Progress in Essential Oils

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Rhododendron anthopogon Oil

The genus *Rhododendron* is a member of the Ericaceae family. Most species are found in their natural habitat in the Himalayan region of Southeast Asia and Melanesia (Popescu and Kopp, 2013). *Rhododendron anthopogon* Maxim. (known as *balu*, or *sunpat*, in Nepalese) grows as a shrub on the open slopes of the Himalayas in northern India, Bhutan and, particularly, Nepal. An oil produced by steam or steam and water distillation from the fragrant leaves and flowers is produced annually in amounts of 250–450 kg. A summary of the published information reveals that the oil has not been the subject of much study.

Using GC/MS as their only method of analysis, Yonzon et al. (2005) analyzed a commercially available oil of *R. anthopogon* that was produced by steam distillation of the aerial parts. They found that the oil contained the following constituents:

α-pinene (8.3%)
β-pinene (6.2%)
myrcene (2.1%
limonene (7.1%)
(Z)-β-ocimene (3.7%)
p-cymene (1.2%)
α-copaene (1.8%)
β-caryophyllene (6.5%)
(E)-β-farnesene (2.2%)
α-humulene (1.5%)
α-amorphene (5.3%)
α-muurolene (5.9%)
α-selinene (1.7%)
δ-cadinene (11.4%)
ar-curcumene (1.0%)
cis-calamenene (2.2%)
α-cadinol (1.6%)
T-cadinol (1.5%)

An oil that was produced from the fresh aerial parts (leaves and flowers) of *R. anthopogon* of Nepalese origin was analyzed using GC-FID and GC/MS by Innocenti et al. (2010). The constituents characterized in this oil were as follows:

α-thujene (0.2%)
α-pinene (37.4%)
camphene (0.2%)
β-pinene (16.0%)
myrcene (1.1%)
p-cymene (2.6%)
limonene (13.3%)
(Z)-β-ocimene (5.3%)
γ-terpinene (1.5%)
α-copaene (0.7%)
β-caryophyllene (2.3%)
α-humulene (0.2%)
allo-aromadendrene (0.2%)
germacrene D (1.8%)
α-amorphene (3.2%)
α-muurolene (2.7%)
δ-cadinene (9.1%)

Inouye et al. (2010) reported that a commercial oil of *R. anthopogon* of Nepalese origin was found to contain:

α-pinene (32.6%)
β-pinene (15.6%)
myrcene (12.5%)
p-cymene (2.4%)
cadina-1,4-diene (6.9%)
α-amorphene (3.8%)
α-bisabolene* (2.2%)
2-isopropenyl-5-isopropyl-7,7-dimethylbicyclo[4.1.0]-3-heptene (2.2%)

*correct isomer not identified

Leaves of *R. anthopogon* harvested from flowering plants were collected from alpine western Himalaya at an altitude of 3,000–4,500 m (Guleria et al., 2011). The fresh leaves were shade-dried, and 500 g were subjected to hydrodistillation for 3 hr. A second aliquot (950 g) of the shade-dried leaves were extracted with supercritical fluid CO_2 at 140 bar, 40°C for 3 hr., and a 60 mL/min CO_2 flow rate. Finally, 1 g of the shade-dried fresh leaves were placed in a 20 mL auto-sample vial, sealed and heated to 80°C with an incubation time of 45 min. The headspace was absorbed on a polar phase. The results of the analysis of the oil, supercritical fluid extract and the leaf headspace as determined by GC-FID and GC/MS can be seen in **T-1**.

Two commercial oils of *R. anthopogon* of Nepalaese origin that were analyzed by GC/MS only were reported (Vossen, 2013) to possess the following composition:

α-thujene (0–0.2%)
α-pinene (21.0–34.3%)
camphene (0.2–0.3%)
sabinene (0–0.2%)
β-pinene (9.9–14.2%)
myrcene (1.4–1.7%)
α-terpinene (0.2%)
p-cymene (0.2–0.4%)
limonene (10.2–13.7%)
(Z)-β-ocimene (6.9–7.3%)
(E)-β-ocimene (1.1–1.2%)
γ-terpinene (2.0–2.4%)
terpinolene (0.4%)
linalool (0.2–0.3%)
terpinen-4-ol (0–0.2%)
α-terpineol (0.3–0.4%)
bornyl acetate (0–0.2%)
α-cubebene (0.3%)
citronellyl acetate (0.1–0.2%)
α-ylangene[a] (0.7–0.9%)
β-bourbonene (0.2–0.3%)
β-elemene (0.1–0.3%)
sesquithujene (0–0.1%)
α-gurjunene (0.1–0.2%)
β-caryophyllene (2.4–2.6%)
β-cubebene[†] (0.2–0.3%)
valencene[†] (0.5%)
muurola-3,5-diene[†] (0.4%)
aromadendrene (0–0.3%)
α-humulene (0–0.5%)
α-cubebene[†] (0–0.2%)
(E)-β-farnesene (1.1%)
γ-muurolene[†] (0.4–0.7%)
β-cubebene[†] (0–0.2%)
cadina-1,4-diene[†] (0–0.5%)
γ-muurolene[†] (1.5–2.7%)
germacrene D (0.5–0.6%)
β-selinene (0.5–1.2%)
muurola-3,5-diene[†] (0.2–0.3%)
α-selinene (1.3–2.0%)
α-muurolene (1.8–3.8%)
cadinene[†] (0.2–0.5%)
β-curcumene (0.3–0.8%)
γ-cadinene (1.9–3.5%)

T-1. Comparative percentage composition of the oil, supercritical fluid CO_2 extract and headspace of the leaves of *Rhododendron anthopogon*

Compound	Oil	Extract	Headspace
α-terpinene	0.6	-	4.9
limonene	11.3	0.8	24.1
β-phellandrene	0.8	-	3.4
(Z)-β-ocimene	3.7	0.7	7.2
γ-terpinene	6.1	0.9	40.7
(E)-β-ocimene	1.1	-	3.2
p-cymene	1.3	-	1.2
terpinene	0.7	-	3.0
(Z)-3-hexenol	-	-	0.1
linalool	1.5	-	-
β-gurjunene	1.3	1.1	1.9
bornyl acetate	1.6	-	-
terpinen-4-ol	2.2	5.5	0.4
β-caryophyllene	11.6	6.0	1.7
citronellyl formate	5.5	3.0	1.1
aromadendrene	6.3	5.6	1.6
γ-gurjunene	2.0	-	-
α-humulene	7.2	4.1	3.5
(E)-β-farnesene	0.9	2.3	-
α-terpineol	3.1	-	0.2
ledene	2.7	2.6	0.4
α-muurolene	2.4	1.7	-
(Z,E)-α-farnesene	-	1.5	-
(E,E)-α-farnesene	1.1	2.3	-
δ-cadinene	2.9	1.8	-
citronellol	1.4	-	-
benzyl alcohol	-	0.8	-
2-phenethyl alcohol	-	1.0	-
(E)-nerolidol	5.8	3.3	-
globulol	1.1	0.8	-
spathulenol	1.4	1.1	-
α-eudesmol	0.7	1.1	-
β-eudesmol	1.6	2.3	-
tetracosane	0.7	-	-
eicosanol	-	16.6	-
2-furan carboxylic acid†	0.6	1.3	-
p-menth-8(10)-ene-2,9-diol	-	7.3	-
isobutyl phthalate†	-	2.5	-
2-phenethyl benzoate	-	1.3	-

†plasticizer, oil contaminant

δ-cadinene (6.3–13.4%)
α-copaene† (0.2–0.3%)
α-cedrene† (0–0.2%)
α-cadinene (0.3–0.7%)
cis-muurola-3,5-diene† (0–0.7%)
g-cadinene† (0–0.5%)
hexahydronaphthalene† (0–0.3%)
γ-eudesmol (0–0.2%)
α-cadinol[b] (0–1.9%)
β-eudesmol (0–0.3%)
α-cadinol (0–1.4%)
α-bisabolol (0–0.2%)

[a]should be α-copaene
[b]should be T-cadinol
†incorrect identification based on GC elution order

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Rosalina Oil

The small-volume oil known as rosalina is produced in Australia from *Melaleuca ericifolia* Smith, which is also known locally as swamp paperbark, or lavender teatree. *Melaleuca ericifolia* is a 1–8 m shrub or small tree with a pale brown to white flaky, papery bark. It possesses alternate, glabrous, narrow, elliptic to linear ovate leaves, which possess oil glands. Commercial oils of rosalina are produced by steam distillation of the leaves and small branches. Oil yields from the northern provinces have been found to be higher than those of the southern provinces (Brophy and Doran, 2004).

A survey of the literature revealed that the oil of *M. ericifolia* has been the subject of a few studies. For example, Baker and Smith (1922) reported that the oil contained 1,8-cineole (>10%) and α-terpineol (ca. 30%). Penfold and Morrison (1935) determined that the major component of the oil was (+)-linalool, not α-terpineol.

Hellyer (1957) examined a commercially distilled oil of *M. ericifolia* and reported that it contained the following constituents: (+)-α-pinene and racemic limonene (monoterpene hydrocarbons totaled ca. 15% of the oil), 1,8 cineole (21%), (+)-linalool (ca. 25%), (+)-α-terpineol (4.5%), some sesquiterpene hydrocarbons and alcohols, and traces of low-boiling aldehydes.

McKern and Willis (1957) found that the (+)-linalool content of rosalina oil ranged from 30–40%.

Lawrence (1993) examined a commercial oil of *M. ericifolia* using GC-FID and GC/MS. The components characterized in this oil were as follows:

α-pinene (9.6%)
β-pinene (1.0%)
myrcene (0.6%)
α-terpinene (0.1%)
limonene (2.7%)
1,8-cineole (17.2%)
γ-terpinene (1.6%)
(E)-β-ocimene (0.4%)
p-cymene (2.0%)

terpinolene (0.6%)
cis-linalool oxide[f] (0.3%)
trans-linalool oxide[f] (0.2%)
α-copaene (0.2%)
α-gurjunene (0.6%)
linalool (44.9%)
β-caryophyllene (0.5%)
terpinen-4-ol (0.9%)
allo-aromadendrene (0.2%)
viridiflorene (0.7%)
α-terpineol (3.8%)
β-selinene (0.3%)
α-selinene (0.1%)
geraniol (1.2%)
caryophyllene oxide (0.2%)
epi-globulol (0.3%)
ledol (2.4%)
globulol (3.0%)
viridiflorol (0.4%)
spathulenol (0.3%)
γ-eudesmol (0.1%)
α-eudesmol (0.1%)
β-eudesmol (0.2%)

[f]furanoid form

Brophy (1999) used a combination of GC-FID and GC/MS to determine that a steam-distilled oil of *M. erificolia* contained the following:

α-pinene (0.4%)
α-thujene (0.6%)
β-pinene (0.1%)
myrcene (0.8%)
α-phellandrene (1.1%)
α-terpinene (0.9%)
limonene (1.4%)
β-phellandrene (0.2%)
1,8-cineole (5.6%)
(Z)-β-ocimene (0.3%)
γ-terpinene (3.5%)
(E)-β-ocimene (0.8%)
p-cymene (1.1%)
terpinolene (24.5%)
p-mentha-1,3,8-triene (0.1%)
p-mentha-1,4,8-triene (0.1%)
p-cymenene (0.4%)
cis-linalool oxide (0.2%)
α-cubebene (0.1%)
bicycloelemene (0.1%)
α-copaene (0.2%)
linalool (39.4%)
terpinen-4-ol (0.8%)
aromadendrene (2.4%)
α-bulnesene (0.2%)
allo-aromadendrene (0.6%)
trans-pinocarveol (0.1%)
neral (0.5%)
α-terpineol (3.3%)
viridiflorene (0.2%)
α-selinene (0.2%)
bicyclogermacrene (0.6%)
calamenene* (0.1%)
geraniol + p-cymen-8-ol (0.5%)
2-phenethylpropionate (0.2%)
palustrol (0.1%)
globulol (2.1%)
viridiflorol (0.6%)
spathulenol (1.0%)
(E,E)-farnesol (0.3%)

*correct isomer not identified; ffuranoid form

In addition, trace amounts (<0.1%) of the furanoid form of *trans*-linalool oxide, δ-terpineol and an isomer of calacorene, along with a number of unknown oxygenated sesquiterpenes, were reported as being found in this oil.

Webb (1999) reported that oils of *M. ericifolia* range in composition as follows:

α-pinene (5.0–10.0%)
p-cymene (1.0–4.0%)
limonene (1.5–5.0%)
1,8-cineole (18–26%)
α-terpinene[a] (1.5–4.0%)
terpinolene (2.0–5.0%)
linalool (35–55%)
terpinen-4-ol (0.5–3.5%)
α-terpineol (1.5–4.0%)
aromadendrene (1.5–4.0%)
viridiflorol (0.5–3.0%)

[a]should be γ-terpinene

Brophy and Doran (2004) examined the small twig and leaf oil compositions

T-2. Percentage composition of the oils of two populations of *Melaleuca ericifolia*

Compound	N. population oil	S. population oil
α-pinene	6.6	13.1
camphene	-	0.1
β-pinene	0.4	1.0
myrcene	0.4	0.2
α-terpinene	-	0.1
limonene	1.9	7.1
1,8-cineole	13.3	43.6
(Z)-β-ocimene	0.1	-
γ-terpinene	0.6	1.8
(E)-β-ocimene	0.4	-
p-cymene	0.5	2.2
linalool oxide*f	0.9	0.1
α-cubebene	0.9	-
linalool oxide*f	0.1	0.1
α-copaene	0.7	-
α-gurjunene	0.2	0.1
linalool	56.2	5.1
β-caryophyllene	0.8	-
aromadendrene	2.0	1.7
hexenyl butyrate*	0.2	0.1
allo-aromadendrene	0.7	0.3
viridiflorene	0.8	-
α-terpineol	2.7	6.5
β-selinene	0.2	0.2
α-selinene	0.1	0.2
geranial	0.7	-
δ-cadinene	0.1	0.6
nerol	0.3	0.3
geraniol	0.3	0.3
caryophyllene	0.1	0.1
epi-globulol	0.3	0.2
ledol	0.1	0.7
cubeban-11-ol	0.4	0.2
globulol	1.7	1.0
viridiflorol	0.5	0.5
spathulenol	1.0	1.7
γ-eudesmol	-	0.2
α-eudesmol	-	1.0
β-eudesmol	-	1.1

*correct isomer not identified; [f]furanoid form

of *M. ericifolia* that were collected from northern and southern populations distributed in southeastern Australia. The northern population was from the New South Wales to central Victoria coastal region, while the southern population was from southern Victoria and Tasmania. Oils produced steam distillation (5 hr.) and cohobation from the northern and southern (Victoria and Tasmania) populations averaged 3.19%, 1.46% and 1.31% yields, respectively. The results of the analyses of the oils using GC-FID and GC/MS can be seen in **T-2**. Trace amounts (<0.05%) of β-phellandrene and β-gurjunene were also found in the southern population oil.

Aerial parts of *M. ericifolia* were collected from trees grown at the arboretum associated with the Federal University of Viçosa (Viçosa, Minas Gerais, Brazil) by Silva et al. (2007). An oil that was produced in the laboratory by hydrodistillation in 0.7% yield was subjected to analysis by GC-FID and GC/MS. The only components characterized in the oil were:

α-thujene (5.9%)
1,8-cineole (79.5%)
γ-terpinene (0.3%)
α-terpineol (8.0%)

This is the first time that an oil of *M. ericifolia* has been reported to be rich in 1,8-cineole. It is possible that the shrub was misnamed, or a new chemotype has been found, which, according to the existing literature on this species, is highly unlikely.

Brophy et al. (2013) examined three oils from the northern provinces and one from the southern provinces using GC-FID and GC/MS. Their results can be seen summarized in **T-3**.

T-3. Percentage composition of four oils of *Melaleuca ericifolia*

Compound	Northern provinces oil		Southern provinces oil	
	1	2	3	4
α-pinene	3.7	17.0	16.3	7.4
camphene	-	-	0.1	-
β-pinene	0.3	0.9	4.8	0.3
myrcene	0.4	0.4	0.2	0.1
α-terpinene	<0.1	0.1	<0.1	0.1
limonene	1.7	4.1	7.8	5.4
β-phellandrene	-	-	<0.1	-
1,8-cineole	12.6	18.6	47.1	38.2
(Z)-β-ocimene	-	0.1	-	-
γ-terpinene	1.5	0.6	1.7	3.5
(E)-β-ocimene	0.3	0.6	-	-
p-cymene	1.7	0.5	2.0	5.0
terpinolene	3.0	0.1	0.1	8.9
linalool*f	0.8	0.3	-	-
α-cubebene	-	0.1	-	-
linalool oxide*f	0.7	0.3	-	-
α-gurjunene	0.2	0.2	-	0.1
linalool	55.3	25.8	0.1	0.9
β-gurjunene	-	0.3	-	0.2
β-caryophyllene	0.3	0.2	0.6	0.5
terpinen-4-ol	2.3	1.8	0.8	0.8
hexenyl butyrate*	0.9	0.4	0.1	1.1
allo-aromadendrene	0.8	0.6	0.4	0.5
viridiflorene	1.0	0.6	0.2	1.7
α-terpineol	2.7	4.6	7.0	5.2
β-selinene	0.1	0.2	0.2	0.3
α-selinene	0.2	0.1	0.2	0.2
geranial	1.0	0.1	-	-
δ-cadinene	0.1	0.1	0.3	0.1
nerol	0.2	0.1	0.3	0.1
geraniol	0.4	0.3	0.6	1.2
2-phenethyl ester*	0.4	0.3	0.7	1.8
caryophyllene oxide	-	0.3	0.5	1.3
epi-globulol	0.4	0.3	0.2	0.2
ledol	0.4	0.3	1.0	2.2
cubeban-11-ol	-	0.3	0.2	0.5
globulol	1.9	1.5	0.8	1.0
viridiflorol	0.5	0.4	0.6	1.1
spathulenol	1.2	1.7	1.6	0.3
γ-eudesmol	-	-	-	0.3
α-eudesmol	-	-	-	0.9
β-eudesmol	-	-	-	1.1

*correct isomer not identified; ᶠfuranoid form

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