Progress in Essential Oils

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Long Pepper Oil

Long pepper, also known as Bengal pepper or Indian long pepper (pippali, peppooli, pipli or pipul in various Indian dialects), is obtained from *Piper longum* L., a member of the Piperaceae family that is endemic to the Indo-Malay region of Southeast Asia. It can be found growing wild in the Indian tropical rainforests. It is a perennial, dioecious, glabrous, slender vine or undershrub, which possesses simple, alternate wide ovate, cordate laves. The female inflorescence is a cylindrical pedunculated spike 2–5 cm long. The fruit are small, shiny ovoid berries ranging in color from green to gray to black and are embedded in the spike. Both the fruit and roots are widely used in traditional medicine (Zaveri et al. 2010), while the fruit are used as a spice (Manoj et al., 2004). In recent years, an oil and an extract of long pepper has become a minor product of India.

A survey of the early literature revealed that Nigam and Radhakrishnan (1968) determined that the fruit oil was produced in the laboratory by water distillation in 0.6% yield. They found that the oil was devoid of monoterpene compounds and was rich in sesquiterpenes with b-caryophyllene being the major hydrocarbon.

Lawrence (1978) examined the composition of a lab-distilled oil of *P. longum* using both GC-FID and GC/MS. The constituents characterized in this oil were:

α-pinene (0.1%)
β-pinene (0.1%)
myrcene (0.2%)
α-phellandrene (0.4%)
limonene (0.3%)
1,8-cineole (0.5%)
γ-terpinene (0.1%)
p-cymene (0.2%)
tridecane (0.8%)
δ-elemene (0.2%)
α-cubebene (0.3%)
α-copaene (0.6%)
trans-α-bergamotene (0.3%)
β-elemene (0.4%)
β-caryophyllene[a] + terpinen-4-ol (10.0%)
α-terpineol + borneol (2.6%)
selina-4,11-diene (1.5%)
germacrene D (10.3%)
pendadecane (1.3%)
β-selinene (12.4%)
δ-cadinene (10.3%)
selina-3,11-diene + ar-curcumene (13.8%)
(E)-anethole (0.5%)
heptadecane (1.3%)
cubebol (4.0%)
caryophyllene oxide (3.7%)
T-muurolol (0.1%)

[a]major component

Trace amounts (<0.05%) of sabiene, isoborneol, (E)-β-farnesene and carvone were also found in this oil.

Shankaracharya et al. (1997) ground a 500 g aliquot of long pepper spikes and subjected the powdered spice to hydrodistillation to yield an oil in 0.9%. The oil, which was analyzed by GC-FID and GC/MS, was found to contain the following constituents:

α-phellandrene (0.1%)
p-cyemene (0.1%)
1,8-cineole (0.4%)
limonene (0.4%)
acetophenone (0.5%)
γ-terpinene (0.6%)
linalool (0.1%)
undecane (0.1%)
terpinen-4-ol (0.1%)
α-terpineol (0.1%)
cuminaldehyde (0.1%)
isopulegyl acetate (0.5%)
undecanone* (0.5%)
tridecane (0.9%)
tridecane (0.8%)
δ-elemene (0.1%)
α-cubebene (0.1%)
α-ylangene (0.1%)
α-copaene (1.6%)
β-bourbonene (0.4%)
β-elemene (0.5%)
β-caryophyllene (17.0%)
(Z)-β-farnesene (3.7%)
α-gurjunene (0.8%)
α-humulene (2.0%)
zingiberene (5.0%)
germacrene D (4.9%)
germacrene B (1.8%)
pentadecane* (1.8%)
β-bisabolene (11.2%)
pentadecane (17.8%)
γ-elemene (0.8%)
globulol (2.6%)
spathulenol (3.0%)
cubenol (0.1%)
T-muurolol (0.3%)
heptadecene* (2.3%)
heptadecane (5.7%)
nonadecane* (0.1%)
nonadecane (0.2%)

*correct isomer not identified

In addition, trace amounts (<0.1%) of α-pinene, β-pinene, myrcene, camphor, naphthalene, γ-muurolene, β-selinene and an isomer of calamenene were characterized in this oil.

Jagan Mohran Rao (2000) repeated the analysis of long pepper oil in which he was a co-author (see Shankaracharya et al., 1997) with no additional information and data.

The dried fruit of long pepper, reputed to be of Indonesian origin, was purchased by Tewtrakul et al. (2000) from a drug store in Songkhla province (Thailand). Hydrodistillation for 3 hr yielded a long pepper oil in 0.6%. Analysis of this oil by GC/MS only revealed that it possessed the following composition:

tridecane (0.3%)
β-elemene (1.1%)
β-caryophyllene (10.2%)
α-bergamotene* (1.4%)
(E)-β-farnesene (1.1%)
α-humulene (2.9%)
9-octadecene (2.3%)

ar-curcumene (4.8%)
germacrene D (16.5%)
pentadecane (6.6%)
β-selinene (3.9%)
β-bisabolene (3.3%)
7-epi-α-selinene (3.0%)
caryophyllene oxide (1.5%)
8-heptadecene* (7.4%)
8-heptadecane* (11.4%)
heptadecane (9.6%)
nonadecane* (1.8%)
nonadecane* (3.1%)
nonadecane (1.0%)

*correct isomer not identified

Fruit spikes of *P. longum* were purchased from a drug store in Shanghai (China), ground and subjected to microwave-assisted hydrodistillation to yield an oil by Liu et al. (2007). The authors also determined the headspace volatiles of the ground *P. longum* using solid-phase microextraction with a divinylbenzene/Carbowax/polydimethylsiloxane fiber (DVB/CAR/PDMS). Analysis of the oil and headspace volatiles was performed using GC/MS only. The results of this study are shown in **T-1**. Trace amounts of a-thujene and an isomer of β-ocimene were also found in this oil.

T-1. Comparative percentage composition of the oil and headspace volatiles of Piper longum

Compound	Oil	Headspace[a]
α-pinene	0.8	t
camphene	0.1	-
β-pinene	2.3	t
myrcene	0.6	-
α-phellandrene	1.6	-
δ-3-carene	7.6	0.1
o-cymene[†]	0.7	-
limonene	6.7	t
γ-terpinene	0.1	-
sabinene[†]	0.1	-
terpinolene	0.3	t
linalool	0.2	-
camphor	0.1	-
piperitone[†]	0.2	0.1
terpinen-4-ol	0.1	-
α-terpineol	0.2	0.1
piperonal	0.1	0.2
p-cymene[†]	0.3	0.1
eugenol	7.4	0.4
α-copaene	0.1	-
β-cubebene	1.8	0.1
β-elemene	2.3	0.2
β-farnesene*	1.5	0.1
β-caryophyllene	33.4	0.6
α-humulene	0.5	0.3
β-selinene	0.9	0.3
α-farnesene*	0.5	0.3
zingiberene	6.7	0.3
β-bisabolene	1.5	0.2
α-cadinene	0.6	0.1
calamenene*	1.8	0.3
cadina-1,4-diene	2.5	0.5
germacrene B	0.6	0.1
caryophyllene oxide	1.4	0.1
spathulenol	1.5	0.4
β-eudesmol	2.3	0.2
cubenol	3.6	0.5
heptadecane	2.7	0.4
benzyl benzoate	0.2	0.1
2-phenethyl benzoate	0.5	0.1
hexadecanol	0.8	0.3
nonadecane	0.2	0.1

*correct isomer not identified; [†]incorrect identification; [a]the headspace volatiles totaled 6.8%, so there is little value in the quantitative data

Bhuiyan et al. (2008) collected leaves and inflorescence-rich spikes of *P. longum* that were grown on the campus of Chittagong University (Bangladesh). Separate hydrodistillation of the leaves and inflorescences for 4 hr yielded oils that were analyzed by GC/MS only. Unfortunately, it would appear that many of the constituents found were probably misidentified. As a result, rather than list the 70 and 32 constituents reputed to be from the leaf and inflorescence oil, only the major constituents will be listed. So, in the leaf oil, the major constituents were β-caryophyllene (12.3%) and (E)-nerolidol (19.1%), while in the inflorescence oil it was eugenol (33.1%), β-caryophyllene (9.3%) and (E)-cinnamyl acetate (5.9%).

Fresh leaves and mature fruiting spikes of long pepper were collected by Rameshkumar et al. (2011) from the Tropical Botanic Garden and Research Institute (Palode, Kerala, India) and separately subjected to 3 br hydrodistillation. The oil yields were 0.05% (leaves) and 0.60% (fruiting spikes). Each oil was analyzed using both GC-FID and GC/MS. The constituents characterized in the leaf oil were:

2-heptyl acetate (1.5%)
linalool (0.5%)
2-undecanone (1.0%)
β-caryophyllene (2.2%)
myristicin (26.9%)
(E)-nerolidol (13.0%)
apiole (50.0%)

Trace amounts of β-copaene and α-humulene were also found in this leaf oil.

In contrast, the composition of the flowering spike oil was determined to be:

1-tridecene (1.5%)
tridecane (4.7%)
δ-elemene (0.7%)
α-copaene (2.6%)
β-elemene (2.4%)
γ-elemene (0.6%)
(Z)-β-farnesene (1.1%)

(E)-β-farnesene (6.8%)
α-acoradiene (0.7%)
trans-cadina-1(6),4-diene (5.4%)
γ-muurolene (0.6%)
1-pentadecene (7.1%)
γ-amorphene (0.9%)
pentadecane (15.8%)
β-bisabolene (5.9%)
myristicin (3.0%)
germacrene B (0.4%)
(E)-nerolidol (1.3%)
spathulenol (6.6%)
caryophyllene oxide (5.4%)
globulol (1.5%)
humulene epoxide II (0.8%)
muurola-4(10(14)-dien-1β-ol (1.7%)
cubenol (1.4%)
14-hydroxy-isocaryophyllene (1.9%)
apiole (3.9%)
δ-heptadecene* (1.8%)
heptadecane (4.7%)

*correct isomer not identified

Druce (2013) produced an oil of *P. longum* that was purchased from a market in Australia. He reported that the oil contained the following constituents: α-pinene, camphene, β-pinene, myrcene, α-phellandrene, δ-3-carene, limonene, 2-heptanol, a β-ocimene isomer, linalool, undecane, camphor, isoborneol, bornyl acetate, (E)-5-tridecene, eugenol, δ-elemene, α-cubebene, methyl eugenol, cyclosativene, α-copaene, β-elemene, *trans*-α-bergamotene, α-gurjunene, β-caryophyllene, *cis*-α-bergamotene, (Z)-β-farnesene, (Z,E)-α-farnesene, α-humulene, arcurcumene, γ-muurolene, germacrene D, α-selinene, β-bisabolene, γ-cadinene, δ-cadinene, α-parnasinene, (Z)-α-bisabolene and caryophyllene oxide. Unfortunately, Druce did not present any quantitative data on the constituents listed above.

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