Progress in Essential Oils

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Cinnamon Bark Oil and Extract

Maurer and Hanser (1989) reported at the 16th "Journées des Huiles Essentielles de Digne" that cinnamyl formate, cinnamyl propionate, cinnamyl isobutyrate, isobutyl cinnamate, l-phenethyl isobutyrate, α-terpinyl isobutyrate and 2-methylbutyl cinnamate were found as trace constituents in an extract of cinnamon (*Cinnamomum zeylanicum* Blume).

A commercial oil of cinnamon back (*C. zeylanium*), which was screened for its antifungal activity, was reported by Simic et al. (2004) to possess the following composition:

α-pinene (1.8%)
benzaldehyde (1.7%)
myrcene (0.4%)
α-phellandrene (0.4%)
p-cymene (0.8%)
limonene (8.3%)
benzyl alcohol (1.0%)
linalool (1.2%)
hydrocinnamaldehyde (0.3%)
(Z)-cinnamaldehyde (0.2%)
(E)-cinnamaldehyde (62.8%)
safrole (0.4%)
thymol (0.3%)
(E)-cinnamyl alcohol (0.2%)
eugenol (7.1%)
α-copaene (0.1%)
α-cedrene (0.2%)
(E)-cinnamyl acetate (0.3%)
α-humulene (0.1%)
methyl (E)-isoeugenol (0.1%)
ethyl p-methoxycinnamate (0.7%)
eugenyl acetate (0.4%)
cinnamaldehyde propyleneglycol acetal (5.6%)
benzyl benzoate (0.6%)

The identification of cinnamaldehyde, propylene glycol acetate, ethyl p-methoxycinnamate and methyl (E)-isoeugenol in this oil proves that it was not a pure oil, but one that had been adulterated and yet was available commercially.

Mallavarapu and Rajeswara Rao (2007) compared the composition of cinnamon bark oils produced in Bangalore and

T-1. Comparative percentage compositions of cinnamon bark oils produced in two different locations in Karnataka

Compound	Bangalore oil	Mysore oil
α-thujene	0.1	0.1
α-pinene	1.9	0.3
camphene	0.7	-
sabinene	-	0.1
β-pinene	0.2	-
myrcene	0.1	0.1
α-phellandrene	0.4	0.2
δ-3-carene	0.1	-
α-terpinene	0.2	0.6
p-cymene	4.7	0.3
limonene	0.6	0.5
1,8-cineole	2.8	2.2
(Z)-β-ocimene	t	0.1
(E)-β-ocimene	0.1	t
γ-terpinene	0.1	0.1
cis-linalool oxide[f]	0.4	t
trans-linalool oxide[f]	0.4	0.1
terpinolene	0.1	t
linalool	13.8	4.4
hydrocinnamaldehyde	0.1	0.3
borneol	0.4	0.1
terpinen-4-ol	1.6	0.7
methyl chavicol	1.3	1.3
(Z)-cinnamaldehyde	0.1	0.1
nerol	0.1	t
neral	0.1	-
(E)-cinnamaldehyde	59.4	60.5
(E)-cinnamyl alcohol	0.2	0.2
eugenol	1.4	1.7
3-phenylpropyl acetate	t	0.2
α-copaene	0.2	0.1
coumarin	0.4	-
(E)-cinnamyl acetate	t	13.6
β-caryophyllene	1.5	5.6
α-humulene	0.3	1.0
β-selinene	0.1	t
(E)-nerolidol	0.1	0.1
spathulenol	0.1	t
caryophyllene oxide	0.4	0.5
humulene epoxide I	0.1	0.1
humulene epoxide II	t	0.1
1-epi-cubenol	t	0.1
T-cadinol	0.1	0.2
α-cadinol	0.3	0.1
benzyl benzoate	1.5	2.2

t=trace (<0.05%)
[f]furanoid form

Mysore (Karnataka, India). A summary of their results can be seen in **T-1**. In addition, trace amounts (<0.05%) of cuminaldehyde, bornyl acetate, β-elemene, γ-cadinene, δ-cadinene, *cis*-calamenene, elemol, safrole and 2-phenethyl benzoate in one or both of the oils.

The comparative composition of an oil and an oleoresin produced from a cinnamon bark purchased at a local market in Gorakhpur (U.P., India) was studied by Singh et al. (2007). Using a combination of gas chromatographic techniques, the oil, which was produced by hydrodistillation in 2.5% yield, was found to contain:

(E)-cinnamaldehyde (97.7%)
α-copaene (0.8%)
α-amorphene (0.5%)
δ-cadinene (0.9%)

Trace amounts (<0.1%) of α-pinene, camphene, sabinene, β-pinene, limonene, 1,8-cineole, camphor and (Z)-cinnamaldehyde were also found in this oil. It should be pointed out that it is not usual for cinnamon bark oil to contain so much cinnamaldehyde and also be devoid of eugenol.

Singh et al. (2007) also analyzed the volatile composition of an oleoresin of the same batch of cinnamon bark using the same techniques. The volatile profile of this cinnamon bark oleoresin was determined to be as follows:

(Z)-cinnamaldehyde (1.5%)
(E)-cinnamaldehyde (50.0%)
α-copaene (4.6%)
δ-cadinene (7.8%)
terpinen-4-ol (0.1%)
β-caryophyllene (1.0%)
coumarin (16.6%)
α-muurolene (4.4%)
β-bisabolene (1.4%)
cadina-1(2),4-diene (1.8%)
o-methoxy cinnamaldehyde (0.5%)
cubenol (0.2%)
l-heptadecene (0.2%)
l-nonadecene (0.4%)
tetracosane (0.1%)
octacosane (0.1%)
nonacosane (0.2%)

The level of coumarin in this cinnamon bark oleoresin is surprising, and probably indicates that the oleoresin from which the oil was obtained was adulterated.

Koroch et al. (2007) examined an oil of cinnamon bark produced in Madagascar. They found that the main components of this oil were:

α-pinene (5.7%)
α-phellandrene (5.2%)
β-phellandrene (18.4%)
(E)-cinnamaldehyde (29.2%)
β-caryophyllene (5.8%)
(E)-cinnamyl acetate (12.9%)

This is a very atypical oil because of the low level of cinnamaldehyde and the very high levels of β-phellandrene. Previously, the highest level reported for β-phellandrene was 7.4% (Lawrence, 2002). Also, the highest level of (E)-cinnamyl acetate reported was 10.6% (Lawrence, 1994), although this oil was a commercial sample. It is worth noting that high levels (45–54%) of (E)-cinnamyl acetate have reported in *C. zeylanicum* fruit oil (Lawrence, 2004).

Koch et al. also compared the atypical oil with two commercial samples of cinnamon bark oil and determined that the main components of these oils were as follows:

α-pinene (0.3–2.8%)
α-phellandrene (0.1–1.0%)
(E)-cinnamaldehyde (73.1–79.4%)
β-caryophyllene (0.4–4.0%)
(E)-cinnamyl acetate (0.7–5.6%)

It is surprising that the authors did not characterize eugenol in the oil because it is a known important component of all cinnamon bark oils. Perhaps the origin of this oil was not *C. zeylanicum*.

Baruah et al. (2010) analyzed the composition of an oil produced from the bark of *C. zeylanicum* collected from the Pathshala area (Assam, India) using a combination of gas chromatographic techniques. The oil, which was produced by hydrodistillation was found to possess the following composition:

p-cymene (1.5%)
1,8-cineole (2.1%)
linalool (6.3%)
(E)-cinnamaldehyde (24.2%)
(E)-cinnamyl alcohol (<0.1%)
eugenol (10.0%)
methyl eugenol (3.4%)
β-caryophyllene (10.4%)
ethyl (E)-cinnamate (1.8%)
methyl isoeugenol* (7.8%)
isoeugenol* (4.1%)
eugenyl acetate (0.4%)
benzyl benzoate (15.1%)

*correct isomer not identified, and were probably misidentifications

An extract of air-dried cinnamon bark that was ground to 0.15–0.25 mm size was produced using 1,1,1,2-tetrafluoroethane at 0.5 MPa pressure, 18°C and

T-2. Comparative percentage composition of the oils of cultivated and wild *Helichrysum italicum* subsp. *microphyllum*

Compound	Cultivated plant oils	Wild plant oil
α-pinene	0.11–0.44	0.42
camphene	0.21–0.25	0.27
β-pinene	0.12–0.15	0.19
p-cymene	0.13–0.14	0.17
limonene	0.62–1.47	2.03
γ-terpinene	0.11–0.16	0.13
1,8-cineole	0.13–2.21	0.14
linalool	3.45–7.13	4.91
α-terpineol	0.66–2.83	1.25
nerol	4.42–9.11	11.12
thymol	0.14–0.19	0.14
carvacrol	0.11–0.12	0.17
neryl acetate	42.46–43.08	33.53
geranyl acetate	0.11–0.15	0.12
β-caryophyllene	0.31–0.63	0.55
neryl propionate	5.63–5.87	5.03
γ-curcumene	2.05–2.19	1.91
curcumene*	0.11–6.55	6.03
guaiol	0.13–0.61	0.71
β-eudesmol	2.29–2.48	2.04
α-eudesmol	0.89–0.99	1.31

*correct isomer not identified

an extraction time of 75 min by Nenov et al. (2011). Analysis of the extract that was produced in 0.8% yield revealed that it contained:

α-pinene (1.1%)
camphene (0.3%)
sabinene (0.2%)
β-pinene (0.5%)
myrcene (0.19%)
limonene (0.5%)
1,8-cineole (1.9%)
γ-terpinene (0.1%)
linalool (0.3%)
borneol (0.8%)
terpinen-4-ol (0.3%)
α-terpineol (0.3%)
(E)-cinnamaldehyde (77.3%)
(E)-cinnamyl alcohol (0.4%)
hydrocinnamyl alcohol (0.2%)
(E)-anethole (0.5%)
bornyl acetate (0.6%)
α-cubebene (0.3%)
α-copaene (2.9%)
β-caryophyllene (1.5%)
coumarin (4.3%)
(E)-cinnamyl acetate (0.8%)
α-humulene (0.2%)
α-bergamotene* (0.3%)
α-muurolene (0.5%)
δ-cadinene (0.6%)
calamenene* (0.2%)
caryophyllene oxide (0.2%)
cubenol (0.1%)

* correct isomer not identified

Fathi et al. (2012) analyzed a lab-distilled oil of *C. zeylanicum* using GC-FID and GC/MS. The constituents characterized in this oil were:

α-pinene (0.1%)
camphene (0.1%)
benzaldehyde (0.2%)
p-cymene (0.1%)
(E)-cinnamaldehyde (90.3%)
eugenol (0.4%)
α-copaene (1.2%)
β-caryophyllene (0.1%)
β-bergamotene* (0.1%)
(E)-cinnamyl acetate (0.3%)
germacrene D (0.3%)
α-muurolene (0.4%)
β-bisabolene (0.2%)
δ-cadinene (0.6%)
cis-calamenene (0.4%)
p-methoxy-cinnamaldehyde (2.3%)
caryophyllene oxide (0.2%)
dillapiole† (0.4%)
α-muurolol (0.3%)
farnesol* (0.2%)

†incorrect identification
*correct isomer not identified

T-3. Comparative average percentage composition of two chemical forms of *Helichrysum italicum* subsp. *microphyllum*

Compound	1	2
α-pinene	0.2	0.1
fenchene*	-	0.1
limonene	1.2	1.2
1,8-cineole	0.2	0.8
(E)-β-ocimene	-	0.2
linalool	9.1	14.9
α-terpineol	0.2	0.2
nerol	10.7	-
neryl acetate	28.9	-
α-ylangene	0.7	-
α-copaene	0.8	2.2
italicene	2.3	4.2
α-cedrene	-	0.2
cis-α-bergamotene	2.1	-
β-caryophyllene	0.2	3.2
trans-α-bergamotene	1.1	-
aromadendrene	0.3	0.3
neryl propionate	11.4	-
allo-aromadendrene	0.9	2.2
α-acroadiene	-	0.4
β-acoradiene	-	0.4
γ-muurolene	-	0.8
γ-curcumene	11.4	18.2
ar-curcumene	4.5	4.8
β-selinene	1.8	1.9
α-selinene	0.9	0.7
α-muurolene	-	1.4
γ-cadinene	1.2	4.1
δ-cadinene	0.8	5.6
guaiol	0.7	2.8
rosifoliol	3.9	20.2
β-eudesmol	0.8	2.6
bulnesol	-	0.7

*correct isomer not identified

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Helichrysum Oil

Weyerstahl et al. (1984) reported that an oil of helichrysum of Yugoslavian origin was determined to contain the following components:

α-pinene (21.7%)
camphene (0.2%)
α-fenchene (0.3%)
β-pinene (0.4%)
myrcene (0.1%)
α-terpinene (0.2%)
p-cymene (0.4%)
limonene (2.4%)
γ-terpinene (0.3%)
terpinolene (0.2%)
α-cubebene (0.3%)
α-ylangene (0.2%)
α-copaene (1.6%)
isoitalicene (1.5%)
heliofolene (0.2%)
italicene (4.0%)
isoheliofolene (0.2%)
cis-α-bergamotene (1.3%)
β-caryophyllene (5.0%)
trans-α-bergamotene (1.2%)
α-humulene (0.5%)
ar-curcumene (4.0%)
γ-curcumene (10.4%)
α-selinene (3.6%)
β-selinene (6.0%)
selina-4,11-diene (2.0%)
γ-cadinene (0.4%)
δ-cadinene (0.9%)
italicene ether (0.2%)
isoitalicene ether (0.2%)
cyclodehydro-α-acorenol (0.4%)
cyclo-epi-β-acorenol (0.2%)
α-acorenol (0.1%)
10-epi-β-acorenol (0.3%)

Usui et al. (1997) examined the lab-distilled oil of two strains of cultivated *Helichrysum italicum* subsp. *microphyllum* and one strain of the same species collected from its natural habitat in northern Sardinia. Using GC/MS as their only method of analysis, the results of this study are presented in **T-2**.

Helichrysum italicum subsp. *microphyllum* was collected from eight locations in Sardinia while the plants were in full flower by Satta et al. (1999). Oils produced from each of the collections were subjected to analysis by GC/MS. Satta et al. found that the oils obtained could be grouped into two distinct chemotypes, as shown in **T-3**.

Six oils of *H. italicum* (probably subsp. *italicum*) were produced in the laboratory from plants collected in Calabria (Italy) by Gionfriddo et al. (2001). The major constituents of these oils were found to be as follows:

β-pinene (41.2–55.2%)
eugenol (12.8–18.2%)
camphor (1.0–5.0%)

It should be noted that eugenol and camphor have never been found as constituents of *H. italicum* oils so the value of this analysis is only for the β-pinene content.

The major components from four samples of *H. italicum* (Roth) G. Don subsp. *microphyllum* (Willd.) Nyman were determined by Angioni et al. (2003), and the data obtained can be found in **T-4**. These same authors also found that the oils produced from flowers and leaves (and stems) harvested between June and September in Esterzili (Cagliari, Italy) ranged quantitatively as shown in **T-5**.

Bianchini et al. (2003) collected plants of *H. italicum* subsp. *italicum* and *H. italicum* subsp. *microphyllum*, the former from Tuscany (Italy) and Corsica (France), and the latter from Sardinia (Italy) and Corsica. Oils produced from four different collections of *H. italicum* subsp. *italicum* from both areas were analyzed by both GC-FID and GC/MS. The summarized results of these analyses can be seen in **T-6**. Oils produced from three Sardinian collections and four Corsican collections were also subjected to analysis, and the composition of these oils is summarized in **T-7**. It is of interest to note that there appeared to be two chemical forms of *H. italicum* subsp. *italicum* from Tuscany, which differed slightly from the oils from Corsica, while the oils of *H. italicum* subsp. *microphyllum* were all rich in neryl acetate irrespective of origin.

Marongiu et al. (2003) compared an oil produced from the flowers of *H. italicum*

T-4. Percentage composition of the oils of four different individual plants of *H. italicum* subsp. *microphyllum*

Compound	Oil A	Oil B	Oil C	Oil D
limonene	4.5	4.9	2.5	9.0
linalool	7.4	15.2	26.5	8.0
α-terpineol	0.3	0.2	0.1	0.4
nerol	5.3	7.1	6.3	13.5
neryl acetate	35.7	36.4	20.0	27.2
neryl propionate	5.2	10.2	1.9	15.6
γ-curcumene	12.2	16.5	17.1	7.3
ar-curcumene	4.5	4.8	6.8	4.0
guaiol	0.9	0.2	1.0	0.2
rosifoliol	15.1	6.5	6.8	5.8

T-5. Seasonal compositional range in oil composition of the leaf and flower oils of *Helichrysum italicum* subsp. *microphyllum*

Compound	Leaf oil	Flower oil
limonene	2.4–17.8	1.5–7.7
linalool	3.6–5.9	12.9–22.9
α-terpineol	0.6–0.7	0.6–0.7
nerol	9.5–20.0	8.6–12.0
neryl acetate	18.8–23.9	16.6–26.6
neryl propionate	11.9–13.2	9.7–14.2
γ-curcumene	6.1–9.3	4.1–11.4
ar-curcumene	1.5–5.4	1.1–8.3
guaiol	1.0–1.4	0.4–1.0
rosifoliol	-	5.6–18.2

subsp. *microphyllum* with a supercritical fluid CO_2 extract of the same batch of flowers. The flower oil was found to possess the following composition:

α-pinene (0.1%)
myrcene (0.6%)
α-phellandrene (0.6%)
α-terpinene (0.8%)
limonene (2.9%)
1,8-cineole (0.2%)
(Z)-β-ocimene (0.4%)
γ-terpinene (0.4%)
terpinolene (0.7%)
2-nonanone (0.3%)
linalool (2.8%)
isoamyl isovalerate (<0.1%)
(E)-tagetone (0.8%)
3-decanone (1.0%)
α-terpineol (1.0%)
nerol (5.4%)
α-terpinyl acetate (0.1%)
neryl acetate (16.9%)
α-copaene (0.6%)
geranyl acetate (0.2%)
isoitalicene (0.2%)
α-cedrene (1.2%)
cis-α-bergamotene (1.1%)
β-caryophyllene (0.2%)
trans-α-bergamotene (1.0%)
aromadendrene (0.3%)
(Z)-α-farnesene (0.6%)
neo-α-clovene (0.4%)
neryl propionate (4.6%)
allo-aromadendrene (1.5%)
9-epi-β-caryophyllene (0.3%)
α-acoradiene (0.2%)
β-acoradiene (0.2%)
γ-curcumene (4.6%)
ar-curcumene (3.6%)
γ-muurolene (0.6%)
α-muurolene (0.5%)
cis-β-guaiene (2.5%)
viridiflorene (0.6%)
zingiberene (0.7%)
γ-cadinene (1.8%)
trans-β-guaiene (0.4%)
δ-cadinene (1.3%)
β-sesquiphellandrene (0.3%)
β-bisabolene (0.3%)
(E)-γ-bisabolene (0.3%)
α-cadinene (0.4%)
α-calacorene (0.2%)
cis-sesquisabinene hydrate (0.2%)
germacrene B (0.4%)
(E)-nerolidol (0.2%)
ledol (0.5%)
tridecanol (0.4%)
globulol (0.3%)
guaiol (1.5%)
widdrol (1.3%)
trans-β-elemenone (0.2%)
cis-dihydro-occidentalol (7.6%)
isoamyl nerate (0.3%)
1-epi-cubenol (0.6%)
γ-eudesmol (0.3%)
β-eudesmol (1.1%)
α-eudesmol (1.3%)
valerianol (0.2%)
7-epi-α-eudesmol (2.5%)
β-bisabolol (0.8%)
α-bisabolol (0.5%)
epi-α-bisabolol (0.2%)
curcuphenol (0.2%)
(65,7R)-bisabolone (0.2%)
xanthorrhizol (0.3%)
β-bisabolenol (0.6%)
1-octadecene (1.5%)
(E,E)-farnesyl acetate (0.9%)
(Z)-lanceol acetate (0.2%)
nonadecane (0.4%)
tetracosane (0.1%)
heptacosane (0.2%)

T-6 *Helichrysum italicum* subsp. *microphyllum* produced from the oils produced from plants collected in Sardinia and Corsica

Compound	Sardinian oils	Corsican oils
3-pentanone	-	0.4–0.7
2-methyl-3-pentanone	-	0.5–0.8
4-methyl-3-hexanone	-	0.7–1.2
2,4-dimethylheptan-3,5-dione	-	1.6–2.6
4,6-dimethyloctan-3,5-dione	0.8–1.2	0.8–1.0
α-pinene	-	1.4–3.0
α-fenchene	-	0.5–1.3
camphene	-	0.1–0.5
β-pinene	-	0.1–0.7
limonene	0.6–1.9	7.5–13.7
(E)-β-ocimene	-	0–0.2
terpinolene	-	0.1–0.3
1,8-cineole	-	0–0.1
linalool	2.9–5.6	1.4–3.5
nerol oxide	0.1–0.6	0.7–1.6
α-terpineol	0.3–1.0	1.5–2.0
nerol	5.3–8.1	3.9–5.7
neryl acetate	44.7–52.5	33.9–47.8
neryl propionate	5.8–6.1	2.1–3.4
neryl isovalerate	0.5–0.9	-
α-copaene	0–1.4	0.6–1.1
isoitalicene	0–0.2	-
italicene	0.6–1.4	0–0.2
cis-α-bergamotene	0.1–0.5	0–0.3
β-caryophyllene	0.3–0.6	-
allo-aromadendrene	0–1.2	0.8–1.4
ar-curcumene	1.3–3.7	0.2–0.4
γ-curcumene	0.7–2.4	0.1–0.7
γ-cadinene	0–2.4	1.0–2.6
δ-cadinene	0–2.2	1.8–3.2
nerolidol*	0–0.9	-
guaiol	0.5–0.7	0.3–0.5
selin-5-en-11-ol	3.6–11.5	1.6–2.6
T-cadinol	0–0.3	1.5–2.4
β-eudesmol	0.3–0.5	0.1–0.5
α-eudesmol	0.1–0.2	0–0.7
α-cadinol	0–0.1	4.9–6.9

*correct isomer not identified

The composition of the volatile portion of the supercritical fluid CO_2 extract of the same batch of flowers was quite similar to that of the flower oil.

An oil of *H. italicum* of Croatian origin was analyzed by Mastelic et al. (2005) using column chromatographic fractionation into hydrocarbons and oxygenated compounds. The hydrocarbons characterized in this oil were as follows:

α-pinene (10.2%)
β-pinene (0.6%)
α-terpinene (0.3%)
limonene (3.8%)
γ-terpinene (0.7%)
p-cymene (0.2%)
terpinolene (0.3%)
tridecane (0.4%)
tetradecane (0.2%)
α-copaene (0.2%)
α-bergamotene* (0.7%)
β-caryophyllene (4.2%)
allo-aromadendrene (0.2%)
α-humulene (1.6%)
β-selinene (1.6%)
α-cedrene† (9.6%)
aromadendrene (4.4%)
α-selinene (0.4%)
δ-cadinene (0.5%)
ar-curcumene (2.3%)
α-amorphene† (<0.1%)
α-patchoulene† (0.5%)
γ-gurjunene† (2.1%)

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

The oxygenated constituents characterized in this same oil can be seen as follows:

1,8-cineole (0.3%)
2-methyl-(E)-2-butenoic acid (0.1%)
(Z)-3-hexenol (<0.1%)
6-methyl-3-heptanone (0.2%)
nerol oxide (0.1%)
linalool (1.4%)
α-fenchyl alcohol (0.2%)
trans-pinocarveol (0.2%)
α-terpineol (1.4%)
neryl acetate (11.5%)
geranyl acetate (4.7%)
nerol (0.2%)
geraniol (0.2%)
2-methylcyclohexyl valerate (8.3%)
2-methylcyclohexyl octanoate (4.8%)
(E)-nerolidol (0.6%)
guaiol (0.6%)
2-phenethyl tiglate (0.9%)
thymol (1.1%)
α-muurolol (1.1%)
α-bisabolol (0.8%)
β-eudesmol (0.5%)
decanoic acid (0.6%)
undecanoic acid (<0.1%)
dodecanoic acid (0.7%)
β-costol (<0.1%)
tridecanoic acid (0.2%)
tetradecanoic acid (0.3%)

Oils of *H. italicum* subsp. *italicum* produced from plants collected from Gorgona Island, Giannutri Island, Giglio Island, Capraia Island, Pianosa Island and Montecristo Island (Tuscan Archipelago, Italy) were analyzed by Paolini et al. (2006). The plants collected were all in various stages of flowering. The range of components found in the 11 oils analyzed can be seen as follows:

4-methyl-3-hexanone (0–0.6%)
α-pinene (0.1–8.6%)
α-fenchene (0–0.9%)
camphene (0–0.4%)
β-pinene (0.1–0.8%)
α-terpinene (0–0.3%)

T-7. Percentage composition of oils of *Helichrysum italicum* subsp. *italicum* from Tuscany and Corsica

Compound	T-1	T-2	C-1
3-pentanone	0–0.2	-	0.4–0.6
2-methyl-3-pentanone	-	-	0.3–0.7
4-methyl-3-hexanone	-	-	0.4–1.4
2-nonanone	-	-	0.2–0.3
2,4-dimethylheptan-3,5-dione	0–0.2	-	0.3–0.9
4,6-dimethyloctan-3,5-dione	-	1.3–2.0	1.1–4.1
4,6,9-trimethyldec-8-en-3,5-dione	0–0.2	1.7–4.0	2.3–5.6
2,4,6,9-tetramethyldec-8-en-3,5-dione*	-	1.0	-
2,4,6,9-tetramethyldec-8-en-3,5-dione*	-	0.7–1.1	-
α-pinene	33.5–53.5	4.1–5.8	0.8–1.4
α-fenchene	0.5–0.9	0–1.4	0.5–0.8
camphene	0.2–0.3	0–0.5	0.2–0.4
β-pinene	0.8–0.9	0–0.5	0.5–0.7
α-terpinene	0.2–0.3	0–0.7	-
p-cymene	-	-	0.2–0.5
limonene	2.3–4.5	2.0–10.7	2.6–4.7
γ-terpinene	0.4–0.6	0–1.3	0.5–0.7
terpinolene	0.2	0–0.5	0.2–0.3
1,8-cineole	-	0–0.3	0.7–0.9
linalool	0.2–1.4	0.8–1.9	1.5–2.7
nerol oxide	-	0.3–0.7	0.5–1.5
terpinen-4-ol	0–0.3	0–1.0	0.4–1.5
α-terpineol	0.4–0.8	1.5	0.7–0.9
nerol	-	2.1–2.8	1.9–3.9
neryl acetate	0.3–1.5	10.0–22.0	33.7–38.9
neryl propionate	0.3–0.4	3.6–5.8	3.4–5.9
α-ylangene	0.6–0.7	-	-
α-copaene	0.4–0.7	-	-
isoitalicene	-	0–0.4	0.2–0.5
italicene	-	0.9–1.0	0.4–2.1
cis-α-bergamotene	0.3–0.7	0.7–3.2	0.4–0.6
β-caryophyllene	5.7–11.0	6.7–6.8	-
trans-α-bergamotene	0–0.2	0.6–2.6	3.3–6.0
α-humulene	0.3–0.4	0.5–0.9	-
ar-curcumene	0.1	0–1.4	1.0–1.8
γ-curcumene	1.4–2.1	3.9–4.9	3.9–13.6
selina-4,11-diene	1.8–2.4	1.6–2.8	-
β-selinene	7.9–12.5	7.2–11.2	-
α-selinene	5.2–7.7	5.1–8.3	-
β-bisabolene	0.8–0.9	0.2–0.4	-
guaiol	0.3–1.5	0–1.0	-
selin-5-en-11-ol	2.0–6.6	0–1.4	2.8–6.1
10-epi-γ-eudesmol	-	-	0–0.2
β-eudesmol	0–0.8	0–1.2	1.2–2.5
selin-11-en-4α-ol	0.7–1.2	1.9–2.3	-
α-eudesmol	0.3–1.1	0–1.3	1.4–2.3
bulnesol	0.2–0.7	0.9–1.4	-

*correct isomer not determined; T-1 and T-2 = two chemical forms of oils from Tuscany; C-1 = Corsican oils

p-cymene (0.1–0.4%)
limonene (0.2–10.4%)
1,8-cineole (0–2.5%)
(E)-β-ocimene (0–0.3%)
γ-terpinene (0–0.6%)
2,4-dimethylheptan-3,5-dione (0.1–2.3%)
2-nonanone (0–0.2%)
terpinolene (0–0.3%)
linalool (0.7–3.9%)
borneol (0–0.2%)
4,6-dimethyloctan-3,5-dione (0.8–2.6%)
terpinen-4-ol (0–1.0%)
α-terpineol (0.5–2.6%)
nerol (1.4–7.6%)
neryl acetate (14.9–44.5%)
α-copaene (0–0.2%)
isoitalicene (0–0.3%)
italicene (0.5–1.2%)
cis-α-bergamotene (0–0.7%)
4,6,9-trimethyldec-8-en-3,5-dione (0.3–19.8%)
trans-α-bergamotene (0–0.8%)
neryl propionate (3.0–16.4%)
2,4,6,9-tetramethyldec-8-en-3,5-dione* (0–5.7%)
2,4,6,9-tetramethyldec-8-en-3,5-dione* (0–8.0%)
ar-curcumene (1.0–2.6%)
γ-curcumene (5.4–13.7%)
β-selinene (0–0.8%)
α-selinene (0–0.6%)
5,7,10-trimethylundec-9-en-4,6-dione (0–0.7%)
β-curcumene (0.1–0.6%)
δ-cadinene (0–0.4%)
neryl butyrate (0–0.2%)
6,11-oxido-acor-4-ene (0–0.2%)
(E)-α-bisabolene (0–0.1%)
(E)-nerolidol (0–0.3%)
3,5,7,10-tetramethylundec-9-en-4,6-dione* (0.1–3.0%)
3,5,7,10-tetramethylundec-9-en-4,6-dione* (0.2–2.4%)
neryl 2-methylbutyrate (0–1.1%)
guaiol (0–1.1%)
selin-5-en-11-ol (1.1–7.6%)
α-eudesmol (0–0.8%)
bulnesol (0.2–1.0%)
α-bisabolol (0–0.3%)

*correct isomer not identified

Jirovetz et al. (2006) analyzed the aroma-rich components of a commercial sample of helichrysum oil. They were reported to be as follows:

citronellol (0.1%)
nerol (9.6%)
neral (0.8%)
geraniol (0.2%)
geranial (0.1%)
neryl acetate (12.2%)
geranyl acetate (0.3%)
neryl propionate (4.8%)
neryl butyrate (1.3%)

Trace amounts (<0.1%) of geranyl formate and geranyl butyrate were also found in this oil.

Rossi et al. (2007) determined that an oil produced from *H. italicum* grown in Corsica contained the following major constituents:

α-pinene (13.9%)
limonene (5.7%)
linalool (1.6%)
α-terpineol (2.4%)
neryl acetate (33.4%)
neryl propionate (5.1%)
ar-curcumene (11.4%)

Hellivan (2009) reviewed the product of *H. italicum* subsp. *microphyllum* (immortelle; Corsican oil). Within this review he reported on the defferences between oils produced from the above-noted subspecies with *H. italicum* subsp. *italicum* (Balkan oil). A summary of these results are shown in **T-8**. In addition, trace amounts (<0.05%) of 2-methylfuran, ethanol, tricyclene, sabinene, δ-3-carene,

α-phellandrene, 2-methylbutyl isobutyrate, 2-amylfuran, (Z)-β-ocimene, *trans*-arbusculone, 6-methyl-5-hepten-2-one, nonanal, hexyl 2-methylbutyrate, p-cymenene, methyl p-cresol, 2-nonanol, camphor, aromadendrene, β-santalene, 2-phenethyl acetate, *cis*-calamenene and geraniol were found in one or both oils.

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T-8. Comparative percentage composition of the oils of immortelle from the Balkans and Corsica

Compound	Balkan oil	Corsican oil
3-methylcyclohexanone	0.1	0.2
2-methyl-3-pentanone	t	0.1
α-pinene	27.5	2.1
α-thujene	-	0.1
α-fenchene	0.4	0.6
camphene	0.4	0.2
4-methyl-3-hexanone	0.1	0.2
β-pinene	1.0	0.6
myrcene	0.1	0.1
α-terpinene	0.1	0.1
limonene	2.3	7.2
β-phellandrene	t	0.1
1,8-cineole	0.2	1.5
γ-terpinene	0.2	0.4
(E)-β-ocimene	t	0.2
p-cymene	0.1	0.2
1-methylbutyl 2-methylbutyrate	0.1	t
terpinolene	0.1	0.2
isobutyl angelate	0.2	t
2-nonanone	t	0.1
isoamyl angelate	0.6	0.1
hexyl angelate	0.1	0.1
artemisia ketone	t	0.2
α-ylangene	0.2	t
linalool	3.3	1.0
italicene	2.7	2.1
cis-α-bergamotene	0.7	0.6
α-cedrene + δ-cadinene†	0.1	t
α-fenchyl alcohol	0.1	t
bornyl acetate	0.1	-
trans-α-bergamotene	0.6	0.3
2-undecanone	t	0.1
4,6-dimethyl-3,5-dione	t	0.6
β-caryophyllene	7.2	0.1
terpinen-4-ol	-	0.3
guaia-6,9-diene	0.3	-
β-maaliene	0.1	-
allo-aromadendrene	0.1	-
trans-pinocarveol	0.1	-
(E)-β-farnesene + zonarene	0.3	0.2
α-humulene	0.3	t
selina-4,7-diene	0.9	-
(Z)-β-farnesene† + unknown	0.2	0.4
γ-curcumene	8.8	8.9
α-terpineol	0.2	0.6
α-terpinyl acetate	0.1	-
borneol	0.1	0.1
germacrene D	0.2	-
neryl acetate	22.4	43.1
β-bisabolene	-	0.1
β-selinene	1.0	-
α-muurolene	0.4	-
α-selinene	1.8	-
7-epi-α-selinene	0.1	-

T-8. Comparative percentage composition of the oils of immortelle from the Balkans and Corsica (Cont.)

Compound	Balkan oil	Corsican oil
β-curcumene	0.4	0.3
geranyl acetate	0.1	0.1
α-farnesene*	0.1	0.1
δ-cadinene	0.7	t
γ-cadinene	0.2	t
α-bisabolene*	0.1	0.1
ar-curcumene	2.0	3.1
neryl propionate	0.6	4.6
cadina-1,4-diene	0.1	-
nerol	1.1	2.9
α-amorphene†	0.1	-
trans-carveol + unknown	t	0.2
neryl butyrate	0.1	-
neryl 2-methylbutyrate	0.1	0.3
neryl isovalerate + unknown	-	0.5
italidione I	1.7	1.3
italidione II	0.5	0.6
α-calacorene	0.1	-
italidione*	0.1	-
italidione III	0.6	0.2
neryl valerate	0.1	0.3
caryophyllene oxide	0.1	t
(E)-nerolidol	0.1	0.2
neryl hexanoate	0.1	-
cubenol	0.1	t
guaiol	0.1	1.1
eudesmol*	-	0.1
trimethylpentadecanone*	t	0.2
selin-5-en-11α-ol	0.2	3.1
eudesmol*	-	0.9
γ-eudesmol	0.1	0.4
eudesmol	0.1	-
cadinol* + unknown	0.2	0.2
bulnesol	-	0.4
α-bisabolol	0.1	-
α-eudesmol	t	0.1
cadalene + α-cadinol	0.1	0.1
β-eudesmol	t	0.7
selin-7(11)-en-4-ol	0.1	0.1

t = trace (<0.05%)
*correct isomer not identified
†incorrect identification based on GC elution order

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