

## Amber Notes in Perfumery

# Ambergris

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Ambergris is among the few materials of animal origin used in perfumery. Because of a late 1970s US law prohibiting the importing of ambergris or any whale products into the US, natural ambergris is no longer used in US perfumery. Ambergris isolates, derivatives and substitutes are used.

Ambergris derives its name from the Arabian term *ambar*,<sup>1</sup> from Old French *ambre gris* (amber + gris, gray).

Ambergris was already used in ancient times, primarily as a medicine and in incense, and only later in fragrances.

The Chinese valued ambergris as medicine and used it chiefly as an aphrodisiac. They called ambergris *lung-yen* (dragon saliva). Medieval Arab medicine held ambergris as a valuable heart stimulant. It was also used as flavor in medieval Arab cuisine. Arabs of the African coast mixed ambergris in their coffee.<sup>2</sup>

Later, Western medicine also placed great faith in ambergris's therapeutic properties. In the 14th century, Marco Polo mentions ambergris as an article of commerce.<sup>2</sup> In a 17th century pharmacopeia, it was reported that besides being a medicine for the heart and brain, ambergris was a good preservative against plague.<sup>3</sup>

### Origin

It is known that the species *Physeter macrocephalus* L. produces ambergris, which is found, especially after storms, in fragmented chunks on the surface of the seas at Madagascar, in Japan and in the southern seas. It is also found inside the killed whale.<sup>4</sup> Brazil, China, India, the Bahamas and many other lands were sources for ambergris, as "the sperm whales roam the seven seas."<sup>3</sup> It was always thought that only the male could produce ambergris, but it is now known that the female sperm whale also produces it.<sup>3</sup>

Theories on ambergris were already devised by Albertus Magnus, the famous German alchemist of the 13th century, but to this day little is known of its formation or its function and the question of its exact origin remains controversial.<sup>5</sup>

Some authors suggest that ambergris is a biliary concre-

tion. Others think of it as a natural secretion. For a third group, ambergris is a pathological concretion produced by whales from incompletely digested food (especially cuttlefish) that injures the whale's digestive tract and forms abscesses which, upon rupturing, release the concretion known as ambergris.<sup>4</sup> The last theory seems to be the most prevalent.

These lumps, or calculus, are found floating on the surface of the ocean, as they are lighter than sea water. Their weight ranges from a few kilograms to several hundred kilograms.<sup>6</sup>

### Properties, Identification and Mode of Production

Ambergris has a specific gravity of 0.8-0.9. It is melted by boiling water and is volatile at higher temperatures, producing a white steam and leaving only slight traces of ash. It is soluble in alcohol, ether and fatty and volatile oils.<sup>7</sup>

A mass of ambergris is similar in consistency to wax. The color varies from white through reddish, gray, brown and even black. The white ambergris is supposed to be the rarest and is found usually in small pieces after prolonged floating in the sea or ocean.<sup>3</sup>

A quick test for genuine ambergris is to dissolve a little piece in a small quantity of hot alcohol, then allow it to cool. True ambergris will crystallize as the alcohol cools. Another test is the hot needle test: the heated needle should enter the mass easily without sticking, a characteristic odor should be given off and an opaque amber-colored molten drop should appear at the point of removal.

Ambergris was used in perfumery in the form of alcoholic infusions. They were valued as fixatives and their odor usually became more refined with proper aging. The infusion was prepared as follows:<sup>8</sup>

- 1 liter alcohol 96°
- 30 grams ambergris
- 60 grams potassium hydroxide 35° or 38°

**Procedure:** Place in the mortar 15 or 20 grams of potassium hydroxide and 30 grams of ambergris and pound until a homogeneous mass is obtained. Add a quarter liter of alcohol to this mass and mix. Decant the liquid. Add the remaining potassium hydrox-

ide to the residue in the mortar and pound to a mass. Pour half of the remaining alcohol and decant the mixed liquid. The remaining alcohol is used to rinse the mortar, and is subsequently added to the liquid. Keep the infusion in a hermetically closed container at room temperature and out of sunlight. Shake it vigorously once a week and age it for five or six months or longer if possible. It is preferable to decant the infusion or, if this is not possible, to filter it before using.

Ambergris was also used as medicine in the form of tinctures:<sup>8</sup>

**Ambergris Tincture** (Codex de Paris, 1758)

Ambergris .....	1 part
Alcoholic rose solution .....	12 parts
Alcoholic carbonated potassium solution .....	12 parts

The above is prepared in a similar way as the infusion. The finished tincture is shaken vigorously from time to time during four or five days and then heated in an open container on a water bath until the alcohol boils. It is then cooled and filtered.

**Chemical Composition**

In 1942, Janistyn disclosed the following findings on gray ambergris:<sup>9</sup>

- coprosterol
- epicosterol
- cholesterol (small amounts)
- dihydrocholesterol (traces)
- ambreine (a crystalline substance)

The dehydration of ambreine with selenium resulted in 1,2,5-trimethylnaphthalin and 1,6-dimethylnaphthalin.

In 1946, Lederer et al. reported the following components of ambergris from various samples studied:<sup>10</sup>

insoluble in ether .....	10-16%
hydrocarbon C <sub>16</sub> H <sub>38</sub> .....	2-4%
ambreine .....	25-45%
epicoprosterol-free and esterified .....	30-40%
coprosterol .....	>1%
ketones (50% of which is 3-coprostanone) .....	6-8%
free acids .....	5%
esterified acids .....	5-8%

Arachidic acid isolated by Tsujimoto was also mentioned by the above researchers, and 3-coprostanone was deemed to be the principal ketone of ambergris. Ambreine was described as a "new triterpene of animal origin, which can be ranged between aliphatic squalene and tetracyclic alcohols of the wool fat."

In 1948, Ruzicka et al.<sup>11</sup> isolated  $\gamma$ -dihydroionone from the volatile part of gray ambergris, and found that it, like the same chemical compound obtained by oxidation from ambreine, had a weak dextrorotation.  $\gamma$ -Dihydroionone possesses a typical amber odor, whereas  $\alpha$ -dihydroionone and  $\beta$ -dihydroionone have more woody, cedar-like odors.

In 1950, the search for adequate amber-type odorants started. Ruzicka and Seidel<sup>12</sup> reported the following components isolated from the volatile part of gray ambergris:

- an oxide C<sub>13</sub>H<sub>22</sub>O
- an oxyaldehyde C<sub>17</sub>H<sub>30</sub>O<sub>2</sub>
- a ketone C<sub>13</sub>H<sub>20</sub>O

In 1957, Seidel and Stoll<sup>13</sup> showed that the volatile

nonketonic fractions of gray ambergris contain mainly  $\gamma$ -cyclohomogeraniol, which has a metallic seaweed note of the ambergris tincture.

Earlier published research on ambergris shows that the major components of ambergris are triterpene alcohol and sterols of the cholestanol type. According to Ohloff,<sup>14</sup> the ratio of the two groups determines the quality of ambergris. The best type of ambergris may contain up to 80% ambreine. Black ambergris, which is considered poorest in quality, is found to contain 45% sterol derivatives.

In 1977, Mookherjee and Patel<sup>15</sup> investigated and identified close to 100 volatile constituents of tincture of ambergris. During the first attempt, the following components were identified in one of the fractions possessing a strong ambergris odor:

diethyl phthalate	70%
norphytan	10%
$\gamma$ -dihydroionone	5%
$\beta$ -ionone	1%
$\alpha$ -ambrinol	1%
p-cresol	0.1%

(Diethyl phthalate was derived from the alcohol for which it is a denaturant.)

After a second attempt, the same researchers believed that their work had revealed most of the important odoriferous constituents of tincture of ambergris. Among these constituents were five which, the researchers felt, play a key role in the characteristic odor of ambergris tincture:

$\gamma$ -homocyclo geranyl chloride .....	ozone-seawater
$\alpha$ -ambrinol .....	moldy-animal-fecal
$\gamma$ -dihydroionone .....	weak tobacco
$\gamma$ -coronal .....	sea water
Ambrox .....	moist, soft, creamy, persistent amber odor with velvety effect

The researchers concluded that the important volatile constituents of ambergris are produced through the auto- or photo-oxidative decomposition of ambreine.

**Syntheses, Isolates, Derivatives**

Starting from sclareol obtained from clary sage (*Salvia sclarea* L.) oil, Stoll and Hinder first synthesized Ambrox (Firmenich) as dodecahydrotrimethyl naphtho furan. This synthesis was reported in 1950.<sup>16</sup>

Mookherjee and Patel first isolated Ambrox from tincture of ambergris, revealing their findings in 1977.<sup>15</sup>

Other perfume houses began to produce this furan chemical compound, some using novel fermentation processes. It is now known under various trade names, such as Ambroxan (Henkel), Amberlyn (Quest) and Amberiff (IFF), to name but a few.

Sensory evaluation of the enantiomers of Ambrox showed that the (+)-enantiomer has a dominant woody note and the (-)-enantiomer has a warm musky animal note.<sup>17</sup>

In 1987, Ambrox was synthesized from non-natural sources, and a year later Ambrox DL Coeur was introduced as a closest version of Ambrox.<sup>18</sup> Ambrox DL (a mixture of isomers of dodecahydro-3a,6,6,9a-tetramethyl naphtho 2-

1-b furan) is a white solid of a powerful amber note with a suggestion of woodiness. It is more diffusive than Ambrox, but less rich in dry-out.

Another important constituent of ambergris is Alpha Ambrinol (Firmenich), which is 2-hydroxy-2,5,5-trimethyl octanile.

The preparation of  $\alpha$ -ambrinol from dihydro- $\gamma$ -ionone was discussed in a Japanese paper.<sup>19</sup>

It was recently reported that the volatile component of ambergris,  $\alpha$ -ambrinol, has been synthesized from 3-methyl-2-hexen-1-one.<sup>20</sup>

New series of ambergris odorants having structures based on 2-cyclo-hex(enyl)-1,3-dioxans have been reported. Various chemical compounds have been prepared with diverse amber-type notes.<sup>21</sup>

- Amber with woody floral and lily-like overtones.
- Amber and green with sandalwood and earthy nuances.
- Woody amber.
- Amber with almond top notes.
- Amber/cinnamate with weaker amber character.
- Green, amber and lily of the valley.

Manool, an oxygenated diterpene obtained from pink pine *Halocarpus biformis* (family *Podocarpaceae*), can be easily converted into acetals with powerful ambergris-type odors.<sup>22</sup>

A new method of obtaining ambergris-type chemical compounds from oxidation products of abietic acid was disclosed.<sup>23</sup>

Alpha pathoulone, prepared during research on patchouly oil, was found to have a strong ambergris odor.<sup>24</sup>

13-Oxabicyclo [10.3.0] pentadecane is claimed to possess a warm amber odor of good persistence.<sup>25</sup>

Tertiary butyl ether of cyclodecanol and some compounds prepared from substituted cyclopentanone have amber-ionone odors.<sup>26</sup>

### Synthetic Compounds

Ambergris was an important part of fragrances and an exceptional fixative. For example, in Tunisia the scent made of ambergris, rose petals and saffron was reputed to last a lifetime. It was worn in beads of a gold necklace.

Here are a few examples of older perfumes, listed in an 1841 French pharmacopeia.

#### Essence Royal<sup>27</sup>

Ambergris .....	2.4 g
Musk .....	1.2 "
Civet .....	0.5 "
Cinnamon oil distilled .....	0.3 "
Rhodes wood oil distilled .....	0.2 "
Rose oil distilled .....	0.2 "
Orange flower oil distilled .....	0.2 "
Potassium carbonate .....	0.6 "
Alcohol 90° .....	86.4 "

The mixture of ambergris, musk and potassium carbonate is triturated. Then it is put in a glass container with the alcohol, and the distilled oils are added. This alcoholic solution is aged at least 15 days, then decanted or filtered.

#### Baume de Vie d'Hoffman<sup>28</sup>

Ambergris pulverized .....	1 g
Succin oil rectified .....	1 "
Rue oil .....	1 "
Cinnamon .....	2 "
Lemon .....	2 "
Cloves .....	2 "
Lavender .....	2 "
Macis .....	2 "
Marjoram .....	2 "
Alcohol 90° .....	480 "

The alcoholic solution is aged for a minimum of 15 days, then filtered.

Both above formulas were used not only for perfumes, but also as preparations for rejuvenation in old age. The suggested dose was 10 to 22 drops in sugar or wine.

Today, cinnamon, lemon and rue oils, used in the above formulas, are considered sensitizers or phototoxic, and their use in fragrances is limited, as per guidelines of the International Fragrance Association (IFRA).

Ambergris was also used in 19th century musk perfumes, as in this example:

#### "Victorian Era" Musk Perfume

Musk tincture .....	4 parts
Ambergris tincture .....	2 "
Rose extract .....	1 part

When aromatic chemicals became available, they were used in amber perfumes. The following formula may serve as an illustration:

#### Ancient Amber II (for extracts)<sup>29</sup>

Ambergris tincture 20% .....	85
Rose compound .....	320
Musk ketone .....	40
Vanillin .....	50
Heliotropin .....	150
Musk ambrette .....	30
Ionone alpha .....	125
Sandalwood .....	25
Jasmine compound .....	25
Cinnamic alcohol .....	150
	1000

Today, cinnamic alcohol is limited to 4% and musk ambrette has a restricted use in limited amounts in fragrance compounds, in accordance with IFRA's guidelines.

### Application

Incense was one of the early uses of ambergris. The ancient Chinese used ambergris as a fixative to preserve the volatility of camphor in an incense, which included musk.<sup>3</sup>

Ancient Orientals believed that ambergris prolonged life, and also that it was an aphrodisiac. The most valued for the latter purpose was white ambergris, which is found in small quantities. It is very brittle and disintegrates into dust. Its odor is very refined.<sup>30</sup>

Special containers were designed and used during the al-Mughira caliph period (dated AH 357, or approximately 968 AD) to hold such precious substances as ambergris and camphor.<sup>31</sup>

Ambergris was also appreciated in the Arab world. The Arabs wore small lumps of ambergris around the neck in order to enjoy its odor and as a symbol of wealth and distinction.<sup>3</sup>

Natural ambergris has a unique subtle note which brings forth a diffusive effect in fragrances, and at the same time gives them homogeneity.

Ambergris does not have the odor intensity of other animal fixatives. It can be used in most luxury fragrances, to which it contributes a velvety effect and gives lift.

Ambergris refreshes rose odors and underlines gardenia and green notes in general.

Ambergris is also an excellent fixative, used both in perfume compounds and in the pre-fixed alcohol for luxury fragrances. Ambergris is especially suitable with musk and civet odors.

Unfortunately, ambergris is no longer available for perfumery use in the US, as mentioned earlier. Also, in 1985, the International Whaling Commission imposed a moratorium on commercial whaling for preservation of the species.

Research work on ambergris has led to identification and synthesis of new ambergris constituents. Their odor is not as subtle and complex as that of natural ambergris, and they have to be used with greater caution. However, they are well suited for today's fragrances, which are less subtle than fragrances of the past.

Among earlier ambergris specialties using some of these constituents are Grisambrol (Firmenich), which is based on  $\alpha$ -ambrinol, and Fixateur 404 (Firmenich), containing Ambrox.

Later, Ambrox (Firmenich), as well as identical or modified versions of this furan compound by other companies (as discussed previously), and Ambrinol (Firmenich) became available.

In a future article we will discuss amber-like odors of vegetable sources and their application to various amber compounds.

**References**

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

1. P Jellinek, *Praktikum des Modernen Parfuemeurs*, Wien: Urban & Schwarzenberg (1949) p 179
2. HH Hart, *Marco Polo Venetian Adventurer*, Norman: University of Oklahoma Press (1967) pp 152-153
3. L Stoller, *Givaudanian*, No 3 (1974) p 8
4. H Fouquet, *La Technique Moderne et les Formules de la Parfumerie*, Paris and Liège: Librairie Polytechnique Ch Béranger (1951) p 59
5. T Mildner, *Givaudanian*, (Mar 1967) p 8
6. Hasslauer, *Ind de la Parfum*, No 7, 307-308 (Jul 1950)
7. Mildner, *ibid*
8. Fouquet, pp 60-61
9. H Janistyn, *Parf u Kosmet* **30** 53, 80 (1942)
10. E Lederer, F Marks, D Mercier and G Pérot, *Helv Chim Acta* **29** 1354-1365 (1946)
11. L Ruzicka, CF Seidel and M Pfeiffer, *Helv Chim Acta* **31** 827-831 (1948)
12. L Ruzicka and CF Seidel, *Helv Chim Acta* **33** 1285-1296 (1950)
13. CF Seidel and M Stoll, *Helv Chim Acta* **40** 1990-1998 (1957)
14. G Ohloff, *The Fragrance of Ambergris in Fragrance Chemistry*, ET Theimer, ed, New York: Academic Press (1982) pp 533-570
15. BD Mookherjee and RR Patel, Proceed 7th Int Congr Ess Oils, Kyoto, Japan, paper No 136 (1977)
16. M Stoll and M Hinder, *Helv Chim Acta* **40** 1251 (1950)
17. MH Boelens, *Perf & Flav* **18**(6) 13 (1993)
18. M Grass, *Perf & Flav* **17**(1) 9 (1992)
19. Takazawa, Matsushita et al, *Chem Lett* (10) 1257 (1980); see also PZ Bedoukian, *Perf & Flav* **7**(2) 13 (1982)
20. Nishi et al, *Chem Express* **4**(1) 33 (1989); see also PZ Bedoukian, *Perf & Flav* **16**(3) 22 (1991)
21. EP 027698, CP Newman, KJ Rossiter and CS Sell (1987) in C Sell, *Chemistry and Industry*, No 16, 516-520 (Aug 1990)
22. NB Perry, MH Douglas and NG Porter, *Perf & Flav* **18**(6) 25-27 (1993)
23. RC Cambie et al, *Aust J Chem* **43**(1) 21 (1990); see also PZ Bedoukian, *Perf & Flav* **16**(3) 22 (1991)
24. BD Mookherjee, RW Trenkle and RA Wilson, 12th Int Congr Fragr Flav and Ess Oils, Vienna, Austria (Oct 4-12, 1992)
25. German Pat 4,222,904, assigned to Henkel KGaA, Germany (1980), in *Perf & Flav* **6**(1) 60 (1981)
26. Eur Pat Appl 21,356, Bruns and Weber (Jan 7, 1981); see also PZ Bedoukian, *Perf & Flav* **7**(2) 13 (1982)
27. Fouquet, p 62
28. Fouquet, p 63
29. RM Gattefossé, *Formulaire de Parfumerie et de Cosmétologie*, Paris: Girardot & Cie (1950) p 91
30. Hasslauer, p 308
31. Louvre Museum, Islamic Section, Paris, France

