Woody Notes in Perfumery

Sandalwood and Sandalwood Compounds

By Danute Pajaujis Anonis, Chemist Perfumer, Rego Park, New York

The term *sandal* is derived from Medieval Latin *sandalum*, from late Greek *sandanon* and *santalon*, and from Sanskrit *candana*.

Sandalwood has been appreciated since ancient times. It was imported from India to Egypt, Greece and Rome. Sandalwood is used for religious purposes in incenses, in fragrances and as medicine. Sandalwood remains much in demand in modern perfumery.

Botanical Origin

Various types of sandalwood trees grow in different countries of the world. Among them are the following:

- *Santalum album* L. (fam. Santalaceae) is native to southern India, particularly in the state of Mysore. The tree is also planted by seed. The semi-parasitic evergreen tree reaches full maturity at an age of 60-80 years.[1] *Santalum album* also grows in Indonesia and in the Yunnan region of China. In the perfumery trade, the oil from this tree is known as East Indian sandalwood oil, or sandalwood E.I.
- *Eucarya spicata* Sprag. et Summ., syn. *Santalum spicatum*, grows in the arid regions of western and southern Australia. It is a comparatively small tree, approximately 12-20 feet in height.[2]
- *Santalum freycinetianum* Gaud. grows in Haiti.[3]
- *Amyris balsamifera* L. (fam. Rutaceae), known in the perfumery trade West Indian sandalwood or sandalwood W.I.(amyris oil), has no relationship to the types mentioned above. It is included here because the oil obtained from the wood of this tree was used as a less expensive substitute of sandalwood E.I. oil in soap and inexpensive fragrances in general. The trees grow wild in Venezuela, Jamaica and Haiti.[4] The main production of the oil since 1942 has occurred in Haiti.

Of the true sandalwood types named here, sandalwood E.I. is the most important in perfumery.

Mode of Production, Yield and Type of Oil

Sandalwood E.I. oil has been obtained in India since ancient times by the so-called water-distillation technique using copper vessels and bamboo pipes. Modern methods include steam distillation of the heartwood and reduction of roots to powder. The yield of sandalwood E.I. oil obtained by this method is 4.5-6.25%.[5] The oil is a viscous pale-yellow liquid with a warm, sweet, heady and lasting odor.

Sandalwood Australian oil has reportedly been obtained by solvent extraction and steam distillation of the concentrated extract.[2] According to the *British Pharmaceutical Codex* of 1949, Australian sandalwood oil is obtained from the wood by distillation and rectification. The yield of the oil varies between 1.4% and 2.6%. The oil is a somewhat viscous, pale-yellow liquid with a strong and lasting woody odor.[2]

Sandalwood W.I. oil is obtained by distilling chopped trunks and large branches that have first been passed through a hammermill. The yield from trees of Jamaican origin is given as 4.5%, while that of the Haitian oil was 3.8%. The oils were somewhat viscous, with a yellow-brown color and a sweet balsamic odor.[6]

Chemical Composition

Sandalwood E.I.: Sandalwood E.I. oil has been investigated by various researchers. Among the earlier were Semmler, Ruzicka, Simonsen and collaborators.[7] Santalol, the main constituent of sandalwood E.I. oil, is a mixture of the two sesquiterpene alcohols α- and β-santalol, with the α- isomer predominating, according to Guenther.[7] Santalol amounts to at least 90% of the oil. Other constituents cited by Guenther as known in the early part of the 20th century are the following:

isovaleraldehyde and other aldehydes
santene
nortricycloekasantalene (tentatively identified)
l-sante none

Editor's note: This series on natural woody notes in perfumery will discuss sandalwood, cedarwood, vetiver and patchouly oils. The series begins with an overview of sandalwood. The next article will discuss miscellaneous sandalwood-type compounds.

0272-2666/98/0005-0019$04.00/0—

santenol
teresantalol
nortricycloekasantalal
santalone
a ketone (not identified)
α- and β-santalene
santalal (not proved conclusively)
teresantalic acid
santalic acid (first reported in 1944)
phenols and lactones (not identified)

During the investigation of the distillation foreruns from sandalwood E.I. oil (amounting to 5-8% of the oil), Demole et al. (1976) isolated and characterized 46 compounds; 32 of them were newly identified constituents. Among the novel substances were:

santalone
4-methyl-cyclohexan-1,3-dien-1-yl methyl ketone
5,6-dimethyl-5-norbornen-exo-2-ol
(E)-5-(2,3-dimethyl-3-nortricyclyl)-pent-3-en-2-one

Demole et al. identified 10 phenols, among which were 4-vinyl phenol and 1-methoxy-4-allyl guaiacol. Some of the other constituents identified were:

1-furfurylpyrrole
α-santalal
nor-α-santalenone
endo-2-endo-3-dimethyl-norbornan-exo-2-ol

The researchers assumed that the phenols may be mostly responsible for the "smoky" note in the sandalwood oil foreruns. But they were astonished that neither the minor constituents (such as epi-β-santalene, α- and β-curcumene and β-farnesene) characterized long ago nor those identified relatively recently (tricyclo-eka-santalal, exo-nor-bicyclo-eka-santalal and 11-methyl-7-oxa-tetracyclo- [6.3.$1^{2,6}0^{4,11}$]dodecane) can truly account for the "peculiar and pleasant fragrance" of the distillation forerun.[8]

In 1976, a comparative analysis of sandalwood E.I. and Java sandalwood oils was done by Mookherjee et al.[9] Of a total of 100 components identified in each oil, 70 components were new to both of these oils, and 30 compounds were novel to natural products. Among the 100 components were:

C_{14} tricyclic ketone of a diffusive woody, amber odor (found only in sandalwood E.I. oil)
C_{14} b-santalene keyone possessing a sweaty, woody, green sandalwood odor
C_{15} trans-b-santalal, of a sweaty, urine sandalwood odor
C_{15} trans-b-photo-santalol with a strong, fatty sandalwood odor

The researchers state that some of these novel trace components play an important role in the total sandalwood odor.[9]

Table 1. α- and β-Santalol composition (%) of Chinese and Indian sandalwood E.I. oils

	Chinese oil		Indian oil	
	Yu[14]	Wang[13]	Yu[14]	Wang[13]
α-santalol	49.99	14.6	48.44	46.6-59.9
β-santalol	18.12	7.3	24.57	24.6-29.0

In 1980, Brunke and Hammerschmidt[10] reported the occurence of the following constituents in sandalwood oil:

cis-epi-β-santalol
trans-epi-β-santalol
cis-lanceol
cis-nuciferol

In 1986, Brunke[11] reported the isolation and identification of two new components: bergamotol and spirosantalol (with a novel carbon skeleton).

Shankaranarayana et al.[12] reported in 1989 that α- and β-santalene were present in sandalwood E.I. oil in the amount of 1.5-3.0%, and other oxygenated sesquiterpenes in the amount of 2.5-4.0%. These minor constituents were considered as having an influence on the overall character of the oil.

Lawrence[13] reviewed the work of various researchers on the chemical composition of sandalwood oil. Ranibai et al. (1986) identified a new trace component: 11-keto-dihydro-a-santalic acid. Nikiforov et al. (1988-1990) identified several new minor components:

dihydro-α-santalol
dihydro-β-santalol
dihydro-α-santalic acid
dihydro-ar-norcurcumenic acid
α-bergamotenic acid

Santalols in sandalwood E.I.: In a comparative composition study of Indian and Chinese sandalwood oils, Yu et al.[14] (1988) showed that the amount of α-santalol is about 1.5% higher in the Chinese oil, and the amount of β-santalol is about 6.5% lower.

Among minor constituents, the percentages of tricycloekasantalal, trans-α-bergamotene and β-santalene are higher in the Chinese oil, while the amounts of α-santalene, ar-curcumene, nuciferol and α-santalal are lower.

Without olfactory evaluation of both oils, it is difficult to judge the quality of these oils, based solely on the given data.

The question of percentages of α- and β-santalols in various types of sandalwood oils is controversial, as shown in Table 1. Vergese et al.[13] (1990) tried to establish a standard for the amounts of α- and β-santalols in sandalwood E.I. oil. Their suggested standard is α-santalol at 40-45% and β-santalol at 17-27%.

Stability of sandalwood E.I.: In 1988, Burke and Hammerschmidt[15] did an interesting stability test of two sandalwood oils that differed in age by more than 80 years. The new oil contained almost twice the amount of cis-α- and cis-β-santalols. It was also richer in β-bisabolol, (Z)-trans-α-bergamotol, epi-β-santalol, cis-nuciferol and spiro santalol. β-Bisabolene, β-curcumene, (E)-nerolidol, α-bisabolol and dihydrosantalol were found only in the new oil.

The old oil contained larger amounts of santene, α-santalene, epi-β-santalene, β-santalene, γ-curcumene, α-ekasantalal, ar-curcumene, β-ekasantalal, α-santalal, (Z)-trans-α-bergamotal and β-santalal. cis-α-Santalyl acetate, cis-β-santalyl acetate, nuciferyl acetate, as well as small amounts of acetic acid and teresantalal were present in the old oil. The occurrence of acetates and acetic acid may be considered normal in the aged oil.

From the stability point of view, the old oil has probably passed the test. But in terms of quality, judging by the amounts of α- and β-santalols, 80 years may be too long a period for the aging of sandalwood oil.

Sandalwood W.I.: The oil of *Amyris balsamifera* L. contains chiefly sesquiterpene alcohols and 30-40% of sesquiterpenes. The following constituents were known in the early part of this century:[16]

β-caryophyllene
d-cadinene
cadinol
amyrolin (seems to be an aromatic lactone)
methyl alcohol
diacetyl
furfural
an unidentified compound found in the distillation residue

Synthetic Compounds

Sandalwood has a warm and sweet odor which is heady, vibrant and lasting. The odor of sandalwood has also been described as having points in common with the green, vegetable odors of oakmoss, lichen and fern (this note is

Formula 1. Sandalwood synthetic No. 3

200	Santalol
150	Copaiba balsam
150	Cedarwood
500	

Formula 2. Sandalwood synthetic No. 4

100.0	Sandalwood W.I.
100.0	Cedrenyl acetate
75.0	Cedrenol
15.0	Cedarwood, Texas
10.0	Phenyl ethyl alcohol
10.0	Hydroxycitronellal
10.0	Musk xylol
7.5	Guaiawood
5.0	Cananga
1.5	Geranium
1.5	Tolu balsam
1.5	Coumarin
0.5	Isoeugenol
0.5	Vanillin
338.0	

essentially underlined in Australian sandalwood); with fruit-peel or citrus-leaf odors; and indistinct common points with musky odors.[17]

Formula 1 and the more complex Formula 2 show examples of synthetic sandalwood compounds used in the first part of the 20th century.

Table 2. Perfume materials traditionally used in sandalwood-type fragrances

	Top note	Floral effect	Woody note	To sweeten	To fix	Accent note
Bergamot	x					
Lavender	x					
Rhodinyl formate	x					
Aldehyde C-16	x					
Rose natural or synthetic		x				
Rhodinol		x				
Jasmin		x				
Ylang		x				
Lilac		x				
Muguet		x				
Neroli		x				
Methyl β naphthyl ketone		x				
Geranium		x				
Geranyl acetate		x				
Sandalwood E.I.			x			
Sandalwood W.I.			x			
Sandalwood Australian			x			
Cedarwood			x			
Cedrol			x			
Cedrenol			x			
Cedrenyl acetate			x			
Guaiacwood			x			
Methylionone			x			
Vetiver			x			
Benzoin resinoid				x		
Coumarin				x		
Tolu balsam				x		
Ethyl vanillin				x		
Vanillin				x		
Natural vanilla				x		
Amber synthetic					x	
Benzophenone					x	
Musk xylol					x	
Macrocyclic or other types synthetic musks					x	
Caraway seed oil						x
Carrot seed oil						x

Formula 3. Sandalwood base	
150	Sandalwood E.I.
75	Cedarwood
50	Geranium
50	Benzyl acetate
45	Methylionone
35	Vetiver
30	Coumarin
25	Musk xylol
15	Petitgrain
15	Patchouly
10	Nutmeg
500	

Sandalwood-type fragrances were developed for colognes, cream, powder, hair oil and soap. Table 2 shows some of the perfume materials traditionally used in such compounds.

Synthetic musks reinforce the odor of sandalwood. The addition of animal notes (such as civet or castoreum) and patchouly refresh and refine the background note.

Formula 3 gives an example of a sandalwood base that can be used in developing a sandalwood fragrance type. We'll discuss miscellaneous sandalwood-type compounds in the second article in this series.

References

Address correspondence to Danute Pajaujis Anonis, 98-41 64th Road #6F, Rego Park, NY 11374.

1. E Guenther, *The Essential Oils*, New York: D Van Nostrand Co (1952) v 5 pp 173-174
2. Ibid, p 189
3. R Cerbelaud, *Formulaire de la Parfumerie*, Paris: Editions Opera (1951) p 310
4. Guenther, v 3, p 385
5. Ibid, v 5, pp 180-181
6. Ibid, v 3, pp 386-398
7. Ibid, v 5, pp 185-187
8. E Demole, C Demole and P Enggist, *Helv Chim Acta* **59** 737 (1976)
9. BD Mookherjee, RW Trenkle and RA Wilson, 12th Intl Congress Essent Oils Fragr Flav (1992) Vienna, Austria
10. E-J Brunke and FJ Hammerschmidt, 8th Intl Congress Essent Oils Fragr Flav, Cannes, France (1980) Paper No 77
11. E-J Brunke, 10th Intl Congress Essent Oils Fragr Flav, Washington DC, USA (1986) Paper No 69
12. KH Shankaranarayana and BS Kamala, *Perfum Flavor* **14**(1) 19 (1969)
13. BM Lawrence, *Perfum Flavor* **16**(6) 50-52 (1991)
14. JG Yu, PZ Cong, JT Lin and HJ Fang, *Yaoxue Xuebao* **23** 868-872 (1988); cf Lawrence, p 50
15. E-J Brunke and FJ Hammerschmidt, *Dragoco Report* (4) 107-113 (1988); cf Lawrence, p 50
16. Guenther, v 3, pp 390-391
17. Cerbelaud, p 309