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Material Review

Woody Notes in Perfumery — Vetiver and Derivatives. Part I

Botanical origin, production, composition and fragrance compounds

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Vetiver is an important woody note in perfumery. The word vetiver, vetyver in French, originated in Tamil:* vettiveru = vetti, worthless + veru, useless.[1] The Indian term for vetiver is Khus, and in Indonesia is known as Akar Wangi.

Botanical origin: Vetiver, *Vetiveria zizanioides* Staph., is a grass growing wild, semi-wild or cultivated in many parts of the world, including India, Haiti, Java, Réunion Islands, China and Indonesia.

Mode of production, yield, type of oil: Vetiver oil is obtained by distillation of *Vetiveria zizanioides* roots. Steam distillation is a more recent method used, and it gives a better yield of the oil. The yield of the dried vetiver Java roots is from 1.5 to 2 percent, and that of vetiver Haiti varies from 1 to 1.5 percent.[2] A more recent source gives the yield of air-dried vetiver Java roots as 2 to 3 percent.[3]

The following types of vetiver oil are available commercially:

- . vetiver Java
- . vetiver Haiti
- . vetiver Réunion
- . vetiver China
- . vetiver Indonesian
- . vetiver redistilled
- . vetiver de-ironized
- . vetiver resinoid

Chemical Composition

The chemical composition of vetiver oil was studied in the beginning of the 20th century. Theulier studied the physicochemical properties of fractionated vetiver oils distilled in France and on Réunion Island. Other investigations were carried out by various researchers, among them Semmler.[4] In the 1950s, the following components of vetiver oil were identified:[5]

- **α- *and* β-*Vetivone (vetiverone):*** Java and Réunion oils were found to contain 7.5 to 35.1 percent of ketones, depending on the method used. The odor of vetiver is due chiefly to ketonic sesquiterpenes. Only two of them, listed above, have been isolated.

- ***Vetivenols (vetiverols):*** These alcohols were investigated by various researchers in the beginning of the 20th century, but the results were inconclusive. Only by the middle of the century did it become apparent that at least 60 percent of these sesquiterpene alcohols occurring in vetiver Java oil seemed to consist of a mixture of primary alcohols in which a tricyclid alcohol predominates, while bicyclic alcohols amounted only to 10 percent.

- **Vetivenyl vetivenate:** An ester that vetivenic acid forms with vetivenol and which readily hydrolyzes.

- ***Palmitic acid.***

- ***Benzoic acid:*** In considerable amounts.

- ***Vetivene:*** A colorless and odorless sesquiterpene.

In 1976, a study of the carbonyls of Haitian vetiver oil was done. Seven novel sesquiterpenoid and norsesquiterpenoid carbonyls were characterized. The major isomer of dihydro β-vetivone had "a strong rich woody peppery odor," while the remaining novel carbonyls were of a general woody type odor. The researchers believed that all of the carbonyls play a role in achieving the complex woody odor of vetiver oil.[6]

Among vetiver oil components characterized in the early 1970s were α- and β-vetivones, the norsesquiterpene khusimone and three biogenetically derived C-12 ketones, which were deemed to be the

*A language spoken by members of the Dravidians, an ethnic group from southeastern India and Ceylon.

most interesting. Spiroketone and khusimone appear to play an important role in the reconstruction of vetiver oil. Therefore, total new syntheses of these compounds were developed.[7]

In the study of vetiver oils of different geographical origins, other researchers reported 95 compounds in the hydrocarbon-rich section, fractionated via distillation of vetiver oil Haiti, and suggested that more than 150 components were present in the total vetiver oil.[8]

In 1977, a synthesis of β-vetivone via base-catalyzed spiroannelation of phenolic tosylates was reported.[9] A 1978 patent covered a new synthesis of khusimone.[10] 6,6,7-Trimethyl-tricyclo [5.2.2.0^{1,5}] undec-8-en-2-one was given as the starting material for this synthesis. This compound was described as having a woody, sandalwood-like odor with vetiver nuances, thus being of interest. In 1989, another synthesis of khusimone was reported, starting from (S)-6,6-dimethyl-5-methoxycarbonylmethyl-2-cyclohexen-1-one. Overall yield was 6.9 percent.[11]

In 1996, an analysis of vetiver Haiti was reported that showed that the main constituents were isovalencenol, β-vetivone and khusimol. Because vetiver was a very complex oil, it is a difficult task to separate and elucidate the structure of its components.

Using flashchromatography, two olfactory important fractions were obtained: (1) medium polar (hydrocarbons, ethers and ketones), and (2) polar alcohols and α,β-unsaturated ketones. The combination of distillation and repeated FC yielded several new compounds.

In the medium polar fraction, one of the sesquiterpene hydrocarbons that never isolated before in vetiver oil was *cis*-eudesmadiene. Among other isolated ethers were α-agarofuran and 4,7-epoxy spirovetiva-1,11(12)-diene.

In the polar fraction, the transformation of secondary alcohols to methyl ethers; subsequent split tube distillation gave 30 new sesquiterpene ethers after repeated FC. Olfactory comparison of the odor of several methyl ethers and their corresponding alcohols showed that the odor of the methyl ethers was more earthy, khusimone-vetiver or patchouly-like, while the alcohols had woody odor tonalities with amber, sweet and grapefruit undertones.[12]

Synthetic Compounds

Vetiver has a lasting woody odor with a hint of camphoraceous, earthy and musty undertones. It has points in common with violet-orris and patchouli type odors, and it blends well with sandalwood and rose odors. Vetiver is especially effective with musky odors. Several of the modifiers of vetiver odor are listed in T-1.

Vetiver Imitations

Because of the complexity of vetiver oil it is difficult to reproduce the vetiver odor. Several early imitations were developed; some served in the past to fraud the natural oil. Here are several examples:

Odor characteristics of tridecan-x-ones (x = 2,3,4,5 and 6) **T-1**

For lift and freshness	To add floralcy	To add sweetness	Folial/green	Spicy	Woody	Fixatives
Aldehyde C-10	Aurantiol	Coumarin	Hexenyl acetate	Isoeugenol	Cedarwood	Amyl salicylate
Aldehyde C-11	Jasmine	Labdanum resinoid	Methyl octine carbonate		Sandalwood	Benzophenone
Aldehyde C-12 (MNA)	Lilial	Musk ketone	Phenylacetaldehyde dimethyl acetal			Dimethyl hydroquinone
Bergamot	Nerol	Styrax resinoid				Diphenyl oxide
Cassie	Neroli	Tolu balsam				Isobutyl salicylate
Citraldimethyl acetal	Rhodinol	Vanilla resinoid				Musks (various types)
Clary sage	Rose	Vanillin				
Geranonitrile	Terpineol					
Lavender	Ylang ylang					
Orange oil						
Thyme						
Ylang ylang						

Complex of Vetiver Oil No. 1[13]

vetiver oil	50.00
sandalwood	40.50
copaiba balsam	8.00
Rhodinol	0.50
Exaltone	0.01
	99.00

Vetiver Synthetic No. 2

vetiver bourbon	225
cedarwood	150
copaiba balsam	100
solvent	25
	500

Vetiver Synthetic No. 3

cedarwood	145.0
sandalwood	135.0
guaiacwood	75.0
hercolyn Atlas	70.0
vetiver Haiti	55.0
vetiver acetate	40.0
labdanum resinoid	20.0
aldehyde C-18	20.0
methyl ionone	15.0
tolu balsam	12.5
isobutyl quinoline	7.5
cade oil 10%	5.0
	600.0

More recent vetiver specialties approximate the odor of vetiver oil, but leave much to be desired in regard to lastingness and fixative power.

Traditional Fragrance Compounds

Let us take a look at a number of illustrative fragrance compounds containing vetiver or its derivatives.

Aldehydic Chypre[14]

clary sage	35
mousse de chene absolute	50
nutmeg	35
patchouli	50
vetiver	95
bergamot	125
orris concrete	25
orange oil	30
sandalwood	90
orange flower absolute	30
jasmin absolute	30
ionone	95
methylionone	90
labdanum absolute	40
coumarin	25
heliotropin	90
vanillin	20
musk ketone	50
aldehyde C-11 10%	75
aldehyde C-10 10%	75
aldehyde C-12 (MNA) 10%	50
	1205

Chypre I[15]

mousse de chene	50
bergamot	225
vetiver Bourbon	75
lavender	50
sandalwood EI	70
patchouli	10
cloves	35
jasmin synthetic	100
rose synthetic	80
isobutyl salicylate	70
cinnamic alcohol	50
heliotropin	100
coumarin	50
tonka resinarome	20
aldehyde C-12 (MNA) 10%	15
	1000

Cuir de Russie[16]

birch tar oil	60
castoreum 10%	150
rose otto	20
styrax resinoid	100
bergamot	100
sandalwood EI	10
patchouli	5
jasmin absolute	50
musk ambrette	50
musk ketone	80
Exaltolide 10%	20
vetiver acetate	100
tonka resinoid	30
vanilla resinoid	20
vanillin	50
labdanum resinoid	100
clary sage	5
oakmoss decolorized	10
tuberose absolute	7
acetophenone	3
cassie absolute	10
lemon oil	20
	1000

Foin Coupé (New Mown Hay)[17]

bergamot	90
coumarin	120
jasmin absolute	100
rose absolute	20
cassie absolute	10
oakmoss absolute	12
anisic aldehyde	18
linalool	20
lavender	36
clary sage	6
vetiveryl acetate	24
hydroxycitronellal	20
methyl anthranilate	6
civet infusion 3%	50
musk tonkin infusion 3%	200
ylang ylang	12
amyl salicylate	60
isobutyl phenylacetate	30
isobutyl benzoate	12
tuberose absolute	20
mimosa absolute	18
ionone a	20
methoxyacetophenone	30
aldehyde C-12 (MNA) 10%	6
sandalwood EI	60
	1000

Traditional illustrative perfume compounds presented in this article were developed before dermatological consideration took effect. Therefore, few components in these formulas would be acceptable today unless a) used in limited percentages or b) spe-

cially processed. In the first case, relevant materials include angelica, cinnamon, cinnamic alcohol, citrus oils and oakmoss, and in the second, bergamot and styrax resinoid. Other components have been completely eliminated, including musk ambrette. We shall discuss this subject matter in greater detail in the second part of this article.

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