylbutyrate (0.03-0.34%)
normenthone† (0.01-0.50%)
camphor (3.15-12.44%)
borneol (0.49-4.26%)
terpinen-4-ol (0.90-2.78%)
α-terpineol (0.18-0.76%)
3-isopropylbenzaldehyde (trace-0.05%)
carvone (trace-0.46%)
carvotanacetone (trace-0.19%)
thymol (0.79-1.79%)
decanoic acid (0.01-0.09%)
α-copaene (trace)
9-(1-methylethylidene) cycloundeca-1,5-diene† (0.01-0.08%)
β-elemene (0.15-0.73%)
β-caryophyllene (0.81-1.63%)
α-humulene (0.04-0.23%)
γ-muurolene + γ-curcumene (0.03-0.16%)
germacrene D (0.45-1.62%)
7α,5-hydroaristolochene† (0.26-0.80%)
γ-cadinene (0.31-0.56%)
δ-cadinene (0.12-0.64%)
elemol (0.18-0.71%)
caryophyllene oxide (0.48-1.00%)
2,5,8-trimethylnaphthol (0.60-3.07%)
cubenol + γ-eudesmol (0.72-2.70%)
hinesol (0.30-0.85%)
methyl jasmonate (0.01-0.99%)
β-eudesmol (3.50-6.68%)
α-cadinol + β-bisabolol (0.14-0.41%)
α-bisabolol (0.04-0.37%)
chamazulene (17.05-38.34%)
4',4'-dimethylbiphenyl + 3',3'-dimethylbiphenyl (0.01-0.12%)†
tetradecanoic acid (0.02-0.28%)

† questionable component identity

In a follow-up paper, Greche et al. (1997) performed a more detailed analysis of Moroccan tansy oils using GC and GC/MS. The components identified in a range of samples were as follows:

tricyclene (trace)
ethyl 3-methyl-2-butenoate (trace)
α-thujene (0.01-0.16%)
α-pinene (0.74-1.80%)
camphene (0.29-0.92%)
propyl isovalerate (trace)
benzaldehyde (trace)
sabinene (4.12-8.60%)
β-pinene (1.65-4.98%)
myrcene (1.15-13.83%)
octanal (trace-0.30%)
isobutyl 2-methylbutyrate (0.13-0.55%)
α-phellandrene (1.38-4.76%)
δ-3-carene (trace)
α-terpinene (0.17-1.19%)
2-methylbutyl isobutyrate (trace)
o-cymene (trace)
p-cymene (1.15-3.38%)
limonene (0.83-2.09%)
1,8-cineole (0.39-1.73%)
2,2,6-trimethylcyclohexanone (trace-0.27%)
p-tolualdehyde (trace)
phenylacetaldehyde (trace-0.29%)
butyl 2-methylbutyrate (trace-0.09%)
γ-terpinene (0.17-0.53%)
cis-linalool oxide-furanoid (0.01-0.22%)
α-p-dimethylstyrene (0.03-0.29%)
terpinolene (0.05-0.23%)
ethyl heptanoate (0.03-0.35%)
linalool (0.03-0.30%)
α-thujone (trace)
6-ethenyl-2,2,6-trimethyl-2H-pyran-3(4H)-one† (0.01-0.26%)
2-methylbutyl 2-methylbutyrate (trace-0.18%)
perillene (trace)
α-fenchol (trace-0.04%)
β-thujone (trace-0.08%)
β-fenchol (trace-0.02%)
trans-p-menth-2-en-1-ol (0.01-0.51%)
4-acetyl-1-methylcyclohexane (trace)
α-campholenal (trace)
nopinone (trace)
trans-p-mentha-2,8-dien-1-ol (trace)
terpinen-1-ol (trace)
trans-pinocarveol (trace)
camphor (3.16-12.44%)
camphene hydrate (trace)
5-(1-methylethyl)-bicyclo[3.1.0]hexan-2-one† (trace-0.11%)
menthone (trace-0.06%)
isopinocamphone (trace-0.31%)
pinocarvone (trace)
borneol (0.50-4.27%)
p-methylacetophenone (0.18-0.77%)
creosol (trace)
menthol (trace-0.04%)
terpinen-4-ol (0.91-2.79%)
cryptone (trace-0.24%)
p-cymen-8-ol (trace-0.04%)
3-hexenyl butyrate* (0.02-0.12%)
α-terpineol (trace-0.29%)
geranial (trace)
myrtenal (0.01-0.19%)
2-pinen-4-one† (trace-0.13%)
pinocamphone (trace-0.15%)
decanal (trace-0.05%)
trans-piperitol (trace-0.02%)
trans-dihydrocarvone (trace)
β-cyclocitral (trace-0.05%)
bornyl formate (trace-0.20%)
2-methyl-5(1-methylethyl)-cyclohexa-1,3-diene† (trace-0.16%)

(Z)-3-hexenyl 2-methylbutyrate (trace-0.10%)
pulegone (trace-0.22%)
cuminaldehyde (trace-0.01%)
2,3-dimethoxytoluene (trace)
carvone (0.09-0.54%)
menth-6-en-2-one* (trace-0.06%)
3-ethyl-5-methylphenol (trace-0.07%)
piperitone (trace)
perillaldehyde (trace)
isobornyl acetate (trace)
thymol (0.80-1.80%)
carvacrol (trace-0.05%)
cuminyl alcohol (0.07-0.25%)
(E,E)-2.4-decadienal (trace-0.03%)
1-(2,3,4-trimethylphenyl) ethanone (0.02-0.40%)
1-(2,4,5-trimethyphenyl) ethanone (trace-0.14%)
piperitenone (trace-0.03%)
mentha-1,4-dien-7-ol* (trace-0.03%)
octyl isobutyrate (trace-0.02%)
α-cubebene (trace-0.03%)
thymyl acetate (0.01-0.09%)
eugenol (trace-0.02%)
carvacryl acetate (trace)
α-copaene (0.01-0.09%)
methyl p-anisate (trace-0.04%)
damascenone* (trace)
geranyl acetate (trace)
β-elemene (0.16-0.73%)
2-phenethyl isobutyrate (trace)
(Z)-jasmone (trace-0.01%)
benzyl isovalerate (trace)
3,4-dimethylquinoline (trace-0.02%)
methyl eugenol (trace)
dodecanal (trace-0.04%)
4-(2,6.6-trimethyl1-cyclohex-1-enyl)-3-buten-1-oneÜ (trace)
α-gurjunene (0.01-0.16%)
β-caryophyllene (0.82-1.63%)
β-gurjunene (trace-0.02%)
cuminyl acetate (trace-0.02%)
2,6-dimethyl-6-(4-methyl-3-pentyl) bicyclo[3.1.0]hept-2-eneÜ (trace)
geranyl acetone (T-0.05%)
patchoulene* (trace)
allo-aromadendrene (0.05-0.23%)
dihydropatchoulene* (0.12-0.40%)
4-(2,6,6-trimethyl-1-cyclohex-1-enyl)3-buten-2-one† (0.27-0.80%)
curcumene* (trace)

Table XIV. Comparative Percentage Composition of Moroccan Tansy Oil Produced from Leaves, Flowers and Flowering Plants Harvested over a 3-month Period

Leaf Compound	Flower Oil	July Oil	August Oil	Sept. Oil	Oil
α-pinene	1.15	0.83	0.99	1.30	1.47
sabinene	5.93	3.61	6.62	6.83	5.77
β-pinene	2.58	2.79	2.40	3.02	3.88
myrcene	1.33	13.36	2.16	1.98	8.93
α-phellandrene	1.84	4.35	1.74	2.26	3.72
p-cymene	4.84	1.98	1.47	2.44	2.68
limonene	0.96	0.66	1.22	1.45	1.23
camphor	13.82	3.45	4.94	9.77	6.94
borneol	1.90	0.80	1.59	1.98	1.40
terpinen-4-ol	1.35	0.58	1.85	1.63	1.09
thymol	1.34	0.23	1.10	1.41	0.99
β-caryophyllene	0.83	1.09	1.08	1.14	1.26
β-sesquiphellandrene	1.71	0.60	0.87	1.06	1.02
3,6-dihydrochamazulene	2.16	4.65	4.63	3.80	2.60
2,5,8-trimethyl-1-naphthol	0.70	1.48	2.51	1.85	0.88
7,12-5,6,7,8-tetrahydrochamazulene	1.15	1.15	2.23	1.90	1.01
b-eudesmol	6.16	5.02	4.85	5.34	5.03
chamazulene	33.79	28.79	32.51	29.00	22.57
9-(15,16-dihydro-15-methyl-enegeranyl)-α-pinene	1.23	3.13	1.53	1.37	1.66

3,4-dihydro-4,5,6-trimethyl-1(2H)-naphthalene† (trace-0.13%)
2-phenethyl 2-methylbutyrate (trace-0.01%)
2-phenethyl isovalerate (0.03-0.17%)
4-hydroxy-3-methylundecalactone† (0.31-0.57%)
valencene (0.46-1.62%)
2-tridecanone (trace-0.10%)
3,6-dihydrochamazulene (2.18-5.31%)
2,4-bis(1,1-dimethylethyl) phenol† (0.08-0.53%)
cis-calamenene (trace-0.18%)
δ-cadinene (0.12-0.64%)
β-sesquiphellandrene (0.19-1.81%)
8-(1-methylethylidene)-bicyclo[5.1.0] octane† (0.01-0.13%)
elemol (0.18-0.71%)
(E)-nerolidol (trace-0.16%)
spathulenol (0.11-0.37%)
ledol (trace)
caryophyllene oxide (0.49-1.01%)
davanone (trace)
globulol (trace)
eudesm-5-en-11-ol† (trace)
guaiol (trace-0.17%)
methyl 2,6,10-trimethyl-undecanoate (trace)
2,5,6-trimethyl-1-naphthol (0.61-3.07%)
5,6-dihydrochamazulene (0.51-2.10%)
2-hydroxy-4-isopropylnaphthalene (trace-0.05%)
eudesm-4(14)-en-6-ol† (trace-0.12%)
7,12-dehydro-5,6,7,8-tetrahydrochamazulene (0.72-2.71%)
γ-eudesmol (trace)
hinesol (0.30-0.86%)
cadina-1,4-diene† (trace)
decahydro-tetramethyl-2-naphthalene methanol† (trace)
β-eudesmol + (Z)-dihydro-5-(2-octenyl)-2(3H)-furanone† (3.5-6.68%)
γ-dodecalactone (trace)
α-bisabolol (0.15-0.41%)
chamazulene (17.05-38.34%)
benzyl benzoate (0.15-0.38%)
3,3ˡ-dimethylbiphenyl* (0.01-0.13%)
4,4ˡ-dimethylbiphenyl* (trace)
cis-3,3a,4,5-tetrahydro-3a-methyl(2H)benz[e]inden-3-ol† (0.01-0.07%)
6-ethenylhexahydro-3,6,dimethyl-7-(1-methylethenyl)-2(3H)-benzofuran† (0.01-0.11%)
isopropyl myristate (trace)
6,10,14-trimethyl-2-pentadecanone (trace)
cis-(2-methylpropyl)-1,2-benzenedicarboxylate† (trace)
2-heptadecanone (trace)
(E,E)-6,10,14-trimethyl-5,9,13-pentadecatrien-2-one (trace)
a palmitate* (trace)
phytol (trace-0.10%)
hexadecyl acetate (trace)
9-(15,16-dihydro-15-methyleneg-eranyl)-α-pinene (0.23-0.58%)
9-(15,16-dihydro-15-methyl-enegeranyl)-p-cymene (1.20-2.56%)

Table XV. Comparative Percentage Composition of two Moroccan Tansy Oils Produced by Different Distillation Methods

Compound	Water Distilled Oil	Steam Distilled Oil
α-pinene	1.4	2.9
camphene	0.4	1.0
sabinene + β-pinene	7.3	17.3
myrcene	2.5	7.1
α-phellandrene	2.2	3.4
p-cymene	2.1	2.1
limonene	1.5	1.7
1,8-cineole	1.0	1.4
camphor	9.4	4.5
borneol	3.3	0.4
terpinen-4-ol	3.3	-
α-terpineol	1.3	trace
thymol	1.6	0.3
β-elemene	0.3	0.5
β-caryophyllene	0.8	1.6
(E)-β-farnesene	1.0	1.2
3,4-dihydro-4,5,6-trimethyl-1 (2H)-naphthalene	0.3	0.5
3,6-dihydrochamazulene	5.9	7.4
cis-calamenene	trace	1.4
5,6-dihydrochamazulene	2.8	2.7
7,12-dehydro-5,6,7,8-tetrahydrochamazulene	1.6	2.5
β-eudesmol	3.5	3.1
chamazulene	26.1	14.8
9(15,16-dihydro-15-methylenegeranyl) p-cymene	0.9	1.5

octadecanol (trace-0.03%)
(Z,Z)-9,12-octadecadienoic acid (0.08-0.26%)
octadecanal (trace-0.09%)
tricosane (trace-0.02%)
2-nonadecanone (trace)
eicosanol (0.03-0.13%)
nonadecanol (trace-0.11%)
heneicosanyl formate (trace)
dioctyl hexanedioate† (trace-0.05%)
pentacosane (trace-0.07%)
diisooctyl 1,2-benzenedicarboxylate† (trace-0.04%)
a behenate* (trace)
heptacosane (trace)
oxirane† (trace)

* correct isomer not identified
† questionable component identity

The authors also compared the main component comparisons of Moroccan tansy oil produced from the leaves and flowers separately, and from oils produced from flowering plants harvested over three separate months. The compositions of these oils can be seen in Table XIV.

The following year, Greche et al. (1998) examined a fraction of an extract of *T. annaum* L. and found that it contained five sesquiterpene lactones, e. g.

tannunolide B
tannunolide C
tannunolide D
tannunolide E
8α-acetoxytannunolide E

The compounds were structurally elucidated by their IR, MS, U.V. and ^{1}H-NMR spectra. It was proposed the authors that they were the precursors of chamazulene that were formed during distillation of *T. annuum*.

Also in 1998, Greche et al. compared the composition of a water distilled oil of Moroccan tansy with a steam distilled oil. The results of this study can be seen in Table XV. They also examined the composition of a hexane microwave extract of Moroccan tansy and found that it contained the following constituents:

α-pinene (1.5%)
camphene (0.6%)
sabinene (8.4%)
β-pinene (2.9%)
myrcene (1.9%)
α-phellandrene (6.7%)
p-cymene (2.3%)
limonene (1.0%)
camphor (10.7%)
borneol (1.7%)
thymol (0.6%)
β-elemene (0.8%)
β-caryophyllene (0.8%)
(E)-β-farnesene (1.0%)
3,6-dihydrochamazulene (1.3%)
cis-calamenene (0.7%)
5,6-dihydrochamazulene (0.6%)
7,12-dihydro-5,6,7,8-tetrahydrochamazulene (1.3%)
β-eudesmol (2.3%)
chamazulene (4.8%)
tannunolide C (3.5%)
tannunolide D (4.1%)
tannunolide E (7.6%)
tannunolide B (1.3%)
8α-acetoxylannunolide (4.2%)

In 1999, Greche et al. published another report on the composition of Moroccan tansy oil. The average amounts of non-trace constituents identified in *T. annuum* oil were:

α-thujene (0.1%)
α-pinene (1.3%)
camphene (0.5%)
sabinene (6.4%)
β-pinene (3.1%)
myrcene (4.4%)
octanal (0.2%)
isobutyl 2-methylbutyrate (0.4%)
α-phellandrene (2.6%)
δ-3-carene (0.3%)
α-terpinene (0.4%)
p-cymene (2.2%)
limonene (1.3%)
1,8-cineole (1.0%)
γ-terpinene (0.4%)
terpinolene (0.1%)
linalool (0.1%)
α-thujone (0.1%)
trans-pinocarveol (0.1%)
camphor (9.6%)
borneol (2.1%)
terpinen-4-ol (1.8%)
α-terpineol (0.4%)
myrtenal (0.1%)
carvone (0.3%)
thymol (1.2%)
carvacrol (0.2%)
β-elemene (0.4%)
β-caryophyllene (1.2%)
(Z)-β-farnesene (1.0%)
allo-aromadendrene (0.1%)
2-phenethyl isovalerate (0.1%)
valencene (0.5%)
3,6-dihydrochamazulene (3.7%)
cis-calamenene (0.3%)
δ-cadinene (0.4%)
elemol (0.4%)
spathulenol (0.2%)
ledol (0.3%)
caryophyllene oxide (0.7%)
5,6-dihydrochamazulene (1.7%)
7,12-dehydro-5,6,7,8-tetrahydrochamazulene (1.7%)
hinesol (0.7%)
β-eudesmol (5.1%)
α-bisabolol (0.6%)
chamazulene (28.0%)
benzyl benzoate (0.3%)

In addition, trace amounts of tricyclene, ethyl 3-methyl-2-butenoate, propyl isovalerate, benzaldehyde, 2-methylbutyl isobutyrate, o-cymene, phenylacetaldehyde, *cis*-linalool

oxide (furanoid), α-p-dimethylstyrene, ethyl heptanoate, 2-methylbutyl 2-methylbutyrate, α-fenchol, β-thujone, β-fenchol, *trans*-p-menth-2-en-1-ol, α-campholenal, nopinone, *trans*-p-mentha-2,8-dien-1-ol, terpinen-1-ol, camphene hydrate, menthone, isopinocamphone, pinocarvone, p-methylacetophenone, menthol, cryptone, p-cymen-8-ol, safranal, pinocamphone, decanal, *trans*-piperitol, *trans*-dihydrocarvone, bornyl formate, (Z)-3-hexenyl 2-methylbutyrate, pulegone, cuminaldehyde, 2,3-dimethoxytoluene, piperitone, perillaldehyde, bornyl acetate, cuminyl alcohol, (E,E)-2,4-decadienal, octyl isobutyrate, α-cubebene, thymyl acetate, eugenol, carvacryl acetate, α-copaene, methyl p-anisate, (E)-β-damascenone, geranyl acetate, 2-phenethyl isobutyrate, (Z)-jasmone, benzyl isovalerate, methyl eugenol, α-gurjunene, β-gurjunene, cuminyl acetate, geranyl acetone, α-patchoulene, γ-decalactone, ar-curcumene, 2-tridecanone, (E)-nerolidol, davanone, globulol, guaiol, γ-eudesmol, γ-dodecalactone, isopropyl myristate, 6,10,14-trimethyl-2-pentadecanone, 2-heptadecanone, methyl palmitate, phytol, hexadecyl acetate, octadecanol, (Z,Z)-9,12-octadecadienoic acid, octadecanal, tricosane, 2-nonadecanone, eicosanol, nonadecanol, heneicosyl formate, pentacosane and heptacosane were also found in these oils.

Recently, Greche et al. (2000) also reported the results of another analysis of Moroccan tansy oil. The components that were identified using GC (retention indices and quantitation) and GC/MS (component identity confirmation) were as follows:

α-thujene (0.7%)
α-pinene (4.9%)
camphene (1.8%)
sabinene (22.3%)
β-pinene (10.1%)
myrcene (6.0%)
α-phellandrene (7.6%)
α-terpinene (0.9%)
p-cymene (8.9%)
limonene (4.2%)
1,8-cineole (0.3%)
γ-terpinene (1.5%)
camphor (13.2%)
borneol (2.7%)
terpineol (trace)
thymol (0.8%)
β-elemene (0.2%)
β-caryophyllene (1.7%)
(Z)-β-farnesene (0.8%)
valencene (1.1%)
3,6-dihydrochamazulene (1.9%)
caryophyllene oxide (trace)
5,6-dihydrochamazulene (trace)
7,12-dehydro-5,6,7,8-tetrahydrochamazulene (trace)
β-eudesmol (0.3%)
chamazulene (2.8%)

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