Progress in Essential Oils

Brian M. Lawrence, Consultant

Patchouli Oil and Extracts

The current world production of patchouli oil ex *Pogostemon cablin* (Blanco) Benth. (syn. *P. patchouli* Pellet) is ca. 1,000 metric tons produced in Indonesia. A further 75 metric tons are also produced in China and India, respectively.

An acetone extract of the dried herb of *P. cablin* was examined for its activity against trypanosomiasis (Chaga's disease) by Kiuchi et al. (2004). Because the extract showed strong trypanocidal activity, it was subjected to repeated column chromatography to yield three active sesquiterpenes. Structural elucidation of the three components revealed that they were hydroperoxides (**see F-1**). The reason that these hydroperoxides have not been previously characterized in patchouli oil is because they will not survive steam distillation.

A collection of 18 *P. cablin* plants from different areas in Guangdong Province and Hainan Province that were dried and ground to a powder were subjected to pressurized liquid extraction using methanol by Hu et al. (2006). Analysis of the volatiles from these extracts using GC/MS only revealed that the nine major constituents varied as follows:

β-patchoulene (0–5.8%)
β-caryophyllene (0.5–3.7%)
α-guaiene (0–10.2%)
seychellene (0–4.6%)
β-guaiene (0–3.3%)
δ-guaiene (0–12.5%)
patchouli alcohol (22.9–78.2%)
pogostone (0–39.5%)

The authors noted that there were both patchouli alcohol and pogostone chemotypes amongst the *P. cablin* collections examined.

Samples of patchouli were collected from Rabaul, Port Moresby and Mekeo areas of the Central Province (Papua New Guinea) by Wossa et al. (2006). Oils produced from each of the areas were analyzed by GC-FID and GC/MS. The comparative results of this study are presented in **T-1**.

Sharma (2007) compared the main component composition of hydrodistilled oils of Indian-grown patchouli leaves in various states of dryness. The results of this study are shown in **T-2**.

Wei and Shibamoto (2007) analyzed commercial sample of patchouli oil and characterized the following main components:

β-patchoulene (4.1%)
α-guaiene (18.2%)
methyl benzoate (14.3%)
γ-guaiene (20.5%)
patchouli alcohol (28.8%)

The fact that the authors characterized methyl benzoate and γ-guaiene as components of this oil indicates that the oil analyzed was adulterated.

The dried leaves of an Indonesian population that was cultivated in Pantnagar (Uttarakhand, India) were subjected to hydrodistillation for 11–12 hr to produce an oil in 0.54% yield. GC-FID and GC/MS analysis by Prakash et al. (2007) revealed that the oil possessed the following composition:

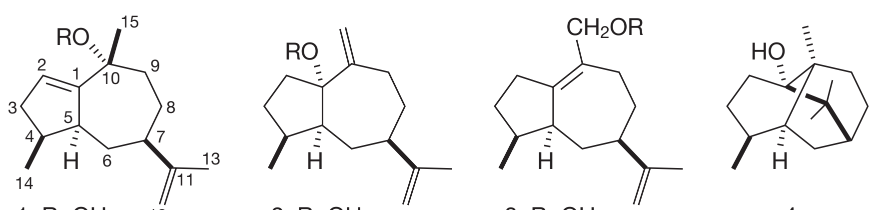
β-pinene (0.2%)
β-patchoulene (2.3%)
β-cubebene (0.6%)
β-caryophyllene (4.8%)
α-guaiene (23.3%)
γ-patchoulene (6.3%)
α-patchoulene (2.5%)
seychellene (3.2%)
α-bulnesene (21.4%)
longicamphenylone† (0.8%)
pogostol (0.3%)
patchouli alcohol (32.3%)

†incorrect identificatio

Ranade (2007) reported that the typical composition of patchouli oil was as follows:

β-patchoulene (2.8%)
β-caryophyllene (4.0%)

F-1. The structures of the newly identified sesquiterpene hydroperoxides in patchouli plants, their corresponding alcohols and patchouli alcohol



1: R=OH 1a: R=H
2: R=OH 2a: R=H
3: R=OH 3a: R=H
4

1. 10α-hydroperoxy-guaia-1,11-diene
1a. guaia-1,11-dien-10α-ol
2. 1α-hydroperoxy-guaia-10(15),11-diene
2a. guaia-10(15),11-dien-10α-ol
3. 15α-hydroperoxy-guaia-1(10),11-diene
3a. guaia-1(10)-dien-5α-ol
4. patchouli alcohol

α-guaiene (14.5%)
α-patchoulene (4.5%)
α-gurjunene[a] (0.3%)
γ-patchoulene (8.5%)
bulnesene[b] (17.0%)
nor-patchouli alcohol (0.4%)
pogostol (2.0%)
patchouli alcohol (31.0%)

[a]should be γ-isomer; [b]should be α-isomer

Williams (2008) reported the results of an analysis of patchouli oil using both polar and non-polar GC columns (GC-FID and GC/MS). The constituents characterized in this oil were as follows:

α-copaene (0.5%)
β-patchoulene (2.0%)
β-elemene (1.1%)
cycloseychellene (0.6%)
isocaryophyllene (0.5%)
β-caryophyllene (2.2%)
α-guaiene (15.2%)
seychellene (5.2%)
α-humulene (1.0%)
α-patchoulene (6.2%)
γ-gurjunene (1.4%)
aciphyllene (2.9%)
γ-patchoulene (0.9%)
α-bulnesene (16.8%)
δ-cadinene (<0.1%)
patchouli alcohol (22.9%)

A sample of patchouli oil that was produced in Banda Aceh (Sumatra, Indonesia) was analyzed by a combination of fractional distillation and GC/MS only (Aisayah et al., 2002). The main identified constituents of this oil were determined to be:

β-patchoulene (2.3%)
β-elemene (1.2%)
β-caryophyllene (3.5%)
α-guaiene (15.9%)
seychellene (7.0%)
α-humulene (0.7%)
α-patchoulene (5.5%)
α-gurjunene (1.5%)
allo-aromadendrene (0.6%)
δ-guaiene (23.1%)
patchouli alcohol (32.6%)

Ramachandra et al. (2008) used various doses of gamma rays to develop a high-yielding mutant patchouli. To study the effect of gamma rays, plantlets derived from tissue culture were irradiated at a dose rate of 250 rad per minute. After greenhouse and field cultivation, the plants were harvested five months after planting, dried and subjected to hydrodistillation. The authors found that best treatment was 8 kR, from which an oil yield of 3.45% was obtained. The major components characterized by GC-FID and retention times in the oil can be seen compared with those of an oil from control plants is shown in **T-3**.

Leaves of patchouli that were collected from Imphal (Manipur, India) were shade-dried for 15 days after which they were hydrodistilled for 6 hrs to produce an oil in 2.7% yield. GC/MS analysis of the oil by Rana and Amparo Blazquez (2009) revealed the following constituents in the oil:

δ-elemene (0.1%)
β-patchoulene (1.1%)
β-bourbonene (0.1%)
β-elemene (0.9%)
thujopsene (0.4%)
β-caryophyllene (2.2%)
α-patchoulene (3.8%)
α-guaiene (0.3%)
germacrene D (0.2%)
γ-patchoulene (0.6%)
α-selinene (1.8%)
α-bulnesene (9.5%)
7-epi-α-selinene (0.2%)
caryophyllene oxide (0.6%)
patchouli alcohol (54.9%)

Trace amounts (<0.1%) of benzaldehyde, β-pinene, limonene and hexadecanoic acid were also characterized in this oil.

Kumar (2009) compared the oil yield and main component composition from dry patchouli leaves versus leaves that were soaked in water for 12 hr and 24 hr. Hydrodistillation of the dry and soaked leaves resulted in oil yields of 3.0%, 3.2% and 3.3%, the latter being from the leaves soaked for 24 hr. The three oils were analyzed by GC-FID and GC/MS. A comparison between the main

T-1. Percentage composition of patchouli oils from different locations in Papua New Guinea

Compound	Mekeo oil	Rabaul oil	Port Moresby oil
α-pinene	1.2	-	-
β-patchoulene	1.8	-	-
β-caryophyllene	2.4	-	1.1
α-guaiene	7.8	7.5	4.6
seychellene	6.2	3.9	3.2
α-patchoulene	1.4	1.7	1.5
aciphyllene	-	-	1.2
γ-patchoulene	3.7	-	-
δ-guaiene	9.5	9.9	9.5
selina-3,7(11)-diene	5.1	-	-
viridifloro	-	-	1.4
pogostol	-	5.1	-
patchouli alcohol	43.7	71.8	71.7
benzyl benzoate	1.7	-	-

T-2. Comparative percentage composition of patchouli oil produced from fresh and dried leaves

Compound	Fresh leaf oil	Dried leaf oil
β-patchoulene	5.9	7.5
β-caryophyllene	2.7	2.2
α-guaiene	7.7	7.0
α-patchoulene	3.1	3.0
seychellene	3.2	3.7
γ-patchoulene	9.4	8.2
pogostol	2.4	1.6
patchouli alcohol	57.4	62.4
oil yield	0.3	3.6

components of these oils can be seen in **T-4**.

Another study on the use of gamma rays to develop an improved patchouli mutant was performed by Rekha et al. (2009). A comparative percentage composition of the oil produced from control plants and the mutant clone are presented in **T-5**.

Analysis of an oil produced from patchouli grown in an experimental garden of the gene bank of CIMAP (Lucknow, Uttar Pradesh, India) by Sundaresan et al. (2009) using GC-FID and GC/MS revealed that the oil contained:

α-pinene (0.2%)
β-pinene (0.4%)
β-patchoulene (4.2%)
β-caryophyllene (4.5%)
α-guaiene (14.6%)
α-humulene (0.7%)
seychellene (5.6%)
α-patchoulene (3.3%)
selinene* (3.9%)
patchouli alcohol (23.2%)

*correct isomer not identifie

Cornwell (2010) analyzed commercial patchouli oils from China, India and Indonesia using GC-FID and GC/MS. The main components identified in these oils can be seen in **T-6**. In addition, the author characterized trace amounts (ppm levels) of toluene, isovaleric acid, 2-methylbutyric acid, 2-heptanone, α-thujene, camphene, benzaldehyde, 5-methylfurfural, sabinene, 1-octen-3-one, 1-octen-3-ol, 3-octanone, 2-pentylfuran, myrcene, 3-octanol, α-phellandrene, α-terpinene, p-cymene, limonene, β-phellandrene, 1,8-cineole, γ-terpinene, acetophenone, terpinolene, linalool, 2-phenethyl alcohol, (E)-4,8-dimethylnona-1,3,7-triene, α-campholenal, *trans*-pinocarveol, terpinen-4-ol, p-cymen-8-ol, α-terpineol, myrtenol, verbenone, citronellol, p-vinylguaiacol, eugenol, β-cubebene, 9-epi-β-caryophyllene, β-selinene, α-selinene, viridiflorene, bicyclogermacrene, aciphyllene, γ-patchoulene, 7-epi-α-selinene, *trans*-calamenene, δ-cadinene, elemol, (E,E)-farnesol, (E,E)-farnesyl acetate, hexahydrofarnesyl acetate, phytol and (E)-nerolidol were found in one or all three of the commercial samples of patchouli oil. Cornwell also pointed out that allo-aromadendrene is not a component of pure patchouli oil, it is only found in oils adulterated with gurjun balsam oil.

Milchard et al. (2010) reported the results of the collaborative analyses of one Chinese and two Indonesian commercial samples of patchouli oil. The results are an update on the earlier study by Milchard et al. (2004), in which they incorrectly reported two constituents—γ-patchoulene instead of seychellene, and ledene instead of aciphyllene and γ-patchoulene. A summary of the new results of these three samples of patchouli oil can be found in **T-7**.

T-3. Comparative percentage composition of the oils of an irradiated and a control type of patchouli

Compound	Irradiated patchouli oil	Control patchouli oil
δ-elemene	1.0	0.2
β-patchoulene + β-elemene	3.1	5.3
β-caryophyllene + α-guaiene[a]	18.2	32.9
seychellene	0.5	1.7
(E)-β-guaiene + α-bulnesene	38.1	25.9
α-guaiene oxide	0.5	0.2
caryophyllene oxide	0.4	0.5
nor-patchoulenol	2.2	0.3
patchouli alcohol	31.9	32.3

[a]plus γ-patchoulene (probably misidentified

T-4. Comparative percentage composition of the main components of oils produced from dry and soaked leaves of patchouli

Compound	Dry leaves oil	12-hr-soaked leaves oil	24-hr-soaked leaves oil
β-patchoulene	3.2	4.2	9.4
β-caryophyllene	3.3	3.1	2.5
α-guaiene	15.6	12.6	9.2
seychellene	6.9	7.2	6.0
α-patchoulene	4.8	4.6	3.8
selinene*	2.9	2.6	2.2
δ-guaiene	16.1	16.3	12.7
patchouli alcohol	37.6	38.5	40.2

*correct isomer not identifie

T-5. Comparative percentage composition of the oils of a control and mutant clone of patchouli

Compound	Control plant oil	Mutant clone oil
β-elemene	0.4	0.2
β-patchoulene	1.8	1.6
β-caryophyllene	9.2	4.7
α-guaiene	2.9	1.4
seychellene	9.5	8.6
α-humulene	0.9	0.9
α-bulnesene	14.1	6.9
α-guaiene oxide	0.3	0.7
caryophyllene oxide	0.5	0.7
nor-patchoulenol	1.2	2.0
patchouli alcohol	47.8	60.3
pogostol	0.4	0.5

Wu et al. (2011) compared the nine major constituents of the oils of 16 selections of patchouli from Guangdong and Hainan provinces. The compositional range of the constituents was found to be as follows:

β-patchoulene (0.2–0.8%)
β-caryophyllene (0.8–1.6%)
α-guaiene (0–7.8%)
seychellene (0–4.3%)
α-patchoulene (0.2–1.4%)
β-guaiene (0.1–2.7%)
δ-guaiene (0–11.6%)
patchouli alcohol (42.9–64.3%)
pogostone (10.3–27.7%)

King (2012) reported that there are at least three cultivars of patchouli grown in Aceh. The major ones are 'Tapaktuan,' 'Lhokseumawe' and 'Sidikalang.' Oils from these three cultivars have been found to possess the following patchouli alcohol contents:

'Tapaktuan': 28.7–35.9%
'Lhokseumawe': 29.1–34.5%
'Sidikalang': 30.2–35.2%

Fresh leaves of *P. cablin* were collected from the experimental garden of the Central Institute of Medicinal and Aromatic Plants Research Centre (Purara, Uttarakhand, India) and subjected to hydrodistillation to produce an oil in 0.32% yield. The composition of this oil was determined by GC-FID and GC/MS to be as follows:

α-copaene (0.1%)
β-patchoulene (1.0%)
β-elemene (0.8%)
cycloseychellene (0.4%)
β-caryophyllene (2.4%)
α-guaiene (10.0%)
seychellene (3.1%)
α-patchoulene (1.6%)
cis-thujopsadiene[a] (0.3%)
γ-gurjunene (0.2%)
γ-muurolene (0.2%)
germacrene D (0.1%)
valencene (0.3%)
γ-patchoulene (1.3%)
α-bulnesene (8.7%)
7-epi-α-selinene (0.1%)
δ-cadinene (0.1%)
nor-patchoulenol (1.6%)
caryophyllene oxide (0.3%)
pogostol (0.5%)
patchouli alcohol (61.6%)
bulnesol (0.1%)
pogostone (1.0%)

[a]tentative identificatio

Trace amounts (<0.05%) of α-pinene, myrcene, p-cymene, γ-terpinene, borneol, α-terpineol, β-longipinene, *cis*-thujopsene (tentative), α-selinene, α-cadinene, longipinene and guaiol were also characterized in this oil.

Rusydi et al. (2013) examined the morphology of the glandular trichomes in *P. cablin* growing in Malaysia. They found that there were six types of glandular thrichomes (oil glands; short-stalked capitate, long-stalked capitate, peltate, digitform, clavate filiform and fusiform). The most abundant are the short-stalked capitate trichomes, which are found on the upper surface (abaxial) of the leaves, while the peltate trichomes are more densely located on the underside (adaxial) of the leaves and are the largest storage sites for the essential oil. Some trichomes are found subcutaneously, which is why it is important to dry the leaves before distillation so that during drying a small amount of fermentation takes place, which facilitates the oil isolation from the subcutaneous glands.

Analysis of a Chinese patchouli oil purchased locally was examined by He et al. (2013) for its antinociceptive and anti-allergic properties. The oil, which

T-6. Percentage composition of patchouli oil from China, India and Indonesia

Compound	Chinese oil	Indian oil	Indonesian oil
α-pinene	0.2	0.1	0.2
β-pinene	0.4	0.3	0.4
limonene + β-phellandrene[a]	t	t	t
δ-elemene	0.2	0.3	0.2
α-copaene	t	t	0.6
β-patchoulene	6.2	4.4	3.0
β-elemene	1.2	1.3	1.3
cycloseychellene	0.8	0.6	0.7
β-caryophyllene	3.6	4.3	3.9
α-guaiene + seychellene[a]	24.7	21.8	21.8
α-humulene[a] + α-patchoulene	6.8	5.7	5.9
α-bulnesene	18.2	19.8	17.1
nor-patchoulenol	0.7	1.0	0.6
pogostol	1.5	1.8	3.3
patchouli alcohol	19.8	22.4	26.9

[a]minor component of mixture; t=trace (0.05%)

T-7. Comparative percentage composition of the main constituents of patchouli oils from different origins

Compound	Chinese oil	Indonesian oil A	Indonesian oil B
β-patchoulene	9.3	2.3	2.1
β-elemene	1.3	0.9	0.7
β-caryophyllene	3.1	3.8	3.1
α-guaiene	15.3	14.6	13.8
seychellene	6.7	6.3	6.7
α-patchoulene	5.9	5.1	5.1
allo-aromadendrene	5.0	2.4	2.3
aciphyllene + γ-patchoulene	3.9	3.7	3.4
δ-guaiene	20.7	18.8	16.7
nor-patchoulenol	0.4	0.6	0.6
pogostol	1.5	2.2	2.4
patchouli alcohol	17.5	28.2	32.7
pogostone	0.1	1.1	1.0

A = oil sold at 30% patchouli alcohol content; B = oil sold at 35% patchouli alcohol content was analyzed by GC-FID and GC/MS, was found to contain the following constituents:

β-patchoulene (7.0%)
β-elemene (1.0%)
cis-thujopsene† (0.9%)
isocaryophyllene† (6.3%)
β-gurjunene† (3.3%)
α-patchoulene (8.6%)
δ-patchoulene (0.7%)
β-caryophyllene (1.0%)
cis-β-guaiene† (0.7%)
γ-gurjunene† (3.7%)
β-selinene (0.4%)
β-guaiene† (14.2%)
elemol (3.0%)
globulol (0.8%)
trans-longipinocarveol† (0.6%)
caryophyllene oxide (0.8%)
patchouli alcohol (26.5%)
bulnesol (0.7%)
aristolone† (0.6%)

†incorrect identificatio

As can be seen, a number of constituents foreign to patchouli oil that were listed above as "incorrect identifications." It is possible, however, that the oil analyzed was adulterated with a number of the identifications being correct for an adulterated oil.

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