

# **Progress in Essential Oils**

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#### Yarrow Oil

The yarrow oil of commerce is rich in chamazulene; consequently, it is a blue oil. Although it is obtained by steam distillation of *Achillea millefolium* L. that is harvested in full flower, a number of chemical forms are known, of which many are devoid of chamazulene. One such oil produced from plants collected in Serbia was the subject of analysis by Chalchat et al. (1999). These authors found that the oil was rich in 1,8-cineole, camphor and borneol as can be seen from the following listing:

tricyclene (0.1%)  $\alpha$ -pinene (1.8%)  $\alpha$ -thujene (0.4%) camphene (1.8%)  $\beta$ -pinene (3.7%) sabinene (0.2%) δ-3-carene (0.2%) dehydro-1,8-cineole (0.2%) 1,8-cineole (23.3%)  $\gamma$ -terpinene (0.4%) p-cymene (1.4%) 1,2,4-trimethylbenzene(0.1%) $\alpha$ -thujone (4.5%)  $\beta$ -thujone (0.8%) camphor (12.7%) benzaldehyde (0.1%) pinocarvone (0.3%) trans-p-menth-2-en-1-ol (0.9%) bornyl acetate (3.6%)  $\beta$ -carvophyllene (0.4%) terpinen-4-ol (2.5%) myrtenal (0.3%) thuj-3-en-10-al (0.3%) cis-p-menth-2-en-1-ol (0.8%) trans-pinocarveol (0.6%) cis-verbenol (0.2%)  $\delta$ -terpineol (0.3%) trans-chrysanthenol (1.3%) trans-verbenol (0.2%) borneol (15.0%)

 $\alpha$ -terpineol (2.2%) cis-piperitol (0.9%) myrtenol (0.4%) trans-carveol (0.3%) p-cymen-8-ol (0.1%) (Z)-jasmone (< 0.1%) caryophyllene oxide (1.6%) nerolidol<sup>°</sup> (1.0%) spathulenol (0.1%) $\alpha$ -muurolol (0.1%) T-muurolol (0.2%)  $\alpha$ -eudesmol (0.2%)  $\beta$ -eudesmol (0.3%)  $\alpha$ -cadinol (0.2%)  $\alpha$ -selin-11-en-4 $\alpha$ -ol (0.7%) caryophyllen-8-ol (0.7%) 14-hydroxy-9-epi- $\beta$ -caryophyllene (0.4%) \* correct isomer not identified

The oils produced from five clones of *A. millefolium* were analyzed by Orth et al. (1999). The various compositions of these oils are shown in **T-1**. As can be seen from the results, with the exception of the oil that was rich in mono- and sesquiterpene hydrocarbons, all other oils contained more than 45% chamazulene.

An oil produced from *A. millefolium* collected from its natural habitat in the flowering stage from Pulwama, Jammu and Kashmir (India) was found by Shawl et al. (2002) to be devoid of chamazulene. Nevertheless its oil composition was determined to be as follows:

 $\begin{array}{l} (Z)\mbox{-}3\mbox{-}hexenol~(0.3\%) \\ (E)\mbox{-}2\mbox{-}hexenol~(0.1\%) \\ \alpha\mbox{-}thujene~(0.1\%) \\ \alpha\mbox{-}pinene~(0.7\%) \\ camphene~(1.2\%) \\ sabinene~(2.0\%) \\ \beta\mbox{-}pinene~(0.5\%) \\ myrcene~(0.2\%) \end{array}$ 

p-cymene (0.5%) 1,8-cineole (11.5%) (Z)- $\beta$ -ocimene (0.1%) (E)- $\beta$ -ocimene (0.1%)  $\gamma$ -terpinene (0.4%) trans-sabinene hydrate (0.1%) cis-linalool oxide f(0.1%)cis-sabinene hydrate (0.4%)  $\alpha$ -thujone (0.2%) trans-p-menth-2-en-1-ol (0.1%) camphor (28.4%) cis-p-menth-2-en-1-ol (0.1%) pinocarvone (0.3%) menthone (0.3%)isoborneol (0.1%) borneol (2.9%) terpinen-4-ol (1.9%) myrtenal (0.2%)  $\alpha$ -terpineol (0.9%) myrtenol (0.3%) verbenone (0.1%) trans-carveol (0.3%) cis-carveol (0.1%) pulegone (4.4%) piperitone (1.6%) cis-chrysanthenyl acetate (7.6%) bornyl acetate (0.2%) thymol (0.1%) linalyl propionate (0.2%) eugenol (0.1%) thymyl acetate (0.2%)  $\alpha$ -cubebene (0.4%) (Z)-jasmone (0.1%)  $\alpha$ -copaene (0.1%)  $\beta$ -cubebene (0.1%)  $\beta$ -caryophyllene (1.1%)  $\alpha$ -bergamotene ° (0.1%) (Z)- $\beta$ -farmesene (4.0%) geranyl propionate (0.3%)  $\gamma$ -muurolene (0.1%) germacrene D (11.6%) bicyclogermacrene (1.1%)  $\alpha$ -muurolene (0.3%) (Z)- $\alpha$ -bisabolene (0.2%)  $\beta$ -bisabolene (1.1%)  $\delta$ -cadinene (0.3%)  $\alpha$ -cadinene (0.2%)

 $\alpha$ -calacorene (0.1%) (E)-nerolidol (0.5%) spathulenol (0.8%) caryophyllene oxide (0.2%) humulene epoxide I (0.1%)humulene epoxide II (0.3%)hexadecane (0.7%)  $\alpha$ -muurolol (0.5%) T-cadinol (0.3%)  $\beta$ -eudesmol (0.5%)  $\alpha$ -eudesmol (0.1%)  $\alpha$ -cadinol (0.2%) α-bisabolol (0.3%) epi- $\alpha$ -bisabolol (0.1%) heptadecane (0.1%) octadecane (0.2%) pentadecanoic acid (0.1%) 2-heptadecanone (0.1%) (E,E)-farnesyl acetone (0.1%)oleic acid (0.1%)

f = furanoid form

\* correct isomer not identified

In addition, trace amounts (< 0.05%) of dehydro-1,8-cineole, benzyl alcohol, isochrysanthenone (syn. 1(7)-pinen-6-one), cuminaldehyde, *cis*-carvyl acetate, (E,E)-farnesol, hexadecanal and nonadecane were also characterized in the same oil.

An oil produced from *A. millefo-lium* of Turkish origin was found by Candan et al. (2003) to possess the following composition:

 $\alpha$ -thujene (0.1%) α-pinene (2.4%) camphene (2.4%) benzaldehyde (0.2%) sabinene (2.8%)  $\beta$ -pinene (4.2%) dehydro-1,8-cineole (0.6%)  $\alpha$ -terpinene (0.5%) 1,8-cineole (24.6%)  $\gamma$ -terpinene (1.0%) terpinolene (0.2%) linalool (0.6%)camphor (16.7%) borneol (4.0%)terpinen-4-ol (2.8%) α-terpineol (10.2%) myrtenol (0.3%) fragranol<sup>†</sup> (0.5%) 7-methyl-3-methylene-6-octenol (0.2%) 3,7-dimethyl-3,6-octadienol (0.6%) chrysanthenyl acetate ° (0.8%) bornyl acetate (0.1%)myrtenal acetate (0.1%) eugenol (0.2%)  $\alpha$ -copaene (0.1%)  $\beta$ -carvophyllene (0.4%)  $\beta$ -farmesene \* (0.3%)  $\gamma$ -curcumene (0.2%) zingiberene (0.3%) nerolidol<sup>°</sup> (0.1%)

 $\begin{array}{l} \mbox{caryophyllene oxide (0.7\%)}\\ \gamma\mbox{-eudesmol (1.8\%)}\\ \beta\mbox{-eudesmol (1.6\%)}\\ \mbox{bisabolol oxide }^{\circ}(3.8\%)\\ \mbox{bisabolone oxide (3.3\%)}\\ \mbox{$\alpha$-bisabolol (2.1\%)} \end{array}$ 

° correct isomer not identified

<sup>+</sup> also known as 1-(2-hydroxyethyl)-2-isopropenyl-1methylcyclobutane

Mockute and Judzentiene (2003) collected plants of *A. millefolium* from 21 habitats in Lithuania. Oils produced from each of the habitats were analyzed by GC and GC/MS.

Using a cluster analysis on the quantitative results it was found that the oils could be categorized into these four groups:

Group 1: borneol + camphor Group 2: chamazulene +  $\beta$ -pinene Group 3: (E)-nerolidol +  $\beta$ -pinene Group 4: 1,8-cineole +  $\beta$ -pinene

Fourteen oils were found to be devoid of chamazulene and another two oils contained only trace amounts of it. The range in composition of Group 1 oils was as follows: α-pinene (2.3–4.7%) camphene (1.1-2.5%) sabinene (1.5-4.3%)  $\beta$ -pinene (4.0–12.6%) myrcene (0.3-0.8%)  $\alpha$ -terpinene (t-0.7%) p-cymene (0.7-1.5%) 1,8-cineole (5.3–12.5%) γ-terpinene (0.2–2.1%) terpinolene (0-0.4%) trans-pinocarveol (0-0.3%) camphor (4.1–13.1%) cis-chrysanthenol (0.3-3.8%) borneol (11.5–13.2%) terpinen-4-ol (1.9-4.5%)  $\alpha$ -terpineol (0.5–2.2%) cis-chrysanthenyl acetate (0.9–2.8%) bornyl acetate (0.5-1.9%) α-cubebene (0-0.8%)  $\beta$ -bourbonene (0-0.2%)  $\beta$ -caryophyllene (0.7–3.5%)  $\alpha$ -humulene (0.2–0.7%) germacrene D (0.3-1.8%)bicyclogermacrene (0.2–0.4%)  $\alpha$ -muurolene (0-0.3%)  $\beta$ -bisabolene (0-0.3%) sesquicineole (0.1-0.2%)  $\delta$ -cadinene (0.3–0.6%) (E)-nerolidol (2.6-4.8%) spathulenol (t-1.3%) caryophyllene oxide (1.9-4.7%) viridiflorol (0.2-1.5%)humulene epoxide ° (0–1.4%) 10-epi-γ-eudesmol (0.9–1.8%) 1-epi-cubenol (0.6-1.9%) T-cadinol (t-0.9%) himachalol ° (0.8–2.7%) selin-11-en-4α-ol (2.2-4.2%) 14-hydroxy-9-epi-β-caryophyllene (0.3–1.5%)  $\alpha$ -bisabolene oxide (0–1.5%) (E,E)-farnesol (t-0.8%) chamazulene (0-1.3%)

° correct isomer not identified t = trace (< 0.1%)

## Group 2 oils were found to contain the following components:

 $\alpha$ -pinene (2.7–5.3%) camphene (0-1.4%) sabinene (3.2-5.2%)  $\beta$ -pinene (9.7–26.5%) myrcene (0.9-1.7%)  $\alpha$ -terpinene (0.2–0.7%) p-cymene (t-1.9%) 1,8-cineole (5.3-10.6%) γ-terpinene (0.2–1.7%) terpinolene (0-0.3%) trans-pinocarveol (0-0.7%) camphor (0.3-1.6%) cis-chrysanthenol (0-0.4%) borneol (0.4-3.8%) terpinen-4-ol (1.2-2.3%)  $\alpha$ -terpineol (0.6–2.2%) cis-chrysanthenyl acetate (0-t)

## Comparative percentage composition of the oils of five clones of *Achillea millefolium* of Russian origin

Compound	1	2	3	4	5
α-pinene	0.2-0.5	1.2-1.3	0.9	0.3-1.0	0.4
α-thujene	0.1-0.2	0.1	-	0-0.3	-
β-pinene	0.5-1.3	16.5-18.6	2.3	2.7-11.6	3.9
sabinene	7.2-17.9	3.6-4.5	0.2	1.4-7.5	4.7
myrcene	0.1-0.2	0-0.1	-	0.1-0.2	1.3
α-terpinene	0.3-0.5	0.1-0.2	-	0.1-0.2	0.2
limonene	0.1	0.2-0.3	-	0.1-0.2	0.1
1,8-cineole	5.3-6.7	0.9-1.2	2.1	0.2-0.4	0.8
(Z)-β-ocimene	-	0-0.1	-	-	0.3
γ-terpinene	0.7-0.8	0.2-0.4	-	0.2-0.5	0.1
(E)-β-ocimene	0-0.1	0.2-0.5	-	0.1-0.2	-
p-cymene	-	-	-	-	0.1
terpinolene	0.1-0.2	0-0.1	-	0-0.1	-
$\alpha$ -cubebene	-	-	-	0-0.1	-
camphor	-	0.1-0.3	-	-	-
β-bourbonene	0-0.1	0.3	0.1	0.1-0.2	-
1-nonen-3-ol	-	0.1-0.2	-	0.1-0.2	-
linayl acetate	0.1-0.2	-	-	-	-
bornyl acetate	-	-	0.8	-	-
β-caryophyllene	38.6-45.5	4.6-5.5	11.6	8.4-11.7	1.5
terpinen-4-ol	3.3-3.7	0.4-0.7	0.1	0.4-1.3	0.8
myrtenal	-	0-0.1	-	-	-
$\alpha$ -humulene	4.0-4.8	0.8-0.9	1.5	0.9-1.2	0.2
$\beta$ -farnesene *	0.1	-	-	0-0.1	-
γ-muurolene	0-0.1	-	-	0-0.1	-
borneol + $\alpha$ -terpineol	-	-	0.2	-	0.2
germacrene D	13.9-14.1	4.9-5.0	7.9	6.2-7.2	4.8
(Z,E)-α-farnesene	0-0.1	-	-	-	-
bicyclogermacrene	0.5	0.2	1.4	1.2-1.4	0.8
(E,E)-α-farnesene	0-0.7	-	0.1	0.2-0.6	0.1
δ-cadinene	0.3-0.6	0.2	0.3	0.3-0.4	0.1
β-sesquiphellandrene	-	-	0.4	0.3	-
ar-curcumene	-	0-0.1	0.1	0.1-0.2	-
myrtenol	-	0-0.1	-	-	-
caryophyllene oxide	3.4-4.0	1.2-1.4	2.8	0.6-0.8	0.4
(Z)-nerolidol	0-0.1	-	-	-	-
germacradienol	0.1	-	-	0.1-0.2	-
(E)-nerolidol	-	0.3-0.5	-	-	0.2
T-muurolol	0.2	-	0.2	0.2	0.1
$\alpha$ -cadinol	0.6	0.1-0.2	0.3	0.4-0.5	0.2
chamazulene	0.2-0.5	52.9-56.4	63.4	46.2-64.6	73.5
dimethylvinylazulene	-	1.0-1.1	1.1	1.4-2.1	1.7
phytol	0.1-0.2	0-0.1	-	0-0.1	-
*					

\* correct isomer not identified

 $\begin{array}{l} \text{bornyl acetate } (0-1.2\%) \\ \alpha\text{-cubebene } (0-0.2\%) \\ \beta\text{-bourbonene } (0-0.4\%) \\ \beta\text{-caryophyllene } (4.5-8.0\%) \\ \alpha\text{-humulene } (0.3-1.5\%) \\ \text{germacrene D } (2.1-5.0\%) \\ \text{bicyclogermacrene } (0.4-1.2\%) \\ \alpha\text{-muurolene } (0-0.7\%) \\ \beta\text{-bisabolene } (0-0.5\%) \\ \text{sesquicineole } (0-0.4\%) \end{array}$ 

$$\begin{split} &\delta\text{-cadinene (0.9-2.4\%)} \\ &(E)\text{-nerolidol (0.3-6.4\%)} \\ &\text{spathulenol (0-1.5\%)} \\ &\text{caryophyllene oxide (1.1-5.4\%)} \\ &\text{viridiflorol (0-6.5\%)} \\ &\text{humulene epoxide }^{\circ}(0-0.6\%) \\ &10\text{-epi-}\alpha\text{-eudesmol (0-1.6\%)} \\ &1\text{-epi-cubenol (0.1-2.2\%)} \\ &\text{T-cadinol (0.4-1.0\%)} \\ &\text{himachalol} ~(0.2\text{-}3.5\%) \end{split}$$

 $\begin{array}{l} selin-11\text{-en-}4\alpha\text{-ol}\;(0.2\text{--}2.2\%)\\ 14\text{-hydroxy-9-epi-}\beta\text{-caryophyllene}\;(0.5\text{--}1.3\%)\\ \alpha\text{-bisabolene}\;\text{oxide}\;(0\text{--}1.1\%)\\ (E,E)\text{-farnesol}\;(0\text{--}0.5\%)\\ \text{chamazulene}\;(9.8\text{--}23.2\%)\\ \end{array}$ 

° correct isomer not identified t = trace (< 0.1%)

### The composition of Group 3 oils was found to be as follows:

α-pinene (2.1–5.1%) camphene (0.4-1.6%) sabinene (2.0-8.5%) β-pinene (5.5–12.0%) myrcene (0.2–1.2%)  $\alpha$ -terpinene (0.2–1.4%) p-cymene (0.5-1.3%) 1,8-cineole (4.4-8.8%) γ-terpinene (0.8–3.8%) terpinolene (0-0.9%) trans-pinocarveol (0-0.4%) camphor (0.6-4.4%) cis-chrysanthenol (0-2.0%) borneol (0.4-6.6%) terpinen-4-ol (0.9–5.5%) α-terpineol (t-1.3%) cis-chrysanthenyl acetate (0-3.8%) bornyl acetate (0.3-4.9%)  $\alpha$ -cubebene (0-0.4%)  $\beta$ -bourbonene (0-0.2%) β-caryophyllene (3.2–7.5%)  $\alpha$ -humulene (0–1.3%) germacrene D (2.1-6.3%) bicyclogermacrene (0.3-1.2%)  $\alpha$ -muurolene (0-0.5%)  $\beta$ -bisabolene (t-1.2%) sesquicineole (0-1.8%) δ-cadinene (0.7–2.8%) (E)-nerolidol (6.4-13.5%) spathulenol (0.5-2.7%) caryophyllene oxide (2.5-6.3%) viridiflorol (0.4–5.1%) humulene epoxide  $^{\circ}(0-1.1\%)$ 10-epi-γ-eudesmol (0.5-8.3%) 1-epi-cubenol (0.6-5.1%) T-cadinol (0.6-1.6%) himachalol ° (0-2.5%) selin-11-en-4α-ol (1.2–6.1%) 14-hydroxy-9-epi-β-caryophyllene (0.9–1.8%)  $\alpha$ -bisabolene oxide (0.3–5.9%) (E,E)-farmesol (0.2-2.8%) chamazulene (0-4.8%)

 $^{\circ}$  correct isomer not identified t = trace (< 0.1%)

Finally, oils in Group 4, which was the major group, possessed the following components:

 $\begin{array}{l} \alpha \text{-pinene} \; (1.9{-}7.4\%) \\ \text{camphene} \; (t{-}2.8\%) \\ \text{sabinene} \; (0.9{-}14.0\%) \\ \beta \text{-pinene} \; (7.3{-}31.1\%) \end{array}$ 

mvrcene (0.4-7.8%)  $\alpha$ -terpinene (0–2.5%) p-cymene (0-2.5%) 1,8-cineole (3.1–17.0%) γ-terpinene (0–3.4%) terpinolene (0-0.6%) trans-pinocarveol (0-1.1%) camphor (t-6.6%) cis-chrysanthenol (0-2.4%) borneol (t-7.8%) terpinen-4-ol (0.9-7.6%) α-terpineol (0.2–3.0%) cis-chrysanthenyl acetate (0-1.7%) bornyl acetate (t-4.7%)  $\alpha$ -cubebene (0-0.6%) β-bourbonene (0-0.7%)  $\beta$ -caryophyllene (1.5–8.7%)  $\alpha$ -humulene (t-1.5%) germacrene D (0.5-4.2%) bicyclogermacrene (0-0.9%)  $\alpha$ -muurolene (0-0.4%)  $\beta$ -bisabolene (0-0.7%) sesquicineole (0-0.7%)  $\delta$ -cadinene (0.3–2.4%) (E)-nerolidol (0-9.5%) spathulenol (0.3-5.7%) caryophyllene oxide (1.6-7.1%) viridiflorol (0-5.1%) humulene epoxide  $^{\circ}(0-1.1\%)$ 10-epi- $\gamma$ -eudesmol (t-5.5%) 1-epi-cubenol (0-7.6%) T-cadinol (0-1.8%) himachalol ° (0-1.9%) selin-11-en-4α-ol (0.3–5.9%) 14-hydroxy-9-epi-β-caryophyllene (0.3-3.8%)  $\alpha$ -bisabolene oxide (0-4.1%) (E,E)-farnesol (0-1.7%) chamazulene (0-13.9%)

° correct isomer not identified t = trace (< 0.1%)

A lab distilled oil of Iranian origin from plants collected near Dakal-e-Derazno (Glolestan state, Iran) was analyzed by Saeidnia et al. (2004). It was found to have the following composition:

 $\alpha$ -thujene (0.1%) benzaldehyde (0.1%)  $\alpha$ -pinene (2.4%) camphene (0.1%)  $\beta$ -pinene (2.9%) dehydrocineole (0.3%) p-mentha-1,4,8-triene (0.1%)  $\alpha$ -terpinene (0.4%) p-cymene (1.0%) salicylaldehyde (0.1%) 1,8-cineole (6.1%) (E)- $\beta$ -ocimene (0.1%)  $\gamma$ -terpinene (1.0%) cis-sabinene hydrate (1.3%) fenchone (0.6%) linalool (4.1%) camphor (5.9%)

trans-verbenol (2.0%) pinocarvone (0.7%) isoborneol (3.4%) terpinen-4-ol (2.6%)  $\alpha$ -terpineol (2.6%) myrtenol (0.9%) trans-carveol (0.2%) cis-carveol (0.1%) nerol (0.2%) pulegone (0.4%) linalyl acetate (0.9%) cis-chrysanthenyl acetate (0.2%) (E)-anethole (0.9%) bornyl acetate (0.1%)lavandulyl acetate (2.3%) thymol (2.2%) carvacrol (0.3%) piperitenone (0.1%)*cis*-carvyl acetate (0.1%)eugenol (0.4%) bicycloelemene (0.1%) neryl acetate (0.1%)  $\alpha$ -cubebene (3.3%)  $\alpha$ -longipinene (2.7%) (Z)-jasmone (0.1%) α-copaene (11.1%)  $\beta$ -patchoulene (0.7%)  $\beta$ -bourbonene (0.2%)  $\beta$ -elemene (0.3%)  $\alpha$ -gurjunene (1.3%)  $\beta$ -caryophyllene (2.1%)  $\beta$ -bergamotene ° (0.4%)  $\alpha$ -humulene (0.3%) allo-aromadendrene (1.3%) 1-hvdroxv-1-methyl-7-methylethyl-1,2,3,3a,4,5,6,7-octahydro-azulene (1.0%)  $\beta$ -bisabolene (0.3%)  $\gamma$ -muurolene (0.1%)  $\gamma$ -cadinene (0.7%) (Z)-nerolidol (0.7%) (E)-nerolidol (8.8%) caryophyllene oxide (4.7%) (E,E)-farnesyl acetate (0.1%) hexadecanoic acid (0.1%)phytol (0.1%) eicosane (0.1%) methyl linoleate (0.1%)heneicosane (0.1%)

° correct isomer not identified

Oils produced from A. *millefolium* grown at five different altitudes in Italy were studied by Giorgi et al. (2005). Plants from the same wild collection were transplanted at five different locations at altitudes ranging 250 m to 1100 m. It was found that the oil compositions only varied quantitatively. The only effect of altitude was on the robustness of the growth habit and the increased time taken to reach maturity at the higher elevations. The range in oil composition was as follows:

#### Comparative percentage composition of the oils of Achillea millefolium of Lithuanian origin

## **T-2**

Compound	White Flower Plants		Pink Flow	Pink Flower Plants		Deep Pink Flower Plants	
	Flower oil	Leaf oil	Flower oil	Leaf oil	Flower oil	Leaf oil	
tricyclene	t	t	_	t	1.4	0.1	
α-thujene	t	t	t	0.1	0.1	0.1	
α-pinene	4.6	0.2	0.1	0.1	2.0	0.2	
camphene	2.5	0.2	0.1	0.5 t	2.0 t	t t	
sabinene	6.0	0.1	6.6	3.0	3.0	0.4	
β-pinene	19.3	1.5	18.0	4.2	13.1	1.0	
, ·	0.1	1.5 t	0.1	4.Z 0.1		1.0 t	
myrcene	0.1				t		
α-terpinene		t 0.5	t 0.1	t 2.8	t 0.9	t 0.5	
p-cymene	t 01						
1,8-cineole	8.1	2.6	5.4	2.5	7.2	1.6	
γ-terpinene	2.8	0.3	2.5	t	3.3	t	
terpinolene	0.1	t	t	0.1	t	0.1	
camphor	1.7	1.1	1.7	1.9	t	0.9	
<i>cis</i> -chrysanthenol	0.4	t	t	-	-	t	
borneol	2.1	2.0	5.6	10.7	2.1	2.3	
terpinen-4-ol	2.8	0.6	2.6	2.0	3.9	1.2	
lpha-terpineol	1.2	0.7	t	t	t	t	
<i>cis</i> -piperitol	t	2.9	-	-	t	t	
piperitone	6.3	0.5	t	t	10.8	10.0	
bornyl acetate	5.6	2.8	3.9	2.9	t	t	
β-bourbonene	t	0.2	0.1	t	0.1	t	
β-elemene	-	t	1.2	t	t	t	
β-caryophyllene	4.3	2.3	6.7	0.9	3.6	1.2	
α-humulene	0.7	0.5	1.2	t	0.7	t	
β-farnesene <sup>*</sup>	-	-	-	-	0.8	t	
allo-aromadendrene	2.5	0.4	t	-	t	0.1	
β-acoradiene	-	1.0	-	-	2.4	0.5	
(E)-β-ionone	-	0.5	-	0.8	-	t	
bicyclogermacrene	-	-	-	-	1.9	-	
β-bisabolene	t	0.6	1.2	-	0.9	t	
cubebol	-	0.4	-	0.6	-	0.9	
δ-cadinene	0.8	0.7	-	0.4	-	3.0	
α-cadinene	-	-	-	-	4.1	t	
(E)-nerolidol	7.0	1.9	14.0	3.0	16.1	4.2	
spathulenol	t	4.0	t	6.1	t	6.1	
<i>trans</i> -sesquisabinene hydrate	t	2.1	1.6	1.0	t	t t	
caryophyllene oxide	3.0	8.1	3.7	10.4	1.6	6.4	
$\beta$ -copaen-4 $\alpha$ -ol		0.6	3.7	-	1.0	0.4	
			-		-		
viridiflorol	0.7	0.1	2.0	3.0	t	1.0	
humulene epoxide II	-	0.2	-	1.7	-	1.6	
β-eudesmol	8.4	12.8	3.4	3.9	3.1	5.0	
himachalol *	0.8	1.8	-	1.3	1.6	4.1	
selin-11-en-4α-ol	1.8	6.5	4.0	5.1	8.3	7.5	
14-hydroxy-9-ep- $\beta$ -caryophyllene	-	1.1	-	1.3	-	0.9	
$\alpha$ -bisabolone oxide A	1.8	2.4	0.8	-	t	2.3	
eudesma-4(15),7-dien-1β-ol	t	1.4	-	-	t	2.9	
(E,E)-farnesol	1.1	1.1	3.5	1.0	0.5	-	
(6R,7R)-bisabolone	-	-	-	-	2.3	-	
(E,Z)-farnesol	0.4	1.0	0.5	0.5	0.5	t	
(Z,E)-farnesyl acetate	2.6	1.0	2.4	1.3	0.3	0.5	

t = trace (< 0.1%)

\* correct isomer not identified

limonene + 1,8-cineole (3.97-5.07%) trans-sabinene hydrate (0.73-1.17%) α-thujone (0–1.67%) β-thujone (0-3.50%) camphor (5.43-10.33%) α-terpineol (0.73–1.63%) bornyl acetate (1.30-3.53%) lavandulyl acetate <sup>+</sup> (0–1.03%) α-copaene (0.53-1.33%) β-caryophyllene (3.77-7.73%) α-humulene (0.63-1.03%) γ-curcumene + germacrene D (2.03-5.63%) cubebol (1.10-3.43%) δ-cadinene (0.50–3.80%) (E)-nerolidol (6.27-15.70%) caryophyllene oxide (2.93-5.90%) chamazulene (0-0.43%) hexadecanoic acid (2.30-8.23%) ethyl hexadecanoate (1.47-3.47%) phytol (1.23-3.37%)

<sup>+</sup> probable misidentification

Oils produced from the aerial parts of A. millefolium plants that possessed white, pink and deep pink flowers collected from their natural environment on Tauras hill (Vilnius, Lilhuania) were subjected to analysis by Judzentiene and Mockute (2005). A comparison of the flower and leaf oils of the different plants differentiated by flower color can be seen in T-2. The authors also identified a phthalate in the oils; however, it was a plasticizer that was leached out of the plastic bags in which the plant materials were collected and sent to the laboratory for oil isolation. Also it is well-known that the valuable oil of yarrow is one rich in chamazulene and as can be seen, these Lithuanian plant oils were devoid of chamazulene. However as A. millefolium is a genetic complex and as in some cases it is not fully cultivated as a plantation crop "sport" plants possessing high levels of  $\beta$ -pinene, (E)-nerolidol,  $\beta$ -eudesmol and other uncommon components can occur in chamazulene-rich oils.

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#### **Spikenard Oil**

Spikenard oil is obtained from the underground rhizomes of *Nardostachys jatamansi* (Roxb.) DC. In India and Nepal the roots of *N. jatamansi* have been used as a substitute for valerian. They are used as a tranquilizer, and sedative and hypotensive agent, and as such have been used to treat epilepsy, hysteria, heart palpitations and intestinal colic. A decoction of the powdered roots is used to treat hair loss and the graying of hair (Amatya and Sthapit, 1994, and Khare, 2007).

Rücker et al. (1978) examined the biological activity of valeranone (also known as jatamansone) isolated from the roots of *Nardostachys jatamansi*. It was found that valeranone had some tranquilizing activity and a weak hypotensive effect; however a low oral LD50 was found with both rats and mice, which suggested therapeutic potential.

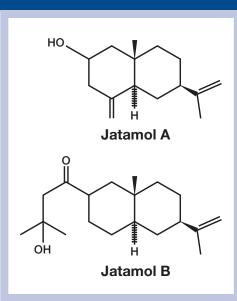
From a methylene chloride extract of the dried rhizomes

of *N. jatamansi*, Bagchi et al. (1991) isolated two new eudesmane sesquiterpenoids. They named the two compounds jatamol A and jatamol B (see **F-1**).

Using a combination of GC-FID and GC/MS, Mahalwal and Ali (2002) analyzed an oil they produced in the laboratory from fresh *N. jatamansi* rhizomes that were obtained from the Himalayan region close to Srinagar (Uttarakhand, India). The oil was contained the following components:

formic acid (9.4%) propionic acid (3.4%) hexane (0.2%) nonane (0.4%)  $\alpha$ -pinene (0.1%)  $\beta$ -pinene (0.4%) myrcene (0.1%) p-cymene (0.4%) 1,8-cineole (0.2%) terpinen-4-ol (0.1%)  $\alpha$ -terpineol (0.2%) myrtenol (0.1%) bornyl acetate (0.1%)  $\alpha$ -copaene (0.3%)  $\beta$ -elemene (0.6%)  $\beta$ -copaene (0.4%)  $\alpha$ -cubebene (0.4%)  $\alpha$ -gurjunene (2.5%)  $\beta$ -caryophyllene (3.3%) selinene isomer ° (3.9%) selinene isomer  $^{\circ}(0.3\%)$ cubebol (2.9%) jatamansinol (0.1%)  $\beta$ -gurjunene (0.4%) cadina-1(10),6,8-triene (0.9%)  $\alpha$ -humulene (2.3%)

#### Jatamol A and Jatamol B



(Z)- $\beta$ -farmesene (0.3%)  $\gamma$ -gurjunene (2.3%) 7-hexadecene <sup>†</sup> (2.0%) ledol isomer  $^{\circ}$  (0.5%) valencene isomer  $^{\circ}(0.4\%)$ valencene isomer  $^{\circ}(0.5\%)$ gurjunene isomer $\degree(0.6\%)$  $\beta$ -selinene (0.9%) valencene (0.8%) germacrene D (0.8%)  $\alpha$ -selinene (9.2%)  $\beta$ -maaliene (0.6%) selinene isomer  $^{\circ}(0.7\%)$ selinene isomer  $^{\circ}(2.2\%)$ calamenene ° (1.1%) (E)-nerolidol (1.9%) nardol isomer ° (4.8%) nardol (10.1%) ledol (0.1%) dihydro- $\beta$ -ionone (7.9%) nardol isomer  $^{\circ}(0.2\%)$ jatamansone (0.3%) jatamansic acid (0.4%) epoxy-ledene (1.0%) bis-2-ethylhexyl phthalate  $^{\circ}(1.1\%)$ 

° correct isomer not identified

<sup>†</sup> incorrect identification based on GC elution order <sup>°</sup> plasticizer impurity obtained from contact either of the fresh rhizomes or oil with plastic

Vaze (2003) determined that an oil of Indian spikenard (*N. jatamansi*) contained the following constituents:

isovaleric acid (0.03%)  $\alpha$ -pinene (0.03%)  $\beta$ -pinene (0.08%) 1,8-cineole (0.06%) methyl thymol (0.05%)  $\beta$ -patchoulene (0.38%)  $\beta$ -elemene (0.29%) cyperene (2.22%)  $\beta$ -maaliene (5.98%) 5-methyl-1-phenyl-1,3-hexadiene (0.48%) aristolene (3.04%) 8,9-dehydrocycloisolongifolene (0.91%)  $\beta$ -gurjunene (20.60%)  $\alpha$ -guaiene (0.81%) seychellene (3.32%)  $\alpha$ -patchoulene (1.27%)  $\alpha$ -gurjunene (5.40%)  $\beta$ -selinene (1.24%)  $\beta$ -ionone ° (0.88%) valencene (1.43%)  $\alpha$ -selinene (0.94%)  $\gamma$ -gurjunene (0.79%) guia-1(10),7(11)-diene (0.33%)  $\gamma$ -cadinene (0.20%) 7-epi- $\alpha$ -selinene (1.54%)  $\delta\text{-cadinene}\;(0.46\%)$  $\gamma$ -eudesmol (0.30%) maaliol (8.21%) globulol (0.79%) viridiflorol (0.39%) humulene epoxide ° (0.20%) caryophyllene oxide (0.13%)

patchouli alcohol (5.92%) 9-aristolen-12-ol (5.97%) valeranone (8.05%) valerenal (3.09%)

° correct isomer not identified

Costa et al. (2007) used linear retention indices for GC/MS peak assignments of a commercial oil of spikenard. Although no quantitative data was reported, they did present a GC profile of the oil. The qualitative composition of the oil was noted as follows: methyl thymol, methyl carvacrol, 2-undecanone, myrtenyl acetate,  $\delta$ -elemene,  $\alpha$ -cubebene, cyclosativene,  $\alpha$ -copaene,  $\beta$ -patchoulene,  $\beta$ -cubebene, cyperene,  $\beta$ -maaliene, isocaryophyllene, aristola-1(10),8diene,  $\beta$ -gurjunene,  $\alpha$ -guaiene, guaia-6,9-diene, seychellene,  $\alpha$ -humulene, 9-epi- $\beta$ -caryophyllene,  $10\beta$ -cadina-1(6)-4, diene,  $\gamma$ -muurolene, (E)- $\beta$ -ionone,  $\beta$ -selinene, valencene,  $\alpha$ -bulnesene,  $\gamma$ -cadinene,  $\delta$ -cadinene, zonarene, cadina-1,4-diene, spathulenol, viridiflorol, carotol, epi-cubenol, T-muurolol, cadin-4-en-10-ol, eudesma-4(15)7-dien-1β-ol, valeranone, valerenal and cyclocolorenone. Based on the GC profile, it can be concluded that the major components of the oil were  $\alpha$ -copaene, aristola-1(10),8-diene,  $\beta$ -gurjunene,  $\delta$ -cadinene and eudesma-4(15),7-dien- $1\beta$ -ol.

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## Dwarf Pine and Mountain Pine Oils

Dwarf pine oil is obtained by steam distillation of the needles and twigs of *Pinus mugo* Turra (syn. *P. montana* Mill.). There are two well-known varieties of this species: *P. mugo* var *mugo* (mountain pine) and *P. mugo* var *pumilio* (Haenke) Zenari (syn. *P. pumilio* Haenke) (the dwarf pine).

Kolesnikova (1985) reported that a needle oil of *P. mugo* var. *pumilio* contained the following major components:

 $\begin{array}{l} \alpha {\rm -pinene}\;(20.0\%) \\ \beta {\rm -pinene}\;(2.1\%) \\ \delta {\rm -3-carene}\;(12.3\%) \\ limonene\;(0.8\%) \\ bornyl acetate\;(9.2\%) \end{array}$ 

She also noted that the main components of *P. mugo* var *mugo* were:

 $\begin{array}{l} \alpha {\rm -pinene}\;(57.0\%) \\ \beta {\rm -pinene}\;(10.3\%) \\ \delta {\rm -3-carene}\;(2.7\%) \\ limonene\;(0.1\%) \\ bornyl acetate\;(0.5\%) \end{array}$ 

Satar (1986) analyzed an oil of *P. mugo* var *pumilio* produced from needles of Mongolian origin and found that it contained:

 $\begin{array}{l} \alpha \text{-pinene (37.6\%)} \\ \beta \text{-fenchene }^{\dagger} (11.6\%) \\ \text{camphene (4.8\%)} \\ \beta \text{-pinene (6.8\%)} \\ \delta \text{-}3\text{-carene (2.7\%)} \\ \text{myrcene (2.7\%)} \\ \text{limonene (8.2\%)} \\ \beta \text{-phellandrene (5.2\%)} \\ \text{terpinolene (0.1\%)} \\ \text{p-cymene (0.6\%)} \\ \text{bornyl acetate (27.0\%)} \end{array}$ 

<sup>†</sup> identification requires corroboration.

Kreis et al. (1990) used a chiral capillary GC column to determine the enantiomeric ratios of three monoterpene hydrocarbons found in *P. mugo* var *pumilio* oil. The ratios were as follows:

(1R,5R)-(+)-α-pinene (44%): (1S,5S)-(-)-α-pinene (56%)  $\begin{array}{l} (1R,\!5R)\mbox{-}(+)\mbox{-}\beta\mbox{-}pinene\ (2\%)\mbox{:}\\ (1S,\!5S)\mbox{-}(-)\mbox{-}\beta\mbox{-}pinene\ (98\%)\mbox{:}\\ (4R)\mbox{-}(+)\mbox{-}limonene\ (40\%)\mbox{:}\ (4S)\mbox{-}(-)\mbox{-}limonene\ (60\%) \end{array}$ 

Reichling and Harkenthal (1998) analyzed an oil produced from *P. mugo* var *pumilio* obtained from the Botanic Garden in Tübingen (Germany). The oil was found to possess the following composition:

 $\alpha$ -thujene (0.4%)  $\alpha$ -pinene (4.5%) camphene (0.8%)  $\beta$ -pinene (2.5%) myrcene (2.3%) δ-3-carene (28.3%) p-cymene (0.5%)  $\beta$ -phellandrene (15.2%) limonene (2.2%)  $\beta$ -ocimene ° (0.3%)  $\gamma$ -terpinene (0.3%) terpinolene (3.1%) terpinen-4-ol (0.9%) methyl thymol (0.8%) bornyl acetate (4.5%)  $\alpha$ -terpinyl acetate (1.6%) α-copaene (0.2%) longifolene (1.5%)  $\beta$ -caryophyllene (6.0%) α-humulene (0.9%) β-cubebene<sup>†</sup>(2.3%)  $\alpha$ -selinene (1.3%) α-muurolene (0.9%) cadinene  $^{\circ}$  (4.0%) caryophyllene oxide (3.7%)

° correct isomer not identified

<sup>+</sup> incorrect identification based in GC elution order.

Trace amounts (< 0.05%) of tricylene,  $\alpha$ -phellandrene,  $\alpha$ -terpinene, borneol,  $\alpha$ -terpineol and  $\beta$ -elemene were also found in this oil.

Reichling and Harkenthal further compared the composition of *P. mugo* oils (varieties not listed) produced from needles harvested from different locations in Germany. The oil composition was found to range as follows:

 $\begin{array}{l} \mbox{tricyclene} (0.4-1.1\%) \\ \mbox{$\alpha$-thujene} (t-3.2\%) \\ \mbox{$\alpha$-pinene} (11.0-23.0\%) \\ \mbox{$camphene} (1.7-4.2\%) \\ \mbox{$\beta$-pinene} (4.0-23.0\%) \\ \mbox{$myrcene} (2.5-29.8\%) \\ \mbox{$\alpha$-phellandrene} (t-0.5\%) \\ \mbox{$\delta$-3-carene} (0.2-29.5\%) \\ \mbox{$\alpha$-terpinene} (t-0.7\%) \\ \mbox{$\beta$-phellandrene} (7.3-19.1\%) \\ \mbox{$limonene} (0.9-8.0\%) \\ \end{array}$ 

 $\beta$ -ocimene ° (t=0.6%)  $\gamma$ -terpinene (t-1.1%) terpinolene (1.1-7.6%) terpinen-4-ol (0.3-1.9%)  $\alpha$ -terpineol (t-0.6%) methyl thymol (t-1.2%) bornyl acetate (2.0-4.8%)  $\alpha$ -terpinyl acetate (0.4–1.2%)  $\alpha$ -copaene (t-0.3%)  $\beta$ -elemene (t-0.2%) longifolene (0.3-1.5%)  $\beta$ -carvophyllene (1.8–9.2%) α-humulene (0.3–1.4%)  $\beta$ -cubebene <sup>+</sup> (t-2.2%)  $\alpha$ -selinene (t-1.4%)  $\alpha$ -muurolene (t-1.0%) cadinene ° (0.4-3.3%) caryopjyllen oxide (t-2.0%)

t = trace (< 0.1%)

correct isomer not identified

 $^{\dagger}$  incorrect identification based on GC elution order.

Trace amounts of p-cymene and borneol were also found in these oils.

Rohloff and Langleite (2005) analyzed an oil produced from the needles and twigs of *P. mugo* var. *mugo* (syn. *P. mughus* Scop.) in Norway. The major components of this oil were:

 $\begin{array}{l} \alpha \text{-pinene} \ (20.6\%) \\ \text{camphene} \ (3.5\%) \\ \beta \text{-pinene} \ (6.9\%) \\ \delta \text{-}3\text{-carene} \ (17.7\%) \\ \text{myrcene} \ (7.0\%) \\ \text{limonene} \ (7.8\%) \\ \beta \text{-phellandrene} \ (9.9\%) \\ \text{terpinolene} \ (2.6\%) \\ \text{bornyl acetate} \ (6.8\%) \end{array}$ 

Kurose et al. (2009) examined the compositions of the needle oils of a number of *Pinus* species including *P. mugo* var *pumilio* (syn. *P. pumilio*). The oil was found to contain the following constituents:

santene (0.2%) tricyclene (0.5%)α-pinene (18.3%) camphene (5.2%)  $\beta$ -pinene (1.3%) sabinene (0.5%)δ-3-carene (10.4%) myrcene (1.7%)  $\alpha$ -phellandrene (0.3%)  $\alpha$ -terpinene (0.1%) limonene (4.9%)  $\beta$ -phellandrene (1.2%) γ-terpinene (0.2%) p-cymene (0.1%) terpinolene (3.1%) 3-hexenol ° (0.1%)

 $\alpha$ -cubebene (0.1%)  $\alpha$ -copaene (0.2%) β-bourbonene (0.1%) bornyl acetate (0.2%)  $\beta$ -elemene (0.3%)  $\beta$ -caryophyllene (2.8%) terpinen-4-ol (0.2%) muurola-3,5-diene (0.1%) trans-cadina-1(6),4-diene (0.2%)  $\alpha$ -humulene (2.0%) (E)- $\beta$ -farmesene (0.1%)  $\gamma$ -muurolene (0.8%)  $\alpha$ -terpinyl acetate (0.4%)  $\beta$ -copaene (7.5%) trans-muurola-4(14),5-diene (0.3%)  $\alpha$ -muurolene (1.4%) bicyclogermacrene (1.9%) γ-cadinene (8.7%)  $\alpha$ -bisabolene ° (0.8%) cadina-1,4-diene (0.2%) germacrene D-4-ol (0.6%) cubenol (0.5%)1-epi-cubenol (0.5%) globulol (0.2%) spathulenol (0.6%) T-cadinol (2.3%) T-muurolol (3.1%)  $\alpha$ -muurolol (1.0%) butyl dodecanoate (1.1%)  $\alpha$ -cadinol (8.4%) ethyl hexadecanoate (0.7%) 3-hexenyl hexanoate  $^{\circ}(1.7\%)$ phytol (7.1%)

° correct isomer not identified

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