Progress in Essential Oils

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Tagetes oil

An oil produced from *Tagetes minuta* collected in the Eastern Cape Province, which was said to have been introduced into South Africa from Argentina during the Anglo-Boer war in 1900, was reported by Osée Muyima et al. (2004) to possess the following composition:

sabinene (3.65%)
limonene (21.26%)
(Z)-β-ocimene (35.56%)
(E)-β-ocimene (1.25%)
dihydrotagetone (28.83%)
allo-ocimene* (1.26%)
(Z)-tagetone (0.98%)
(E)-tagetone (5.38%)
(E)-tagetenone (1.05%)

* correct isomer not identified

Singh et al. (2006) examined the effect of harvest time on oil yield and composition of *T. minuta* grown in an experimental garden in Lucknow (Uttar Pradesh, India). They found that the oil yield was 0.44%, 0.74–0.75% and 1.01% for plants harvested pre-flowering, during flowering and post-flowering (at seed setting time). The main components of the oil produced from the plants harvested at the above mentioned developmental stages can be seen in **T-1**. The data reveals that the variation experienced in a commercial oil can be caused by intrinsic factors such as plant maturity (ontogeny) as well as cultivar (genetics).

Rajeswara Rao et al. (2006) compared the composition of a hydrodistilled oil, a steam-distilled oil and a water-soluble oil of *Tagetes minuta* (cv. Vanphool) grown in an experimental garden in Hyderabad (India). The hydrodistillation used 800 g of freshly harvested biomass chopped into small pieces; the distillation time was 3 hrs. The same batch of unchopped plant material (100 kg) was steam-distilled in a field unit although no time was given. The water-soluble oil was obtained by hexane extraction of cold distillate water from the steam-distillation. Hydrodistillation gave the highest oil yield of 0.35–0.40% compared to 0.27% for the field distillation. Only 2.0–3.3 mL of oil were obtained as water-soluble oil from the hexane extraction of steam distillate water. The composition of the three oils can be seen in **T-2**.

Seeds of *T. minuta* of Namibian origin were planted in Iran and air-dried plants harvested at their full blooming stage were used to produce an oil by hydrodistillation in the laboratory by Moghaddam et al. (2007). Analysis of this oil using GC-FID and GC/MS revealed that it had the following composition:

sabinene (0.3%)
limonene (2.6%)
(Z)-β-ocimene (17.7%)
dihydrotagetone (13.7%)
terpinen-1-ol (2.8%)
(E)-tagetone (1.9%)
(Z)-tagetone (8.4%)
trans-β-terpineol (0.7%)
borneol (0.6%)
terpinen-4-ol (0.8%)
α-terpineol (20.8%)
cis-dihydrocarvone (5.0%)
(Z)-tagetenone (6.1%)
(E)-tagetenone (13.3%)
(Z)-jasmone (0.7%)
β-caryophyllene (0.6%)
α-humulene (0.4%)
bicyclogermacrene (0.5%)
spathulenol (1.8%)

It should be noted that the occurrence of such a high level of α-terpineol in a *Tagetes* oil is very unusual. In the following report Moghaddam et al. (2007) compared the oils produced from the same *T. minuta* plants at their budding,

T-1 Percentage composition of the main components of *Tagetes minuta* oil produced from plants harvested at different developmental stages.

Compound	Pre-flowering oil	Flowering oil	Post-flowering oil
limonene	5.2	8.5–9.0	21.1
(Z)-β-ocimene	2.1	2.6–4.4	-
dihydrotagetone	9.0	29.8–31.4	36.0
(E)-tagetone	4.4	2.5–5.4	1.9
(Z)-tagetone	24.9	31.6–36.0	29.4
(E)-tagetenone	10.0	2.6–3.8	0.9
(Z)-tagetenone	37.7	5.2–11.0	4.9

Comparative percentage composition of a hydrodistilled oil, a steam-distilled oil and a water-soluble oil from *Tagetes minuta* **T-2**

Compound	Hydrodistilled oil	Steam-distilled oil	Water-soluble oil
(E)-2-hexenal	0.9	-	-
ethyl 2-methylbutyrate	-	0.1	0–0.1
(E)-2-hexenol	0.3	-	-
isoamyl acetate	-	0.1–0.2	0–t
ethyl valerate	0.8	0.1	0–0.1
propyl butyrate	-	-	0–t
α-pinene	0.8	0.1	-
sabinene	0.2	0.6	t–2.6
β-pinene	-	-	0–0.6
myrcene	1.6	0.2	0–0.1
α-phellandrene	0.2	0.1	-
limonene + β-phellandrene	1.8	4.2–4.6	0–0.2
(Z)-β-ocimene	13.6	40.8–42.2	1.0–1.4
dihydrotagetone + (E)-β-ocimene	30.3	14.8–18.6	3.9–6.8
octanol	-	0–0.1	0–t
γ-terpinene	0.3	0.1	0.3–0.4
terpinolene	0.2	0.5	0.1–0.2
linalool	0.2	t–0.1	2.0–4.6
2-phenethylalcohol	0.2	0.1	0–0.1
α-thujone	1.2	0.1–0.2	0–0.2
β-thujone	-	0.3–0.4	0.1–0.2
(E)-tagetone	2.0	0.8–0.9	0.4–0.7
(Z)-tagetone	7.1	11.5–11.9	6.2–7.9
isoborneol	0.2	0.3–0.4	0.3–0.6
borneol	0.3	0.1	0.3–0.8
terpinen-4-ol	0.3	t	0.2–0.4
α-terpineol	0.3	-	0.1–0.4
(Z)-tagetenone	5.9	3.7–4.9	1.6–4.3
(E)-tagetenone	1.8	7.1–12.7	10.7–13.0
geraniol[†] + linalyl acetate	3.8	0.7–2.1	47.5–52.0
piperitone	1.2	0.1	0.7–1.3
bornyl acetate	1.1	0.1	0.2
carvacrol	0.3	0–t	0.2–1.2
trans-carvyl acetate	0.9	t	0.4–3.2
eugenol	0.6	-	0–t
geranyl acetate	0.2	0.2–0.6	1.4–1.7
methyl eugenol	0.5	0.1	0.5–0.6
β-elemene	0.3	0.1	-
β-caryophyllene	1.4	0.7–0.8	0.1–0.2
γ-elemene	0.2	t–0.1	0.1–0.2
α-humulene	-	0.3–0.4	-
germacrene D	-	0.1–0.2	-
δ-cadinene	1.2	0–0.1	0.1–0.6
(E)-nerolidol	0.3	t	-
spathulenol	1.5	t–0.1	t–0.2
caryophyllene oxide	1.5	0.1	0.1–0.2
β-eudesmol	0.6	0.1	0–0.1
α-cadinol	0.3	-	t–0.2
(Z, Z)-farnesol	0.4	0.1	0.2–0.3
(E, E)-farnesol	-	0.1–0.2	0.1–0.3

t = trace (< 0.05%)
[†] major component

full flowering and fruit setting stages. They found that the highest oil yield (1.55%) was obtained from the budding stage, while at the flowering and fruit stages the oil yields were 1.44% and 1.0%, respectively. This data is different from that obtained by Singh et al.

Moghaddam et al. explained the difference being the high humidity level experienced at the pre-flowering stage in India versus the low humidity experienced in Iran at the same ontogenetic stage. The composition of the oils obtained from the Iranian plants at the three stages are summarized in **T-3**.

Omidbiagi et al. (2008) examined the effect of nitrogen fertilizer on the yield and composition of the same *T. minuta* grown in Iran as was used in previous Iranian studies. They found that the highest yield of fresh and dried biomass, which as extrapolated from small plot experiments, was 70 tonnes/ha and 20 tonnes/ha, respectively, when nitrogen was applied at 200 kg/ha. Although the authors noted that the level of nitrogen fertilizer used had a significant effect on the oil composition, this reviewer does not believe that these conclusions could be drawn from a single study. Irrespective of nitrogen fertilizer use (0-200 kg/ha) the oil composition was found to vary as follows:

α-thujene (0.1–0.5%)
α-pinene (0.5–1.7%)
camphene (0.6–0.8%)
sabinene (0–0.2%)
β-pinene (0–0.1%)
mycrene (0–0.1%)
octanal (0–0.1%)
α-phellandrene (0–0.1%)
α-terpinene (0–0.6%)
p-cymene (4.3–5.0%)
limonene (7.5–9.3%)
(E)-β-tagetone† (0–0.1%)
(E)-β-ocimene (0–0.1%)
dihydrotagetone (42.5–57.1%)
linalool (0–0.2%)
cis-limonene oxide (0–0.5%)
terpinen-1-ol (0–0.3%)
limonene†† (0–0.2%)
(E)-tagetone (2.3–9.2%)
(Z)-tagetone (14.9–17.9%)
trans-β-terpineol (t–0.3%)
borneol (0.1–0.3%)
terpinen-4-ol (0–0.1%)
α-terpineol (0–0.2%)
(Z)-tagetenone (0.8–4.6%)
(E)-tagetenone (2.0–5.1%)
β-bourbonene (0–0.3%)
β-caryophyllene (0–0.5%)
α-humulene (0–0.2%)
bicyclogermacrene (0–0.2%)
spathulenol (0–0.4%)
caryophyllene oxide (0–0.3%)

t = trace (< 0.1%)
† should have been (Z)-β-ocimene
†† should have been *trans*-limonene oxide

T-3 Comparative percentage composition of oils produced from *Tagetes minuta* harvested at three ontogenetic stages in Iran

Compound	1	2	3
α-pinene	0.4	-	-
sabinene	0.5	0.6	0.4
myrcene	0.5	-	-
limonene	49.2	4.0	2.8
(Z)-β-ocimene	4.4	8.3	7.4
dihydrotagetone	14.8	21.4	20.7
linalool	0.7	-	-
cis-limonene oxide	0.6	-	-
terpinen-1-ol	1.5	1.7	1.2
trans-limonene oxide	1.4	-	-
(E)-tagetone	0.9	2.6	2.1
(Z)-tagetone	4.7	13.0	13.4
trans-β-terpineol	-	0.5	0.6
borneol	-	0.7	-
terpinen-4-ol	-	0.6	0.3
α-terpineol	7.4	15.6	18.4
cis-dihydrocarvone	2.1	3.8	4.4
trans-carveol	1.0	-	-
(Z)-tagetenone	3.6	4.5	3.1
(E)-tagetenone	3.3	11.8	8.6
carvone	0.8	-	-
(Z)-jasmone	-	0.4	0.8
β-caryophyllene	-	0.9	0.7
α-humulene	-	0.6	0.5
bicyclogermacrene	-	0.7	0.6
spathulenol	0.9	4.8	5.6
caryophyllene oxide	-	1.3	1.9

1. Oil produced at budding stage
2. Oil produced at full flowering stage
3. Oil produced at fruit setting stage

This reviewer finds the study somewhat puzzling as the author used the same *T. minuta* plants raised from Namibian seed. In earlier studies the oils were determined to have moderate levels of α-terpineol; however, in the current study no α-terpineol was reported.

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M. Moghaddam, R. Omidbiagi and F. Sefidkon, *Chemical composition of the essential oil of* Tagetes minuta *L.* J. Essent. Oil Res., **19,** 3–4 (2007).

M. Moghaddam, R. Omidbiagi and F. Sefidkon, *Changes in content and chemical composition of* Tagetes minutia *oil at various harvest times.* J. Essent. Oil Res., 18–20 (2007).

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Armoise oil

Armoise oil, which is produced from *Artemisia herba-alba* Asso, is available commercially as thujone-rich oil. However, because it is not a cultivated plant, the existence of infraspecific chemical differences (chemotypes) can mean that plants harvested from the wild may not all be thujone-rich. As a result, it is important to know the range of composition of the other chemotypes. A summary of the chemotypic compositions has been previously published (Lawrence 1989).

A review of the recent literature reveals the following information:

Ravid et al. (1996) determined that the enantiomeric distribution of borneol isolated from a commercial sample of armoise oil was:

(IR)-(+)-borneol (< 1%) : (IS)-(-)-borneol (> 99%)

An oil of *A. herba-alba* produced from plants collected from the Sinai Peninsula (Egypt) was analyzed by Hifnawy et al. (2001). The components identified in this oil were:

3-methyl-3-buten-2-one (0.7%)
α-pinene (0.9%)
4-methyl-3-hepten-2-one (6.4%)
isopinocamphone (0.6%)
1,8-cineole (17.2%)
cis-3-methyl-4-methylene-2-hexanone† (2.0%)
δ-3-carene (0.4%)
trans-3-methyl-4-methylene-2-hexanone† (3.3%)
p-cymene (1.4%)
isoamyl butyrate (0.2%)
1,2-dimethylstyrene† (0.2%)
1-isopropyl-2-isopropenylcyclopropane† (0.2%)
2-methoxyphenethanol (7.9%)
camphor (19.2%)
cis-carvyl acetate (0.4%)
cis-verbenyl acetate (25.0%)
terpinen-4-ol (1.8%)
myrtenol (0.3%)
trans-pinocarveol (3.4%)
α-terpineol (1.6%)
trans-carveol (0.2%)
spathulenol (0.9%)
hexadecanoic acid (0.9%)

† questionable identifications – requires independent corroboration before acceptance as oil constituent

Vincenzi et al. (2002) reported that the 1,8-cineole content of a commercial sample of armoise oil was 0.5–1.5%.

An oil of *A. herba-alba* that was produced from plants collected in the Djelfa region of Algeria was the subject of analysis by Dahmani-Hamzaoui and Baaliouamer (2005). The composition of this oil was found to be as follows:

santolinatriene (0.1%)
2,5-diethyl-2-methyltetrahydrofuran* (0.3%)
4,5-dimethylthiazole (0.1%)
α-pinene (0.1%)
camphene (0.6%)
isopropyl tiglate (0.1%)
β-pinene (0.1%)
1-octen-3-ol (0.1%)
myrcene (0.9%)
yomogi alcohol (0.2%)
α-phellandrene (0.1%)
1,4-cineole (0.2%)
α-terpinene (0.1%)
p-cymene (0.6%)
1,8-cineole (5.8%)
santolina alcohol (0.3%)
lavender lactone (0.1%)
γ-terpinene (0.2%)
(Z)-3-hexenyl butyrate (0.1%)
(E)-3-hexenyl butyrate (0.3%)
artemisia alcohol (0.2%)
terpinolene (0.1%)
linalool (0.3%)
cis-p-menth-2-en-1-ol (0.7%)
trans-pinocarveol (0.2%)
camphor (5.6%)
ipsidienol (0.2%)
camphene hydrate (0.1%)
pinocarvone (0.5%)
borneol (1.2%)
α-phellandren-8-ol (0.2%)
isopinocamphone (0.1%)
terpinen-4-ol (1.4%)
p-cymen-8-ol (0.1%)
α-terpineol (0.2%)
myrtenal + *cis*-piperitol (0.3%)
cis-sabinene hydrate acetate (0.1%)
cis-carveol (0.1%)
nor-davanone (0.5%)
carvone (0.1%)
pipertone (0.1%)
cis-chrysanthenyl acetate (0.1%)
α-terpinen-7-al (0.1%)
eugenol (0.4%)
α-copaene (0.3%)
(Z)-jasmone (0.8%)
methyl eugenol (0.1%)
isocaryophyllene (0.2%)
davana furan (0.6%)
α-humulene (0.1%)
allo-aromadendrene (0.1%)
γ-muurolene (0.6%)
bicyclogermacrene (0.7%)
isodavana ether * (1.7%)
davana ether (5.3%)
artedouglasia oxide C (1.1%)
artedouglasia oxide A (1.6%)
isodavana ether * (1.8%)
isodavanone * (0.6%)
isodavanone * (1.5%)
caryophyllene oxide (1.1%)
β-copaen-4α-ol (0.3%)
davanone (34.0%)

* correct isomer not identified

Trace components (< 0.1%) such as an isomer of 2,5-diethyl-2-methyltetrahydrofuran, tricyclene, α-thujene, sabinene, 3-octanone, β-phellandrene, p-cymenene, α-thujone, β-thujone, *cis*-pinene hydrate, chrysanthenone, isoborneol, pinocamphone, sabina ketone, lavandulol, thuj-3-en-10-al, 3-decanone, myrtenol, verbenone, *cis*-carveol, cuminaldehyde, carvotanacetone, bornyl acetate, cumin alcohol, lavandulyl acetate, thymol, *trans*-sabinyl acetate, thujyl acetate, hexyl tiglate, α-cubebene, neoisodihydrocarvyl acetate, β-bourbonene, (E)-β-damascone, β-cubebene, (E)-jasmone, β-cedrene, β-gurjunene, *trans*-α-bergamotene, viridiflorene, α-muurolene, a calacorene isomer and spathulenol were also found in the same Algerian oil.

Hudaib and Aburjai (2006) analyzed an oil produced from *A. herba-alba* collected from the University of Jordan gardens (Amman, Jordan). Oils of *A. herba-alba* are known to exist in numerous chemotypic forms. As a result, this Jordanian oil, which is of no commercial value, was found to possess the following composition:

santolinatriene (0.9%)
m-mentha-(1)7,8-diene (2.5%)
p-cymene (0.7%)
santolina alcohol (13.0%)
artemisia ketone (12.4%)
dihydromyrcenol (0.5%)
artemisia alcohol (0.9%)
α-thujone (16.2%)
β-thujone (8.5%)
trans-pinocarveol (3.9%)

lavandulol (0.3%)
artemisyl acetate (3.7%)
terpinen-4-ol (0.3%)
methyl chavicol (0.5%)
cuminaldehyde (0.6%)
(E)-anethole (1.4%)
trans-sabinyl acetate (5.4%)
carvacrol (0.4%)
(E)-jasmone (0.1%)
(Z)-jasmone (0.8%)
methyl eugenol (0.7%)
β-caryophyllene (0.4%)
β-gurjunene (0.5%)
trans-α-bergamotene (0.1%)
allo-aromadendrene (0.4%)
β-chamigrene (0.4%)
γ-himachalene (0.4%)
γ-curcumene (0.5%)
germacrene D (4.6%)
(E)-β-ionone and β-selinene (0.1%)
benzyl tiglate (0.1%)
spathulenol (0.5%)
γ-eudesmol (0.9%)
β-acorenol (0.5%)
T-cadinol (0.9%)
α-eudesmol (4.2%)
α-bisabolol (0.5%)
caryophyllene oxide (5.7%)

An oil of *A. herba-alba* obtained from plants collected in M'sila (Algeria) was analyzed by Dob and Benabdelkader (2006) and was found to contain the following constituents:

γ-terpinene (2.8%)
artemisia alcohol (0.1%)
terpinolene (0.1%)
α-thujone (1.5%)
β-thujone (15.0%)
chrysanthenone (15.8%)
trans-pinocarveol (16.9%)
camphor (19.4%)
cis-β-terpineol (0.6%)
isoborneol (0.1%)
cis-chrysanthenol (1.2%)
lavandulol (0.8%)
terpinen-4-ol (2.7%)
myrtenal (0.9%)
myrtenol (0.1%)
verbenone (0.5%)
trans-piperitol (0.4%)
neral (0.1%)
carvone (0.1%)
piperitone (0.2%)
perillaldehyde (0.4%)
geranial (0.7%)
lavandulyl acetate (2.2%)
thymol (0.1%)
carvacrol (0.1%)
α-ylangene (2.6%)
α-copaene (0.2%)
β-cubebene (0.1%)
cyperene (0.1%)
(Z)-β-farnesene (0.1%)
α-humulene (0.1%)
allo-aromadendrene (0.3%)
β-santalene (0.2%)
ethyl (E)-cinnamate (2.8%)
germacrene D (0.7%)
δ-cadinene (0.1%)
(E)-nerolidol (0.1%)
trans-calamenene (0.1%)
spathulenol (0.1%)
caryophyllene oxide (0.9%)
viridiflorol (0.7%)
capillene (0.3%)
humulene expoxide I (0.1%)
1-epi-cubenol (0.7%)
cubenol (0.8%)
β-eudesmol (0.1%)

Trace amounts (< 0.1%) of α-pinene, camphene, sabinene, β-pinene, yomogi alcohol, α-phellandrene, δ-3-carene, α-terpinene, p-cymene, limonene, 1,8-cineole, (E)-β-ocimene, fenchone, borneol, *trans*-carveol, α-cubebene, β-elemene, β-caryophyllene, γ-cadinene, (Z)-nerolidol and α-bisabolol oxide B were also characterized in this oil.

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M.M. Hudaib and T.A. Aburjai, *Composition of the essential oil from* Artemisia herba-alba *grown in Jordan*. J. Essent. Oil Res., **18**, 301–304 (2006).

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