

Woody Notes in Perfumery Part II: Sandalwood Compounds and Aroma Chemicals

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In the first part of this article, we discussed sandalwood oil and its chemical composition,^a gave several examples of synthetic sandalwood compounds, discussed some traditional perfume materials in sandalwood-type fragrances and illustrated a sandalwood base.

In this article we shall look at various sandalwood-type fragrance compounds, discuss the dermatological aspects of their components, and review several aroma chemicals possessing sandalwood-type odors.

Here is an example of a conventional perfume-formula compound for cologne:

Formula 1. Santal Cologne No. 5	
130	Bergamot
120	Sandalwood E.I.
45	Neroli synthetic
30	Benzoin resinoid
20	Lavender 40/42%
15	Methylionone
15	Geranium
10	Vetiver acetate
15	Coumarin
10	Musk xylol
5	Cedrenol IFF
1	Carrot seed oil 1%
<u>416</u>	

Sandalwood fragrances have been popular in India. An example of such a fragrance compound from the early part of century is:

Formula 2. Sandalwood No. 397¹	
350	Sandalwood E.I.
250	Sandalwood W.I.
150	Geraniol
100	Guaiacwood
100	Jasmin synthetic
50	Petitgrain Paraguay
<u>1000</u>	

Another more complex fragrance called "Indian Wood" of the middle of this century is:

Formula 3. Bois d'Inde 8²	
115	Sandalwood E.I.
75	Cedrol crystallized
75	Methylionone delta
38	Cypress oil
25	Ylang
25	Geranium
15	Patchouly
75	Vetiver
300	Rose synthetic
25	Geranyl acetate
30	Amber synthetic
12	Ethyl vanillin
25	Coumarin
30	Musk ambrette
25	Musk xylol
<u>890</u>	

^aAmyris oil (Sandalwood W.I.) components, were also mentioned in the previous article. Readers interested in further analyses of amyris oil are referred to Brian M. Lawrence's article "Progress in Essential Oils" (Perfum Flavor, 1 38 (1996)

During World War II, perfumes without alcohol were innovated in Germany. The perfume oil was dissolved in diethyl phtalate, castor oil or other solvents. An example of such a perfume compound is:

Formula 4. Sandalwood Bouquet³	
850 cm ³	Sandalwood E.I.
50 cm ³	Phenyl ethyl alcohol
35 cm ³	Red rose
10 g	Musk ketone
5 g	Aldehyde C-16

Sandalwood is also an important component of men's fragrances. Here is an example of a conventional formula:

Formula 5. Pagodes⁴	
150	Sandalwood E.I.
100	Methylionone
35	Cedrol
35	Vetiver acetate
170	Bergamot
50	Civet absolute
20	Caraway seed oil
75	Bois de Rose
5	Rose Otto
50	Lavender
95	Coumarin
5	Vanillin
75	Opoponax resinoid
<u>865</u>	

Nineteenth century powders were complexes containing moistly pulverized ambrette seeds, clove buds, orris, lemon and orange peels, and ambergris. Also recommended were rose petals, cinnamon bark, benzoin, styrax, sandalwood, bergamot peel, orange flower buds and angelica roots. Everything was reduced to a fine powder of a particular floral and exotic wood scent, difficult to reproduce.⁵

Sandalwood was a valuable component of later powder perfumes. It gives body covering power and persistence in powder. Sandalwood-type fragrances were also developed for soap. Here are few examples of conventional formulas:

Formula 6. Sandalwood No. 680 for soap⁶	
160	Sandalwood W.I.
270	Sandalwood E.I.
100	Cedarwood
45	Patchouly
10	Cinnamon leaf oil
85	Geraniol
70	Phenyl ethyl alcohol
25	Geranium
130	Cananga
40	Musk ambrette
40	Benzoin resinoid
25	Styrax resinoid
<u>1000</u>	

Formula 7. Santalwood No. 681 for soap⁷	
300	Sandalwood E.I.
200	Sandalwood Australian
100	Terpinyl butyrate
150	Terpinyl isobutyrate
150	Geranium
50	Guaiacwood
30	Heliotropin
20	Moskene L.G.
<u>1000</u>	

Another sandalwood type compound for soap, based on sandalwood W.I. is:

Formula 8. Sandalwood No. 6 for soap	
200	Sandalwood W.I.
125	Cedarwood
50	Benzoin resinoid
35	Ionone
25	Bergamot
25	Geranium
15	Vetiver
15	Musk xylo
<u>515</u>	

The prices of naturals used in the past soap fragrances, such as geranium, sandalwood, vetiver and others would be prohibitive today. In modern soap perfumes many different aroma chemicals, including synthetic musks, are incorporated.

In regard to sandalwood, various aroma chemicals of this odor tonality are now available. Among the first was Sandela (Givaudan).

In the writer's past experiments, Sandela used in an 80:20 proportion with natural sandalwood was found to be an advantageous substitute, both from the odor and price point of view in a specific soap fragrance. Sandela and other sandalwood aroma chemicals possessing sandalwood-like odors will be discussed later.

Dermatological Consideration

In some sandalwood compounds of the past, a number of perfume materials were used that are now prohibited, restricted or must meet certain specifications, according to the International Fragrance Association's Code of Practice, which is continuously updated.

Among such perfume materials are:

- bergamot - limited to 0.4% in consumer products applied to skin exposed to sunshine
- hydroxycitronellal - limited to 5% as a fragrance ingredient
- isoeugenol - limited to 2% in consumer products
- methylionone - specifications of a limit up to 2% of pseudomethylionone as an impurity
- musk ambrette - prohibited

opoponax - specified to preparations obtained from opoponax gum by extraction with suitable solvent or steam distillation
 styrax resinoid - only Asian styrax produced by vacuum distillation or extraction with ethanol

Sandalwood does not pose any incompatibility or stability problems because it contains a large amount of sesquiterpene alcohols. It improves with age.

Sandalwood Aroma Chemicals

In the past, there were very few synthetic aroma chemicals with sandalwood-like odors. Among them was trans-decahydro β naphthyl formate, which was used as sandalwood replacement in inexpensive fragrances. Santalol and some of its derivatives are available, but santalol is obtained from the natural sandalwood oil. It would seem logical to develop synthetic α - and β -santalols. However, the attempts proved futile as complex syntheses were involved, resulting in low yields.

- The first synthetic aroma chemicals possessing sandalwood odors was sandela (Givaudan, 1960): 2(4)-(5,5,6-trimethylbicyclo[2,2,1] hept-2-yl)cyclohexan-1-ol. It is not reported as being found in nature (according to the Givaudan-Roure Index). It is a mixture of isomeric terpenylcyclohexanols, obtained by hydrogenation of condensation product of camphene and phenol. Demole's⁸ (1962) studies of terpenylphenols led to a synthesis of terpenylcyclohexanols. The relationship between their structures and their odor was established.
- Osyrol (Bush Boake Allen, 1970s): 3,7-dimethyl-7-methoxy-2-ethanol.
- Santalydol is condensation production of camphene and guaiacol. The chemical composition of Santalydol was reported by Aulchenko and Kheifits⁹ in 1970. They established that "the santal odor of Santalydol is due to the presence of 3-terpenocyclohexanols which are structurally close to natural α - and β -santalols." Trans-3-isocamphylicyclohexanol was found to have a very strong sandalwood odor, and trans-3-isobornylcyclohexanol possessed a strong sandalwood odor.

With sandalwood prices escalating, earnest research began in the 1970s based on readily available starting materials which were inexpensive. As a result, various types of aroma chemicals with sandalwood odors were developed. Some of the results of this work include:

- Catechol-camphene reaction products:¹⁰ J. B. Hall and W. J. Wiegen; US Patents 4,104,203, August 1, 1978; 4,131,557, December 26, 1978; assigned to International Flavors and Fragrances Inc. Hydrogenation of the reaction product of camphene and catechol obtained in presence of a Friedel-Crafts catalyst produces a mixture of compounds having an intense sandalwood odor. Reaction of camphene and catechol, using an H₂SO₄ catalyst results in a mixture of several chemical compounds possessing a strong sandalwood odor.

- Campholenic aldehyde reaction products: campholenic aldehyde condensation with methyl ethyl ketone and subsequent hydrogenation results in a mixture of secondary alcohols, one isomer of which has a strong sandalwood odor.¹¹ Condensation of campholenic aldehyde with aceto-acetic ester and subsequent hydrogenation gives rise to a mixture of stereoisomers with strong and lasting sandalwood odors.^{12,13} Treatment of campholenic aldehyde with chloroacetal yields a carbinol which is converted into cyclohexenone and subsequently into an alcohol possessing a strong sandalwood note.¹²

Treatment of campholenic aldehyde with methyl vinyl ketone produces a mixture of isomers. Hydrogenation of one of the isomers yields cyclopentanol which has a lasting sandalwood odor.¹² Condensation of campholenic aldehyde with diethyl ketone or propionic aldehyde and subsequent hydrogenation results compounds which have strong sandalwood odor.¹² Condensation of campholenaldehyde with EtCHO, followed by hydrogenation and reductive methylation results in cyclopentenpental, possessing a sandalwood odor.¹⁴ By condensing campholenaldehyde with MeCOEt cyclopentenylpentanol was obtained. It has a sandalwood note.¹⁵

Cyclopentene Derivatives¹⁶

- W Hoffman and K von Fraunberg, US Patent 4,069,258, Jan 17, 1978, assigned to BASF AG, Germany.
- 1-Methyl-2-(2,2-dimethyl-3-hydroxypropyl)-3-isopropenylcyclopent-1-ene has a typical sandalwood odor.
- V Kanath, BD Mookherjee and FL Schmitt, US Patents 4,149,020, Apr 10, 1979 and 4,170,577, Oct 9, 1979, both assigned to International Flavors & Fragrances, Inc.
- 2,3-Dimethyl-5-(2,2,3-trimethyl-3-cyclopenten-1-yl)-2-pentanol (Compound A), possessing a long-lasting sandalwood/santalol-type odor.

An illustrative synthetic sandalwood formula containing 25% of Compound A is given:

100	Amyris oil
220	Amyris acetate
150	Cedarwood oil
100	Tetra decahydro beta naphthol formate
50	Guaiophene 1% in diethyl phthalate
50	Eugenol 10% in diethyl phthalate
30	Galaxolide 2.5% in diethyl phthalate
50	Geranyl phenyl acetate
250	Compound A

It is claimed that the addition of 25% of Compound A to this synthetic sandalwood formula contributes the main sandalwood note to this formulation.

Polycyclic Alcohols¹⁷

JJ Bloomfield and DC Owsley, US Patent 4,119,575, Oct 10, 1978, assigned to Monsanto Company:

5,5,7-Trimethyltricyclo[6.4.0.0^{2,7}]dodecane-3-ol was found to possess a sandalwood odor.

Another new aroma chemical obtained during a study of a rearrangement product of carene epoxide by Dev¹⁸ was:

1'-(3,6,6-Trimethylbicyclo[3.1.0] hexan-3'-yl)-2'-methylpent-1'-(E)-en-3'-ol. It was described as having a lasting floral, sandalwood odor.

Among a variety of aroma chemical specialties offered by many perfume houses, to mention a few, are:

- Bacdanol (IFF): 2-Ethyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)-2-buten-1-ol of a woody sandalwood note.
- BBD (Naarden International): 8-t-Butyl-bicyclo 4.4.0 decanol, possessing a sandalwood odor.
- Ebanol (Givaudan-Roure): 3-Methyl-5-(2,2,3-trimethyl-3-cyclopenten-1-yl)-4-penten-2-ol (and isomers) of a sandalwood, musk, long-lasting odor, not found in nature.
- Sandalore (Givaudan-Roure): 5-(2,2,3-Trimethyl-3-cyclopentenyl)-3-methylpentan-2-ol, possessing a tenacious woody, sandalwood-like odor.

Some researchers investigated structure requirements for a sandalwood odor.

Kheifits et al¹⁹ ascribed sandalwood odor characteristics to compounds:

- containing a hydroxyl group
- having a "rigid" and bulky alkyl radical in direct proximity to atom C₍₅₎
- capable of assuming a configuration similar to the structure of natural cis-santalols

Buchbauer et al²⁰ showed that important requirements odor molecules with sandalwood fragrance are:

- A flat structure, linking a polar group rather exposed to this part to a more crowded "bulky" group
- The distance between the polar and bulky groups
- The shape of the bulky group

Naipawer et al²¹ found that structure requirements for a sandalwood odor are:

- The molecule should have a monohydric alcohol
- The number of carbon atoms should be 12-16
- There should be a highly substituted or quaternary carbon atom in the molecular framework
- The distance of the hydroxyl group and the quaternary carbon should be 4A° in at least one of the conformations.

The researchers acknowledged that not all compounds meeting these criteria have sandalwood odors.

Gora and Gibka²² reported the synthesis of a number of dimethylbornane derivatives. Among them, two saturated cyclic alcohols were found to possess strong and lasting sandalwood odors. The researchers deduced that the sandalwood odor structure requirements for saturated alcohols are:

- having a five- or six-membered ring
- having a hydroxyl group situated axially or quasi axially

- the monocyclic ring size has no influence on the odor of the alcohol.

Application

Sandalwood is an important perfume material. It has been originally used (and still is used) in incenses for religious purposes, and later in perfumery.

References in ancient religious scriptures, sutras and vedas show that people of ancient India were familiar with perfumed waters, among them Chandan (sandalwood).²³

Early Arab perfumers used sandalwood dust as a base for "solid" perfumes and incenses.²⁴

During the Nara Period (710-784) in Japan, sandalwood was among other aromatic materials used in incense burners in temples. Sandalwood was used individually or in mixtures with other materials.²⁵

Sandalwood was also included in the traditional attars of India which consisted of natural floral, herbal, woody, spicy, animal materials. These attars were also used in Muslim countries, especially South Arabia, as body perfumes because they did not contain any alcohol.²⁶

In India, sandalwood was also used, among other materials, in agarbattis: small sticks impregnated with resin paste.

In Western perfume, sandalwood finds application in women's fragrances, especially in oriental or semi-oriental types.

In the early part of this century, sandalwood was used in a violet perfumed pomade. Of earlier fragrances, Chypre, Fougère, Nuit de Noël, Eau de Cologne Ambrée, Eau de Lavande Ambrée may be mentioned. Among other fragrances containing sandalwood are: Interdit, Amazone, Audace, Rafale, Giorgio, Act 2, Must, Jardanel, to quote several.

Most modern fragrances contain small or larger amounts of woody notes which bring smoothness, roundness, and persistence to a perfume.

The use of sandalwood in women's fragrances has increased. It is not only a components of oriental fragrances, but also of diverse perfume types. Here are few examples of newer fragrances containing sandalwood:

Contradiction (Calvin Klein): oriental
 Transparent Blue (Molinari): green type
 Tocadilly (Rochas): floral, fruity, coconut, amber
 Relaxing Fragrance (Shiseido): herbal complex
 Flacon Collection (Lalique): floral, fruity, woody
 212 (Carolina Herrera): light floral, musk
 In Love Again (YSL): green, floral musk

Among the latest fragrances are: Theorema (Fondi), Lalique de Lalique, Paradox (Jacomo) and Cristobal (Balenciaga).

Sandalwood is a natural component of men's fragrance. Oleg Cassini, Quorum and 7922 YSL are but few examples. Among the latest are: Pleasures for Men (Estée Lauder), Sagitaire (Lalique), Eau du Tsar (Van Cleef & Arpels) and Orphée (Maxim's).

Sandalwood also found application in cosmetic fragrances: creams, powder, bath and hair preparations.

A recent Caswell-Massey catalog lists a sandalwood talc, body lotion, shampoo, hair conditioner, foaming bath gel and foaming bath grains.

In powder, sandalwood gives body covering power and persistence. Sandalwood was a component of the early Maréchale face powder perfume.

Indian women in Abeer use a scented powder which is sprinkled on clothes and linen. It is made from sandalwood, rose petals, civet and other ingredients pounded together in a mortar until they are finely powdered.²⁶

Sandalwood plays an important role in soap fragrances. Its sweet and lasting odor is an excellent fixative. However, because of its high price, sandalwood is used only in deluxe-type soaps.

In less expensive soap fragrances, the sandalwood note is achieved by the use of newer aromatic chemicals.

Santal soap by Roger Gallet, originally produced in 1896, is still sold today. So is Caswell-Massey Sandalwood soap, enriched with a warm spicy aroma.

Sandalwood was used in such known soap perfume types of the past as Peau d'Espagne, Ambre Antique and Palmolive. Palmolive survived to our days.

Sandalwood is likely to remain an important component of various types of fragrances in the future. This applies also to sandalwood specialties based on aroma chemicals with sandalwood notes.

During the early part of the 20th century sandalwood oil was widely used as medicine. By the middle of the century, only about 10% of the world production of sandalwood oil served for medicinal purposes.²⁸

The earliest use of sandalwood Australian was for therapeutical purposes. By the middle of the 20th century, it was still used in China, the Malayan Archipelago, and South America for self-medication.²⁹

In India, sandalwood is considered as an antiseptic, antiscabietic and diuretic drug. It is also used for the treatment of bronchitis and bladder infection, and to cure gonorrhoea.³⁰

Sandalwood is also displayed among other exotic items, spices and herbs, used as natural remedies, in the famous soukh (market) Khan el-Khalili in Cairo, Egypt, established in the Middle Ages.

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