Progress in Essential Oils

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Amyris Oil

Amyris oil (*Amyris balsamifera* L.) is produced by steam distillation of the heartwood of a small tree member of the Rutaceae family. The distribution of *A. balsamifera* is mostly limited to islands in the Caribbean, particularly Cuba, Dominican Republic and Jamaica, although it can be found to a limited extent in certain South American countries. The tree is known as *bois chandelle* (candlewood) in Haiti, torchwood in Jamaica, and amyris or West Indian sandalwood in the United States.

Between 1956 and 1967 the quantity of amyris oil produced annually in Haiti ranged from 46 to 104 metric tonnes (Igolen, 1968). Lawrence (1985) reported that in 1984 production had decreased to 40 tonnes, while Champon (2001) reported that the level of amyris oil produced in Haiti had stabilized to ca. 50 tonnes. More recently, oil production seems to have stabilized at around 55–65 tonnes. Amyris oil production in the Dominican Republic has grown from a few tonnes to 20–35 tonnes annually.

Van Beck et al. (1989) used both GC-FID and GC/MS to determine that a commercial oil of amyris presumed to be of Haitian origin was found to possess the following composition:

zingiberene (2.4%)
β-bisabolene (0.8%)
β-dihydroagarofuran (1.0%)
7-epi-α-selinene (0.5%)
β-sesquiphellandrene (4.7%)
ar-curcumene (1.5%)
selina-3(7)11-diene (2.5%)
α-agarofuran (0.5%)
(E)-nerolidol (0.6%)
elemol (9.1%)
10-epi-γ-eudesmol (9.7%)
guai-8-en-11-ol* (1.0%)
guai-4(14)-en-11-ol* (0.9%)
γ-eudesmol (6.6%)
jinkoh-eremol[t] (0.7%)
valerianol (21.5%)
α-eudesmol (4.8%)
7-epi-α-eudesmol (10.7%)
β-eudesmol (7.9%)
4α-hydroxydihydroagarofuran (0.4%)
6R,7R-bisabolone (0.1%)
6S,7R-bisabolone (0.6%)
drimenol (1.1%)

*correct isomer not identified; [t]tentative identification

König et al. (1999) characterized the presence of cadina-4,11-diene and muurola-4,11-diene as minor constituents of amyris oil. Furthermore, they determined that it was the (-)-form that was found in the oil.

Jirovetz et al. (2004) screened numerous sandalwood oils of different origins for their antimicrobial activities. They found that *A. balsamifera* oil contained:

guaiol (22.0%)
elemol (31.2%)
(Z)-α-santalol (0.2%)
(Z)-β-santalol (<0.1%)

It is of interest to note that the leaf oil of *A. balsamifera* of Cuban origin that was produced by hydrodistillation was analyzed by Pino et al. (2006) using GC-FID and GC/MS. The main components (70.1%) were found to be as follows:

linalool (0.3%)
β-bourbonene (0.3%)
β-cubebene (0.1%)
β-caryophyllene (0.7%)
α-humulene (0.2%)
γ-muurolene (0.2%)
7-epi-cubebol (0.5%)
β-dihydroagarofuran (0.6%)
cubebol (1.0%)
δ-cadinene (0.5%)
α-agarofuran (1.1%)
elemol (2.0%)
caryophyllene alcohol (0.2%)
spathulenol (7.1%)
caryophyllene oxide (2.1%)
γ-eudesmol (15.4%)
valerianol (43.8%)
7-epi-α-eudesmol (2.3%)
occidentalol acetate (2.4%)
14-hydroxyl-α-muurolene (1.0%)
carissone[a] (0.8%)
seselin[b] (3.5%)

[a]also known as 11-hydroxy-eudesm-4-en-3-one
[b]also known as amyrolin

Trace amounts (<0.1%) of an additional 34 compounds were also characterized in this oil. The interest in this oil is that it contains the same major constituent and many of the same minor constituents although at different quantitative amounts.

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W.A. König, N. Bülow and V. Saritas, *Identification of sesquiterpene hydrocarbons by gas phase analytical methods.* Flav. Fragr. J., **14**, 367–378 (1999).

L. Jirovetz, G. Buchbauer, Z. Denkova, A. Stoyanova, I. Murgov, V. Gearon, S. Birkbeck, E. Schmidt and M. Geissler, *Comparative study on the antimicrobial activities of different sandalwood essential oils of various origin.* Flav. Fragr. J., **21**, 465–468 (2006).

J.A. Pino, R. Marbot and V. Fuentes, *Aromatic plants from Western Cuba VI. Composition off the leaf oils of* Murraya exotica *L.*, Amyris balsamifera *L.*, Severinia buxifolia *(Poir.) Ten. and* Triphasia trifolia *(Burm. f.) P. Wilson.* J. Essent. Oil Res., **18**, 24–28 (2006).

Anise Oil

The major constituents of anise oil produced in Poland were found by Gora et al. (1997) to be as follows:

limonene (1.1%)
methyl chavicol (1.1%)
(E)-anethole (95.5%)
anisaldehyde (1.0%)

Oils produced from 29 seed sources collected in the regions of Alfyon (2), Antalya (4), Balikesir (2), Burdur (9), Bursa (2), Denizli (5), Izmir (2), Mugla (2) and Usak (1) in Turkey were subjected to analysis by Arslan et al. (2004). The average amount of constituents identified in the various oils was found to be as follows:

α-pinene (0.00425%)
camphene (0.00585%)
β-pinene (0.00850%)
sabinene (0.00929%)
myrcene (0.00864%)
δ-3-carene (0.01300%)
α-phellandrene (0.01551%)
α-terpinene (0.00768%)
β-phellandrene (0.00852%)
1,8-cineole (0.00849%)
(Z)-β-ocimene (0.00530%)
(E)-β-ocimene (0.00217%)
γ-terpinene (0.08981%)
p-cymene (0.13166%)
terpinolene (0.04009%)
linalool (0.80063%)
linalyl acetate (0.00580%)
terpinen-4-ol (0.48511%)
methyl chavicol (0.80530%)
α-terpineol (0.96772%)
(Z)-anethole (0.14377%)
(E)-anethole (89.5421%)
methyl eugenol (0.61695%)
anisaldehyde (0.46536%)
anisic acid (0.13902%)
acetanisole (0.20343%)
anisyl alcohol (0.08984%)
isoeugenol* (0.15997%)

*correct isomer not identified

Zeller and Rychlik (2007) characterized the constituents of a volatile concentrate of the fruits of *P. anisum.* They found the following:

2-isopropyl-1,3-methoxypyrazine (0.007)*
linalool (4.5)
methyl chavicol (530)
(Z)-anethole (57)
(E)-anethole (16,000)
guaiacol (0.071)
β-ionone (0.18)**
p-anisaldehyde (220)
anise ketone (110)
eugenol (0.16)
sotolone (0.011)
vanillin (0.73)

*concentration in fruits (μg/g)
**correct isomer not identified

Ranade (2007) reported that the composition of anise oil ex *Pimpinella anisam* oil was as follows:

α-pinene (0.2%)
camphene (0.1%)
α-phellandrene (0.1%)
β-phellandrene (0.1%)
1,8-cineole (0.1%)
p-cymene (0.1%)
linalool (0.2%)
α-terpineol (0.1%)
methyl chavicol (1.0%)
(Z)-anethole (2.3%)
(E)-anethole (85.0%)
safrole* (0.6%)
anisaldehyde (0.9%)
acetanisole (0.9%)

*incorrect identification

Trace amounts (<0.05%) of β-pinene, sabinene, myrcene, δ-3-carene, α-terpinene, (Z)-β-ocimene, (E)-β-ocimene, terpinolene, terpinen-4-ol and (E)-β-farnesol were also characterized in this same oil.

Orav et al. (2008) compared the methyl chavicol, p-anisaldehyde, (E)-anethole, γ-himachalene and *trans*-pseudoeugenyl 2-methylbutyrate contents of oil produced from 14 seed sources [France (1), Hungary (1), Russia (3), Greece (1), Scotland, UK (1), Lithuania (1), Spain (1), Italy (1), Germany (2), Czech Republic (1) and Estonia (1)]. The authors found the following compositional range of the above listed constituents:

methyl chavicol (0.5–2.3%)
p-anisaldehyde (<0.1–5.4%)
(E)-anethole (76.9–93.7%)
γ-himachalene (0.4–5.4%)
trans-pseudoeugenyl 2-methylbutyrate (0.9–6.4%)

Dawidar et al. (2008) screened anise oil for its biological activities. The lab-produced oil used in this study was found to possess the following major components:

(Z)-anethole (7.35%)
(E)-anethole (61.69%)
safrole* (2.45%)
α-longipinene* (10.09%)
cyclosativene* (5.19%)
isoledene* (3.3%)

*To the best of this reviewer's knowledge, safrole, α-longipinene, cyclosativene and isoledene have never been previously characterized as components of anise oil. It is quite probable that these compounds were incorrectly identified.

Singh et al. (2008) determined (using GC/MS only) that the main constituents of an oil produced from seeds of *P. anisum* purchased from a local market in Gorakhpur (Uttar Pradesh, India) by hydrodistillation were as follows:

α-pinene (0.1%)
p-cymene (0.1%)
limonene (0.8%)
1,8-cineole (0.1%)
fenchone* (5.0%)
camphor (0.2%)
methyl chavicol (2.3%)
α-fenchyl acetate (0.1%)
(Z)-anethole (0.5%)
p-anisaldehyde (0.5%)
(E)-anethole (90.1%)

*It should be noted that fenchone, a major constituent of bitter fennel seed oil has never been unequivocally identified as a constituent of anise oil.

Trace amounts (<0.05%) of sabinene, myrcene, α-phellandrene and (Z)-β-ocimene were also found in this oil.

In addition, the authors also examined the composition of some extracts of the same batch of Indian anise seed that was ground prior to extraction, using GC/MS only. The composition of these extracts can be seen in **T-1**. In addition, trace amounts (<0.05%) of p-cymene, 1,8-cineole, (Z)-β-ocimene, camphor, α-fenchyl acetate, p-anisaldehyde and β-sitosterol were characterized in one or more of the extracts.

De Martino et al. (2009) screened a number of oils for their antimicrobial activity. The commercial oil of *P. anisum* that was screened was determined to possess the following constituents:

α-pinene (0.3%)
α-phellandrene (0.1%)
δ-3-carene (0.1%)
o-cymene (0.1%)

Comparative percentage composition of various solvent extracts of *Pimpinella anisum* seeds **T-1**

Compound	1	2	3	4
limonene	t	-	0.5	t
fenchone*	1.2	0.3	0.9	0.4
undecane	t	-	-	0.3
methyl chavicol	t	-	0.5	t
(E)-anethole	14.1	5.7	19.7	6.4
methyl palmitate	t	0.3	t	t
palmitic acid	8.5	7.9	5.3	5.7
ethyl palmitate	1.2	-	-	-
methyl linoleate	t	0.7	0.1	t
methyl oleate	t	2.8	0.4	0.5
oleic acid	57.9	75.5	57.5	63.5
ethyl oleate	11.0	-	-	-
stearic acid	1.9	-	-	-
glyceryl dioleate	2.3	2.8	2.1	2.6
squalene	-	t	0.2	t
octacosanal	t	t	0.4	0.6
stigmasterol	t	t	0.4	0.5

*never been a component of *Pimpinella anisum* seeds

1 = ethanol extract
2 = methanol extract
3 = hexane extract
4 = petroleum-benzene extract

Comparative percentage composition of star anise oil produced by hydrodistillation or solvent-free microwave distillation **T-2**

Compound	Hydrodistilled oil	Microwave distilled oil
α-pinene	2.1	1.2
δ-3-carene	0.8	-
limonene	11.6	6.6
1,8-cineole	1.5	1.5
linalool	1.1	1.7
methyl chavicol	1.9	3.2
α-terpineol	1.0	-
(E)-anethole	78.0	81.4
anisaldehyde	2.0	3.9

fenchone (0.2%)
linalool (0.4%)
(E)-anethole (97.1%)*

*This oil was obviously not a genuine oil, but one that was formulated using synthetic anethole and a small amount of fennel oil.

Trace (<0.05%) amounts of sabinene, β-phellandrene, (Z)-β-ocimene, γ-terpinene, α-terpineol, β-caryophyllene and aromadendrene were also found in this oil.

J. Gora, T. Majda, A. Lis, A. Tichek and A. Kurowska, *Chemical composition of some Polish commercial essential oils.* Rivista Ital. EPPOS, (Numero Speciale), 761–766 (1997).

N. Arslan, B.B. Gurbuz, E.O. Sarihan, A. Bayrak and A. Gumuscu, *Variation in the essential oil content and composition of Turkish anise* (Pimpinella anisum *L.) populations.* Turk. J. Agric. Forest., **28**, 173–177 (2004).

A. Zeller and M. Rychlik, *Impact of estragole and other odorants on the flavour of anise and tarragon.* Flav. Fragr. J., **22**, 105–113 (2007).

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A.M. Dawidar, M.A. Mogib, A.H. El-Ghorab, M. Mahfouz, F.G. Elsaid and Kh. Hussein, *Chemical composition and effect of photo-oxygenation on biological activities of Egyptian commercial anise and fennel essential oils.* J. Essent. Oil Bear. Plants, **11**, 124–136 (2008).

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L. De Martino, V. De Feo, F. Fratianni and F. Nazzaro, *Chemistry, Antioxidant, Antibacterial and Antifungal Activities of Volatile Oils and their Components.* Nat. Prod. Commun., **4**, 1741–1750 (2009).

Star Anise Oil

Star anise oil, which is obtained from the fruit of *Illicium verum* J.D. Hook., is produced in relatively large quantities in China and Vietnam.

Chen (1986) reported that the two constituent isomers of anethole were found in levels of 85.5% and 0.4% for the (E)-isomer and (Z)-isomer, respectively, in Chinese star anise oil.

Bernard et al. (1989) analyzed the volatiles of a 1,1,2-trichloro-1,2,2-trifluoroethane extract of dried *I. verum* fruit produced in the laboratory using GC-FID and GC/MS.

The constituents characterized in this volatile extract were:

α-pinene (0.1%)
β-pinene (0.1%)
sabinene (0.1%)
limonene (1.5%)
β-phellandrene (0.1%)
1,8-cineole (0.2%)
linalool (0.6%)
trans-α-bergamotene (0.2%)
methyl chavicol (1.3%)
(Z)-anethole (0.1%)
(E)-anethole (86.7%)
several phenols* (2.2%)

*correct isomers not identified

Schultze et al. (1990) noted that star anise (*I. verum*) can be found adulterated with Japanese star anise of shikimi (*I. anisatum* L.). They found that direct mass spectrometric measurement of small fragments of the fruit of *I. anisatum* revealed that shikimi spectra could be characterized by the ion species m/z 192 (from myristicin and 1-allyl-2-methoxy-4,5-methylene dioxybenzene) and 194 (from 1-allyl-3,5-dimethoxy-4-[3-methylbut-2-enyloxy]benzene), whereas star anise was characterized

Percentage composition of volatiles found in the pericarps of *Illicium* species **T-3**

Compound	Iv	Ia	Ib	Ig	Ih	Il	Imj	Imi
limonene	0.0–1.6	t–1.2	1.2–11.1	0.0–t	12.4–32.8	0.1–0.6	0.1–10.3	1.1–17.9
1,8-cineole	0.0–0.6	3.9–20.3	3.0–6.6	t–0.1	1.2–2.1	4.1–36.6	0.7–1.0	0.3–1.6
methyl chavicol	t–49.1	0.0–0.3	-	-	-	-	-	0.0–t
(E)-anethole	5.1–81.3	t–16.0	t–1.1	0.3–0.4	t	t–6.7	t–3.0	t–2.6
safrole	-	0.0–28.5	0.0–t	-	0.4–2.7	0.0–0.2	t–1.7	0.0–1.5
eugenol	0.0–t	0.0–0.6	0.0–t	-	-	t	-	-
methyl eugenol	-	0.0–0.2	t	-	-	0.0–t	-	-
β-caryophyllene	0.0–4.3	2.0–15.6	t–5.0	14.9–17.3	1.5–8.5	0.0–0.8	0.5–6.9	0.9–8.6
asaricin*	-	t–16.9	-	-	-	-	-	-
myristicin	-	0.0–1.9	-	-	-	0.0–2.1	-	-
elemicin	-	-	-	t	-	t–10.3	-	-
methoxy eugenol	-	t–4.0	-	-	-	-	-	-
foeniculin**	0.0–22.4	-	-	-	-	0.0–1.2	-	-
eugenyl derivative	-	0.0–49.5	-	-	-	-	-	-
methoxyeugenol derivative	-	0.0–17.1	-	43.8–57.2	-	-	-	-

Iv = *Illicium verum*, Ia = *I. anisatum*, Ib = *I. brevistylum*, Ig = *I. griffithii*, Ih = *I. henryi*, Il = *I. lanceolatum*, Imj = *I. majus* and Imi = *I. micranthum*

t = trace (<0.1%)
* 1-allyl-2-methoxy-4,5-methylenedioxybenzene
** correct isomer identified

by the ion species 148 (from anethole) and 134 (from foeniculin).

Luchesi et al. (2004) compared the chemical composition of star anise oil produced either by hydrodistillation or solvent-free microwave distillation. A summary of their results can be found in **T-2**.

Guerrini et al. (2006) analyzed a commercial oil of *I. verum* fruit purchased in Italy. The constituents identified in this oil were as follows:

α-pinene (0.4%)
myrcene (0.1%)
α-phellandrene (0.4%)
p-cymene (0.1%)
β-phellandrene (0.8%)
linalool (2.3%)
terpinen-4-ol (0.3%)
α-terpineol (0.3%)
methyl chavicol (6.6%)
p-anisaldehyde (1.8%)
(E)-anethole (78.8%)
p-methoxyphenylacetone[a] (0.4%)
β-caryophyllene (0.5%)
trans-α-bergamotene (0.5%)
(Z)-nerolidol (0.2%)
feoniculin* (2.3%)
hexatriacontone (1.2%)

*correct isomer not identified
[a]also known as acetanisole

Howes et al. (2009) analyzed an oil of star anise using GC/MS. The composition of this oil was found to be as follows:

α-pinene (0.5%)
β-pinene (0.1%)
α-phellandrene (0.1%)
p-cymene (0.2%)
limonene (0.4%)
1,8-cineole (0.2%)
linalool (1.4%)
terpinen-4-ol (0.2%)
methyl chavicol (4.0%)
p-anisaldehyde (3.3%)
(E)-anethole (80.8%)
β-caryophyllene (0.3%)
trans-α-bergamotene (0.3%)
aromadendrene (0.1%)
β-bisabolene (0.1%)
(E)-nerolidol (0.1%)
α-cadinol (0.1%)
foeniculin* (1.5%)

*correct isomer not identified

Trace amounts (<0.1%) of α-thujene, myrcene, γ-terpinene, α-copaene, *cis*-α-bergamotene, (E)-cinnamyl acetate, methyl (E)-isoeugenol, (E,E)-α-farnesene, γ-cadinene, elemol, p-methoxy-cinnamaldehyde, spathulenol and caryophyllene oxide were also found in this oil.

In addition, Howes et al. compared the amounts of selected volatiles obtained from the pericarps of different *Illicum* species. This study is summarized in **T-3**.

S.-H. Chen, *Determination of* cis- *and* trans-*isomers of anethole from star aniseed oil by combined gas chromatography-mass spectrometry.* Sepu, 4(1/2), 120 (1986).

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