Progress in Essential Oils

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Sandalwood Oil

Different qualities of sandalwood oil are produced in India, including unbranded oil, branded oil, Agmarked oil and Mysore oil (Chana 1994). The unbranded oil is used exclusively by the flavor and fragrance industry in India, and it generally does not meet the Indian standard of 90% total santalols. Some of the branded oil is exported, although most is used domestically. Agmark oil is an export-quality material with a santalol content guaranteed to be greater than the Indian standard. Mysore oil is produced at the Mysore and Shimoga distilleries, which were at one time under the control of the Karnataka government; however, they are now controlled by the Karnataka Soap and Detergents Co. Ltd.

Chana (1994) reported that the oil content of the heartwood of 10-year-old sandalwood trees was 0.9% as compared to 30-year-old trees, which possessed 4.0% oil. Furthermore, he noted that the total santalols, santalyl acetate and santalenes in the oil produced from the 30-year-old heartwood were 89.2%, 3.5 % and 2.3%, respectively.

Venkatesha Gowda et al. (2006) disputed the findings of Chana, noting that the heartwood of 30-year-old trees possess ~5% oil, while the heartwood of 12–15-year-old plantation style trees possess an oil content of between 3.5–4.0%. These authors explored the economic feasibility of establishing sandalwood plantations and found that after 15 years the economic return was very lucrative, assuming the farmers could wait that long to generate high profits.

According to Venkatesha Gowda et al. (2006), production of sandalwood and sandalwood oil in India is ~85% of the world demand, with Indonesia (Timor) and other sources (primarily Fiji and New Caledonia) accounting for 10% and 5%, respectively. Of the Indian production, Tamil Nadu accounts for more than 80% of the country's production. The auction sales volume for sandalwood can be seen in **T-1**, with the handicraft industry consuming 360–600 tonnes annually.

However, Venkatesha Gowda et al. estimated that the actual annual production of sandalwood is in excess of 3,000–4,000 tonnes, which results in production of Indian sandalwood oil of 120–150 tonnes. Of these, up to 80 tonnes are consumed by Indian industry, leaving 40–70 tonnes for export.

Composition

In 1988, using a GC-sniffing technique, Nikiforov et al. determined that the most intense aroma compounds found in the oil of sandalwood were:

α-santalene
α-santalal
β-santalal
epi-β-santalal
α-santalol
β-santalol
epi-β-santalol
α-bergamotol
spirosantalol

These components were identified both by GC/MS and GC-FTIR. Of interest to essential oil chemists was the fact that the authors presented FT-IR spectra of each of the previously noted compounds.

Starting with 100 g of East Indian sandalwood oil, Mookherjee et al. (1992) performed a number of silica gel column chromatographic separations to yield fractions that could be divided into classes of compounds that could be further characterized using a combination of gas chromatographic and spectroscopic techniques. They found that the oil contained 3.4% hydrocarbons and 96.6% oxygenated compounds. Although the authors did not list the 100 components identified, they commented on a number of them and their aroma characteristics. A summary of these findings can be seen in **T-2**. In addition, the structures of some of the uncommon constituents can be seen in **F-1**.

Auction sales volume of sandalwood in India **T-1**

Year	Amount (metric tonnes)
1993	2850
1994	2575
1995	2325
1996	995
1997	1288
1998	1475
1999	1800
2000	1850
2001	1800
2002	1850
2003	1800
2004	1505
2005	1275

Percentage compositions of some uncommon components of East Indian and Javan sandalwood oil **T-2**

Compound	% East Indian oil	% Javan oil	Odor character
santalene oxide	3.1	1.6	green melon and lavender like
non-sesquiterpene tricyclic ketone(A)	3.6	-	diffusive woody and amber like
trans-α-santalal	12.8	7.7	pine needle and juniper like
trans-β-santalal	8.2	4.0	sweaty and urinaceous
(E)-nuciferal	0.7	1.6	weak odor
trans-α-photosantalol	4.7	8.4	weak woody odor
trans-epi-β-photosantalol	1.4	1.1	weak woody odor
trans-β-photosantalol	2.8	6.6	fatty, sandalwood like
aldehyde 1 (B)	0.1	0.1	sweet melon like
ketone 1 (C)	0.1	0.1	green, woody, amber like
ketone 2 (D)	0.3	-	green, oily, sandalwood like
ketone 3 (E)	1.2	1.0	weak, woody, melon like
ketone 4 (F)	0.1	0.1	strong, woody, melon like
aldehyde 2 (G)	1.2	-	woody, ambergris like
aldehyde 3 (H)	0.2	-	green, oily, melon like
spiroketone (I)	1.7	1.4	weak, uninteresting odor

Zhu et al. (1993) produced an oil from the heartwood of sandalwood trees growing in the South China Botanical Garden (Guangzhou, China). They found that the oil contained the following components:

α-santalene (1.51%)
β-santalene (1.81%)
epi-β-santalene (2.30%)
α-santalol (22.08%)
β-santalol (1.95%)
cis-α-santalol (11.75%)
α-santalol isomers (7.76%)
β-santalol isomers (5.54%)

Brunke et al. (1995) examined some of the minor constituents of East Indian sandalwood oil. They found that the oil contained the following:

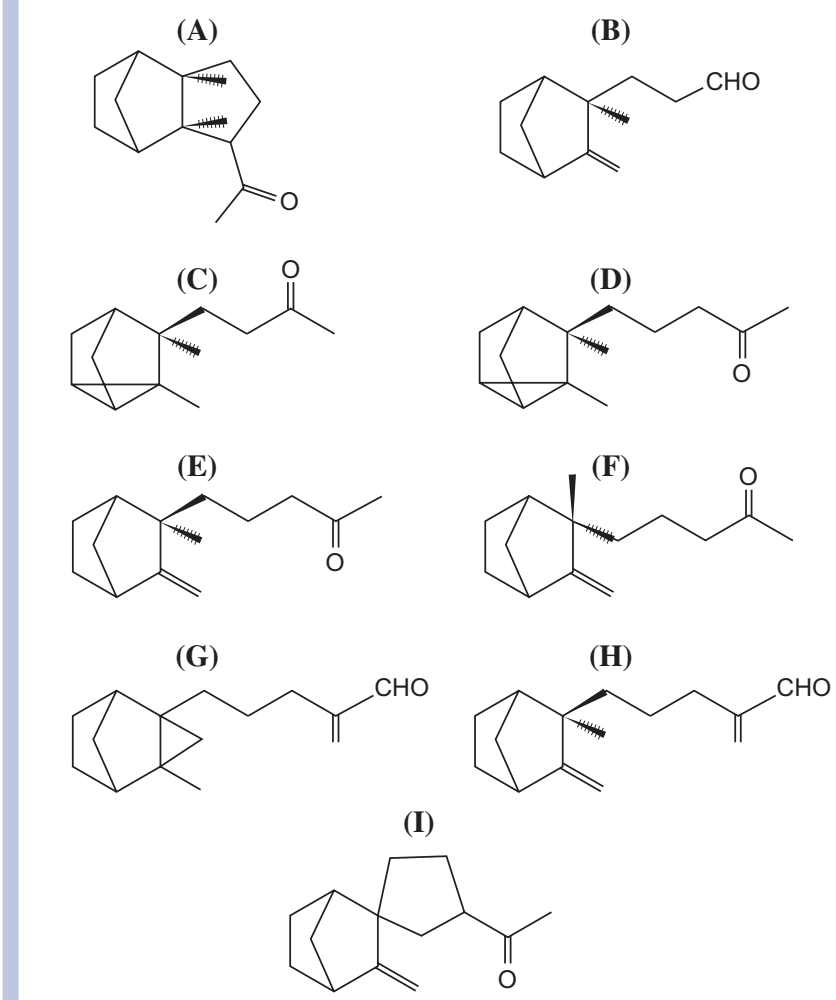
cyclosantalal (1.67%)
epi-cyclosantalal (1.24%)

Trace amounts (< 0.01%) of cyclosantalic acid, epi-cyclosantalic acid, dihydroalbene, acetyldihydroalbene and albene were also found in the oil as oxidation products of the cyclosantalals.

Shukla et al. (1999) examined 13 samples of sandalwood oil in India and found the following physico-chemical data for them:

Optical Rotation (30°C): -15.1° to -20.4°

Structures of some sandalwood components **F-1**



Specific Gravity (30°C): 0.968185–0.974413
Refractive Index (30°C): 1.50000-1.50451

Free OH calculated as:
total santalols (percent by mass): 88.13–97.01%

Esters calculated as:
santalyl acetate (percent by mass): 3.56–6.15%

α-santalol: 46.05–51.32%
β-santalol: 18.36–23.00%

Wei et al. (2000) determined that wind damage to *Santalum album* trees probably accelerates the formation of heartwood. The composition of an oil produced from the heartwood of a 25-year-old tree was found to be as follows:

α-santalene (0.08%)
epi-β-santalene (0.12%)
β-santalene (0.25%)
curcumene* (0.05%)
α-santalol* (43.09%)
(Z)-*trans*-α-bergamotol (9.44%)
epi-β-santalol (3.66%)
β-santalol (22.53%)
nuciferol* (9.65%)
(Z)-lanceol (0.51%)

*correct isomer not identified

Chen and Lin (2001) compared the main component composition of sandalwood oil produced by various isolation treatments. The range of the main components was found to be as follows:

α-santalene (0.08–0.65%)
epi-β-santalene (0.16–0.89%)
β-santalene (0.04–1.42%)
curcumene[1] (0.09–0.33%)
α-santalol[2] (30.76–41.51%)
α-santalol[3] (6.03–8.28%)
epi-β-santalol (3.94–6.74%)
β-santalol (22.64–26.86%)
nuciferol[4] (2.08–2.47%)
lanceol[5] (0.46–0.88%)

[1] should be β-curcumene
[2] should be *cis*-α-santalol
[3] should be *trans*-α-santalol
[4] should be (Z)-nuciferol
[5] should be (Z)-lanceol

Braun et al. (2003) analyzed an oil of East Indian sandalwood obtained commercially in Germany. The composition of this oil was determined to be as follows:

santene (0.2%)
α-santalene (0.7%)
α-cedrene (0.1%)
trans-α-bergamotene (0.2%)
epi-β-santalene (0.8%)
β-santalene (1.2%)
trans-β-bergamotene (0.1%)
γ-curcumene (0.1%)
β-bisabolene (0.1%)
β-curcumene (0.2%)
ar- curcumene (0.3%)
(E)-nerolidol (0.1%)
β-bisabolol/epi-β-bisabolol (0.7%)
cyclosantalal (0.4%)
α-santalal* (1.9%)
α-bergamotal (0.2%)
epi-cyclosantalal (0.3%)
α-bisabolol (0.2%)
dihydro-α-santalol (0.6%)
β-santalal* (0.6%)
cis-α-santalol (41.1%)
trans-α-bergamotol (6.4%)
trans-α-santalol (0.4%)
cis-α-bergamotol (0.2%)
epi-β-santalol (3.5%)
cis-β-santalol (19.8%)
fokienol (0.5%)
trans-β-santalol (1.5%)
(Z)-lanceol (1.4%)
(Z)-nuciferol (3.4%)

spirosantalol (0.9%)
(E)-nuciferol (0.1%)

*correct isomer not identified

Trace amounts (< 0.1%) of epi-sesquithujene, *cis*-α-bergamotene, (E)-β-farnesene, sesquisabinene, β-alaskene, (Z)-γ-bisabolene, α-alaskene, (E)- γ-bisabolene and (E)-α-bisabolene were also found in this same oil. Chiral analysis of the β-bisabolols revealed that all four enantomers were present in the oil, although the main stereoisomer was (6R,7R)-β-bisabolol.

A water-distilled oil of *S. album* was found by Braun et al. (2003) to contain (1R, 4R, 5S)-α-acorenol (0.22%), (1R, 4R, 5R)-β-acorenol (0.11%), (1R, 4S, 5S)-epi-α-acorenol (0.13%) and (1R, 4S,5R)-epi-β-acorenol (< 0.01%).

Three commercial samples of East Indian sandalwood oil were analyzed by Jirovetz et al. (2006). They found that the main components were as follows:

cis-α-santalol (38.8–52.5%)
cis-β-santalol (16.5–32.9%)

Marongiu et al. (2006) analyzed three supercritical fluid CO_2 extracts of sandalwood and compared them to an oil produced by hydrodistillation. The comparative results of this study are shown in **T-3**. As can be seen, this reviewer believes that many of the constituents supposedly characterized in sandalwood oil and extract were misidentified. This conclusion is reached based on the dearth of information on the analysis of sandalwood oil that has been published during the past 30 years (Lawrence 1976, 1981 and 1991; and Brunke et al., 1997.)

Comparative percentage composition of a supercritical fluid CO_2 extract and an essential oil of *Santalum album* **T-3**

Compound	Oil	Extract
santene	0.4	0.1–0.2
linalyl acetate†	-	0.7–1.0
p-menth-1,8-dien-9-al†	0.3	0.2–0.3
β-longipinene†	0.6	0–0.9
longifolene†	0.3	0–0.9
bergamotene*	-	0–0.7
(E)-α-ionone†	4.2	0–0.8
α-santalene	0.6	1.1–1.4
epi-β-santalene	1.4	0.2–0.3
α-humulene	1.0	0.3–1.6
β-santalene	1.0	0.2–0.3
β-acoradiene	0.7	0–t
ar-curcumene	1.0	0–t
zingiberene†	0.5	-
(Z)-α-bisabolene	0.7	0-t
β-curcumene	0.7	-
germacrene C†	t	t–0.4
6,11-oxoacor-4-ene†	0.6	0.3–0.6
cis-muurol-5-en-4α-ol†	0.7	0–0.4
globulol†	0.6	0–0.6
cis-arteannuic alcohol†	5.1	-
caryophyllene oxide	t	0-0.01
β-oplopenone†	0.4	-
trans-isolongifolanone†	1.3	0–0.2
3-iso-thujopsanone†	0.6	-
himachalol*†	0.3	0–0.6
(E)-amyl cinnamic alcohol†	1.0	0.9–1.3
(Z)-nerolidyl acetate†	1.4	-
cis-α-santalol	35.0	46.1–48.7
(Z)-*trans*-α-bergamotol	-	t–5.4
β-sinensal†	5.7	1.1–6.1
epi-β-santalol	1.7	1.4–6.8
(E)-nerolidyl acetate†	4.6	0–1.5
cis-β-santalol	14.0	20.3–21.4
trans-β-santalol	1.4	1.2–3.3
α-sinensal†	0.5	0–2.2
(Z)-lanceol	-	0–0.9
cis-β-santalyl acetate	-	0–0.5

*correct isomer not identified
†constituents probably misidentified

Adulteration

As the price of sandalwood oil is high and its availability sometimes scarce, it is subject to adulteration in the country of production. John et al. (1991) determined that some commercial samples that were available in India were adulterated with polyethylene glycol. Naqvi and Mandal (1995) confirmed the findings of John et al., and also found that in addition to polyethylene glycol, some sandalwood oil contained dioctyl phthalate.

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Australian Sandalwood Oil

Shellie et al. (2004) used a combination of chromatographic techniques such as GC/MS, GC-time-of-flight-mass-spectrometry (TOFMS), GCxGC/FID and GCxGC-TOFMS to characterize the eight most important components of Australian sandalwood oil. They used the two dimensional technique because GC/MS or even GC/FID using a polar capillary column did not possess enough resolving power to differentiate clearly between the eight components. The quantitative composition of these components was determined to be:

(Z)-α-santalol (22.0%)
epi-α-bisabolol (4.8%)
(Z)-α-*trans*-bergamotol (5.2%)
epi-β-santalol (1.7%)
(Z)-β-santalol(5.2%)
(E,E)-farnesol (5.8%)
(Z)-nuciferol (2.8%)
(Z)-lanceol (5.2%)

Six stereo isomers of nor-helifolenal [(1R,2S,5S,6S,7R)-13-nor-helifol-8-en-6-al (0.24%), (1R,2R,5S,6S,7R)-13-nor-helifol-8-en-6-al (0.11%), (1R,2S,5R,6R,7R)-13-nor-helifol-8-en-6-al (0.12%), (1R,2R,5R,6R,7R)-13-nor-helifol-8-en-6-al (0.05%), (IR,2S,5S,6R,7R)-13-nor-helifol-8-en-6-al (0.40%) and (1R,2R,5S,6R,7R)-13-nor-helifol-8-en-6-al (0.17%),(1R,4R,5S)-α-acorenol (0.37-0.52%),(1R,4S,5S)-epi-α-acerenol (<0.01-0.04%), (1R,4R,5R)-β-acorenol (0.04%) and (1R,4S,5R)-epi-β-acorenol (0.10-0.11%) were characterized in an oil of Australian sandalwood by Braun et al. (2003).

Jirovetz et al. (2006) examined the main components of three commercial samples of *S. spicatum*. They found that the (Z)-α-santalol and (Z)-β-santalol varied from 16.1–19.0% and 7.2–13.5%, respectively. One other commercial sample analyzed contained (Z)-α-santalol (26.5%), (Z)-β-santalol (5.9%) and a farnesol isomer (14.4%).

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