Woody Notes in Perfumery:
Cedarwood and Cedarwood Derivatives Part

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Cedarwood is an important perfume material in the woody odor tonality. It finds application in various types of fragrances. The oil is also used to obtain cedarwood derivatives. The term "cedar" is derived from Latin (*cedrus*), Greek (kédros), Old English (ceder) and French (cedre). Cedarwood trees were appreciated in antiquity. The wood was imported to Egypt for various uses. Cedarwood oil was obtained by primitive distillation in ancient India.

Origin

There are several varieties of evergreen trees of the genera *Cedrus* and *Juniperus*. Among them are:

- *Juniperus mexicanus* Schiede (fam. Cupressaceae), also known as Texas cedar. This tree grows in central and western Texas and Central America.
- *Juniperus virginiana* L. (fam. Cupressaceae), also known as red cedar. The principal growing regions are Virginia and North Carolina.
- *Juniperus atlantica* Manetti (fam. Pinaceae), also called Atlas cedar. This tree is native to the Atlas mountains of Morocco, and Algeria.
- *Cypressus funebris* Endl. This tree is found in China, and is thus called Chinese cedar.
- *Cedrus deodara* (Roxb.) Loud (fam. Pinaceae), which is native to the Himalayan Mountain region.

Mode of Production, Yield, Oil Type

Various types of cedarwood oils are used in perfumery. These include: Cedarwood Texas (ex. *Juniperus mexicana*); Cedarwood Virginia (ex. *Juniperus virginiana* L.); Cedarwood Atlas (ex. *Cedrus atlantica* Manetti); Cedarwood Chinese (ex. *Cypressus funebris*, Endl.); and Cedarwood Himalayan (ex. *Cedrus deodara*), which has been recently advertised in trade literature. Steam distillation is used to produce the above cedarwood oils. Cedarwood Texas oil is produced from heartwood and wood shavings. The rectified (redistilled oil) is almost colorless and of a lasting balsamic woody odor.

The yield of the crude oil is 1.8 percent to 2.3 percent, while that of the rectified oil is 15 percent to 20 percent less.[1] Cedarwood Virginia oil is produced from the timber waste, sawdust and shavings. The yield ranges from 2 percent to 2.5 percent.[2] The oil is available in regular or distilled. The color of the regular oil is yellow to orange, while the redistilled oil is almost colorless.

Cedarwood Atlas oil is produced in Morocco. It is of a light-brown color and has a lasting balsamic, woody odor. It is also available as an absolute. The yield of the regular oil is 3 percent to 5 percent.[3] Chinese cedarwood oil is a more recent oil. Cedarwood oil Himalayan from India is new to the industry.

Chemical Composition

According to Guenther, it was known in the late 1950s that Virginia cedarwood oil contains about 80 percent cedrene, 3 percent to 14 percent of cedrol and a small amount of cedrenol. The cedrol occurs in crystalline and liquid form, identical chemically.[4] Cedrene was first isolated by Walter in 1841. In the same year, Walter observed cedrol in cedarwood oil. In the beginning of the 20th century, Semmler and Mayer first noted the sesquiterpene alcohol cedrenol. In the 1940s, Naves et al. reported that cedrene consists of several isomers, the chief components of which are α- and β-cedrene. Despite the work of terpene-chemistry researchers Semmler, Treibs, Ruzicka, Plattner and their collaborators, the structural formulas of cedrene, cedrol and cedrenol could not be definitely established, notes Guenther in the 1950s.[5]

The chemical composition of Atlas cedarwood was first investigated in the beginning of this century by Grimal, who identified d-cadinene, and also noted p-methyl-3-tetrahydroacetophenone in the oil, which was identified by Pfau and Plattner in the 1930s. This ketone is not present in the wood, but originates on steam distillation of the wood. The chief constituents found by the same researchers were α- and γ-atlantone.[6] In 1953, Stork and Breslow first synthesized dl-cedrol and dl-cedrene, and in 1955 achieved the total synthesis of cedrol and cedrene. Technological advances permitted Runeberg to report in 1960 the achievement of analysis of cedarwood Virginia oil by using gas and column chromatography, which showed that the sesquiterpene fraction was mainly a mixture of α-cedrene and thujopsene, the latter reported in cedarwood

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for the first time. Several minor constituents, not previously separated, were also found. They were cuparene, widdrol and curcumene.[7]

In 1967, Wenninger and collaborators reported finding in cedarwood oil Virginia β-elemene, α-and β-humulene, caryophyllene, an "accorene," valencene, two cuprenenes, and cuparene, in addition to previously reported constituents.[8] In 1971, Kitchens, Dorsky and Kaiser reported the results of their study of Virginia and Texas cedarwood oil composition.[9] The main components were: α-cedrene, β-cedrene, thujopsene, cedrol and widdrol. They occur in both oils, but in different percentages: the amount of β-cedrene and cedrol is higher in the Virginia oil, and thujopsene is higher in the Texas oil. Among minor sesquiterpene components of cedarwood oil Texas, the following were reported: β-chamigrene, widdrene, isowiddrene, α-chamigrene, widdrene isomer, cuparenene 2, cuparenene 4 and cuparene.

In 1980, Lawrence isolated and identified several components of Virginia and Texas cedarwood oils using infrared spectroscopy.[10] The results can be seen in Table 1 prepared by the author of this article.

Thus, Lawrence confirmed that the percentage of cedrol was higher in the Virginia oil, while that of thujopsene was significantly higher in the Texas oil. He also found that the amounts of caryopyllene and γ-eudesmol were almost double in the Virginia oil.

In 1985, Baslas and Saxena reported the following components of cedarwood, besides α-cedrene (79.5 percent), cedrol (12 percent) and cedrenol (0.95 percent): α-pinene (0.60 percent); limonene (0.25 percent; β-pinene epoxide (0.35 percent); limonene epoxide (0.10 percent); β-thujone (0.25 percent); methoxy acetophenone (0.20 percent); p-anisaldehyde (0.32 percent); menthol (0.10 percent); neoisomenthol (0.15 percent); α-terpineol (0.25 percent); thymol (0.55 percent); carvacrol (0.34 percent); eugenol (0.26 percent); ethyl vanillin (0.15 percent); bisabolene epoxide I (0.15 percent; bisabolene epoxide II (0.35 percent); methyl naphthyl ketone (0.30 percent); and pseudocedrol (10.90 percent).[11]

The analysis was performed using TLC, and the authors stated that the constituents were confirmed by CO-TLC, refractive index and spectroscopy. Lawrence believes that the description of the above analysis is "an in accurate and misleading publication." From the perfumer's point of view, it would be interesting to compound such a cedarwood oil and see the olfactory effect of such unusual minor components.

In 1986, Srinivas confirmed the presence of four components of cedarwood oil.[12] They were:

α-cedrene (25.15-25.20)>25 percent

β-cedrene (6.07-6.36)>6 percent

cedrol (19.70-23.97)~20-24 percent

thujopsene (20.10-26.97)~20-27 percent

In 1988, R. ter Heide et al. reported that a cedrol and hydrocarbon-free fraction of Virginia cedarwood oil, rich in oxygenated compounds, contains the following constituents: 8-cedren-2-ol; caryolan-1-ol; a sesquiterpene alcohol; betulenal; funebrenal; thujopsenol; chamigrenal; cedran-9-one; 8-cedren-3-one; 8-cedrene-10-one; nootkatone; 2-methyl-6 (4'-methylphenyl)-heptan-2-ol-3-one; and a sesquiterpene ketone.[13]

Results of the analysis of the chemical composition of cedarwood oil Texas, Virginia and Chinese, done by Adams, were reported in 1991.[14] The main difference was in the cedrol, widdrol and thujopsene percentages. Virginia and Texas oils had comparable amounts of cedrol, while the Chinese oil had a much lower percentage. However, the Chinese oil had a larger amount of widdrol, which was about equal in both the Virginia and Texas oils. Thujopsene was higher in the Chinese oil.

In 1997, Shu and Lawrence compared major and minor ones of four different cedarwood oil types.[15] The results showed that the Virginia and Chinese oils had about the same amount of α-cedrene. Both Virginia and Texas oils had similar percentages of cedrol, which was the lowest in the Chinese oil, followed by the Atlanta cedarwood (ex *Chamaecyparisus thyoides* L.). The Texas oil had the largest amount of thujopsene, followed by the Chinese and Atlanta oils. The Virginia oil had the least amount.

The Virginia oil was found to contain the highest percentage of widdrol, followed by the Atlanta oil, Texas oil and Chinese oil.

Table 1. Comparative component percentage of Virginia and Texas cedarwood oils

Component	Virginia cedarwood (percent)	Texas cedarwood (percent)
α-pinene	0.3-0.5	0.2-0.3
α-cedrene	18.2-30.9	23.7-24.5
caryophyllene	2.5-2.8	0.5-0.6
β-cedrene	4.6-8.9	5.5-5.8
thujopsene	14.6-15.6	30.3-34.7
cedrol	21.6-30.6	14.5-17.6
γ-eudesmol	4.1-6.3	2.3-2.6

In 1997, an analysis of six selected components of Virginia cedarwood oil: α-pinene, α-cedrene, β-cedrene, thujopsene, cedrol and widdrol was done by Coleman and Lawrence.[16] GC-based methods were used, which included different headspace methods. A table of the comparative results was shown and an interpretation given.

Cedarwood Derivatives and Isolates

Various cedarwood derivatives are obtained from cedarwood oil. They can be further treated by esterification, epoxidation or acetylation. Some of these possess woody cedar notes with musk or amber tones. In others, the ambergris note is dominating. Some of them have cedar-vetiver or cedar-sandalwood odor tonalities. Most of these derivatives are used per se in various types of fragrances, but some are incorporated in perfume specialties.

Let us look at several examples:

- Cedrol distilled is obtained from cedarwood oil by vacuum distillation. It is a mixture of alcohols and ketones, available in several grades, depending on the percentage of the alcohols. The higher grade is of a pale yellow color and typically contains 65 percent to 70 percent cedrol.
- Cedrol crystals are obtained by the vacuum distillation and crystallization of the cedrol cuts. It is 90 percent cedrol, minimum, and has a balsamic, sweet cedar and sandalwood odor.
- Cedryl acetate is obtained by esterification of the crude cedarwood oil or the cedrol distilled. Several grades are manufactured, depending on the percentages of acetates and hydrocarbons. It is a pale-yellow to yellow liquid or semi-solid.
- Cedryl acetate crystals are obtained by the crystallization of cuts from the vacuum distillation of cedryl acetate. The white crystals have a woody, powdery odor.
- Cedryl methyl ether is of a diffusive ambergris, woody odor tonality. It can be identified as a colorless to pale-yellow liquid.
- Cedrenol is richer in liquid cedrols and ketones than cedrol distilled. A colorless to pale-yellow liquid of a tenacious, dry, sweet, woody cedar odor.
- Cedrenyl acetate is obtained my esterification of cedrenol. It is a colorless to pale-yellow liquid of a long-lasting woody, cedar and vetiver odor tonality.
- Cedrenyl acetate crystals are a purer grade of cedrenyl acetate. It is a white crystalline solid and has a more refined woody, cedar, vetiver dry odor than the liquid form.
- Cedrenyl formate is a colorless to pale-yellow liquid of a dry woody, amber odor.
- α-Cedrene epoxide is obtained by epoxidation of α-cedrene, It has a woody cedar, sandalwood, patchouli and ambergris odor tonality, and is a colorless to pale-yellow liquid.
- Acetyl cedrene is a mixture of ketones derived from the acetylization of cedarwood hydrocarbons. It is available in several grades. A colorless to pale-yellow liquid of a diffusive woody cedar odor of great tenacity with a hint of amber and musk.
- Methyl cedrenyl ketone has a woody, vetiver, musk and leather odor.

There are also different types of aroma chemicals possessing woody odors with powdery, amber, musk or spicy overtones. Some of these are available as specialties. Here are a few examples.

Compounds Synthesized from the Terpene Isolongifolene[17]

- The formate fraction comprised of a mixture of aldehydes which have a cedarwood, vetiver odor of great tenacity with amber and clary sage dry-out.
- The acetate esters have a strong cedar, vetiver odor.
- The saponified mixture of formates and acetates gave corresponding alcohols. The distilled product in each case have an odor reminiscent of cedrol.

Trimethylcyclodecatriene possesses a tenacious woody, cedar and powdery note.

Cyclododecyl methyl ether has a cedarwood and musk odor tonality.

Methyl (methyl ethyl) bicyclo octenyl ethanone (three main isomers) possesses a woody, cedar odor with hints of balsam and amber.

Isolongifolene epoxide is a colorless to pale liquid of a woody, spicy odor with a hint of amber.

Application

The wood itself was used in ancient times for various purposes, such as painted statuettes, mummy portraits and coffins.

Today, cedarwood lining is used in chest and cedarwood blocks in closets, because the odor of the material is known to repel moths and mildew.

Cedarwood oil and/or its derivatives find application in various types of women's and men's fragrances, as well as in cosmetics, soap and household perfume. We shall discuss this subject in the second part of this article, which is forthcoming.

References

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1. E. Guenther, The Essential Oils, New York : D. Van Nostrand Company (1952) v6, p366.
2. Guenther, p355.
3. Ibid., p234.
4. Ibid., p362.
5. Ibid., pp361-363.
6. Ibid., pp235-236.
7. G.C. Kitchens, J. Dorsky and K. Kaiser, Givaudanian No. 1, 3-4 (1971).
8. Ibid., p4.
9. Ibid., pp4-9.
10. B.M. Lawrence, Perf. & Flav. 5(3)63 (1980).
11. R.K. Baslas and S. Saxena, Herba Hung. 24, 27-30 (1985), c.f. B.M. Lawrence, Perf. & Flav. 16(5) 79 (1991).
12. S.R. Srinivas, Atlas of Ess. Oils. Published by the author, Bronx, New York (1986).
13. R. ter Heide, J. Visser, L.M. van der Linde and F.P. van Lier, 10th Int. Congress of Ess. Oils, Frag. & Flav., Washington, DC, 1986, Paper No. 51.
14. R.P. Adams, Ess. Oils and Waxes, v12, pp59-173, Ed. H.F. Liskens and J.F. Jackson, Springer Verlag, New York (1991); c.f. B.M. Lawrence, Perf. & Flav. 23(5)68 (1998).
15. B.M. Lawrence, Perf. & Flav. 23(5)68 (1998).
16. Ibid., pp67-68.
17. H.R. Ansari, N. Unvin and H.R. Wagner, US Patent 4,100,110 (July 11, 1978), assigned to Bush, Boake, Allen Ltd. England. In: Fragrances & Flavors, Recent Developments. Chemical Technology Review No. 156, Ed. S. Torrey, Park Ridge, NJ: Noyes Data Corp. (1980) pp122-123. ■