

Animal Notes in Perfumery

Castoreum and Castoreum Substitutes

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Castoreum is an odorous secretion obtained from certain glands of the beaver.

The word *beaver* is derived from the Sanskrit word *babhru*, *bebras* in Lithuanian (an old Indo-European language), *biber* in German, *bever* in Middle English and *fiber* in Latin.

The word *castoreum* is derived from the Greek word *kastor* (*kastorion*), *castor* in French.

Although the term *castor* is used interchangeably with *castoreum* in dictionaries, *castoreum* is the preferred term in perfumery to denote the perfume material obtained from the beaver.

Origin

There are two species of beavers (belonging to the family Castoridae) of importance in perfumery. The first is *Castor fiber* L. (Siberian beaver), found in Russia and in many parts of Europe, and the second is *Castor canadensis* (Canadian beaver), found in Canada and the northern United States.

Type of Material, Mode of Production and Yield

Castoreum is a secretion from glands situated near the beavers' genital organs. Both female and male beavers have these glands, but those of the female are less developed. The fresh castoreum secretion is a creamy orange-brown substance with a strong, penetrating odor. When dried it turns to a reddish-brown resin with a pungent, acrid, bitter odor.

Castoreum obtained from the Russian beaver has a tarry odor with a secondary creosote-like note, reminiscent of birch bark oil. The Canadian castoreum has a secondary odor reminiscent of pine resin, associated with galbanum. This odor difference may be attributed to the different food eaten by these beavers. The Russian beaver feeds on birch bark, and the Canadian beaver consumes the bark of aspen, pine and fir trees.

In the early part of the 20th century, castoreum was

commercially available in original pouches, and its odor was strong, harsh and ammoniacal.¹ The infusions were prepared in a similar manner to those of amber and musk. Here are a few examples.

Castoreum infusion^{2a}

1 liter	Alcohol 95%
50 g	Castoreum
100 g	Potassium hydroxide

Simple castoreum infusion^{2b}

500 g	Castoreum natural
10 liters	Alcohol 95%

Concentrated castoreum infusion^{2b}

5 kg	Castoreum natural
10 liters	Alcohol 95%

Another method of preparing the infusions was to remove the secretion from the pouch, rubbing it down with either orris root powder or clean silver sand. It was then macerated for several days with 20 times its weight of 90% alcohol, then filtered. The yield of the soluble fraction of the pouches was 45-75% of their original weight.³

Later, volatile solvents were used to obtain the so-called concrete. The yield of the concrete was about 20%. Extraction with alcohol gives the alcohol-soluble absolute.⁴

Alcoholic solutions can be readily prepared from castoreum absolute, and they have replaced earlier infusions.

A modern method of obtaining castoreum is CO₂ extraction.

Chemical Composition

A number of castoreum components were identified in the 1940s, mostly due to the work of Lederer. Among them were the following.⁵

acetophenone
benzyl alcohol
benzoic acid
p-ethyl phenol

1-borneol
o-cresol
o-methoxy phenol (guaiacol)
ammonia
traces of organic bases in the aqueous distillate

It was also generally agreed that castoreum contains a crystalline material called castorin.

The following constituents were found in beaver urine.⁶

Alcohols

manitol
derivatives of tetrahydro ionol

Phenols

p-ethyl phenol
pyrocatechol
hydroquinone

Ketones

hydroxyketones, derived from ionone

Acids

benzoic
salicylic
m- and p-hydroxybenzoic
gentisic
coumaric

The nutty note of castoreum has been attributed to lactones. Other components mentioned are a volatile oil, resin, castorin, small quantities of ammonium carbonate and traces of minerals.⁷

A pyridine compound called musco pyridine has been found in musk. A similar compound has been isolated from castoreum.⁸

The varying results obtained from analyses of castoreum by different researchers may be attributed to the age of the beaver and its environment at the time the secretion was collected. But most researchers agree that castoreum contains castorin, resin, benzoic acid and a volatile oil.⁹

Cerbelaud reported that Siberian castoreum contains up to 2% of castorin, which is soluble in alcohol and benzol. Canadian castoreum contains a maximum of 1% of castorin.¹⁰

E. S. Maurer wrote that the unctuous character of freshly exuded castoreum, as well as civet and other animal secretions, seemed "to be based on some kind of buttery albumen-lanolin complex rich in cholesterol." The same author's study of glyco-proteins and cholic acid revealed "many interesting linkages which help toward the understanding of the remarkable fixative value of these materials."¹¹

Compiled data from different sources on the chemical composition of castoreum is given by Leung and Foster as follows:¹²

1-2% volatile oil
0.33-2.5% castorin
up to 80% of an alcohol-soluble resinoid material

The same authors also mention cinnamic acid, phenol, o-ethyl phenol, p-propyl phenol, acetophenone derivatives, chavicol, betuligenol, cholesterol, cis-1,2-cyclohexadienol and 1.4% calcium phosphate, in addition to the previously listed components.

In a study of castoreum's nitrogen-containing compounds, Maurer and Ohloff¹³ reported 14 constituents that were identified for the first time. Besides castoramine (the only alkaloid previously isolated), seven constituents closely related to castoramine were found:

isocastoramine
desoxynupharidine
7-epi-desoxynupharidine
1-epi-desoxynupharidine
1-epi-,7-epi-desoxynupharidine
7-demethyl-desoxynupharidine

Also identified were:

5-(3-furyl)-8-methyl-octahydroindolizine (trace)
1,3,6,6-tetramethyl-5,6,7,8-tetrahydroisoquinolin-8-one
trimethyl pyrazine
tetramethyl pyrazine
5,6,7,8-tetrahydroquinoxaline
2-methyl-5,6,7,8-tetrahydroquinoxaline
2,3-dimethyl-5,6,7,8-tetrahydroquinoxaline
1,2,3,4,6,7,8,9-octahydrophenazine

Maurer and Ohloff state that, to their knowledge, 7-demethyl-desoxynupharidine is the first known nuphar-alkaloid with 14 carbon atoms.

Synthetic Compounds

Among perfume materials that come close to the animal castoreum odor tonality are dihydrocarveol, dihydrocarvyl acetate and birch tar oil.¹⁴

Castoreum synthetic (LG), produced in the 1930s, was considered the best imitation of the natural.¹⁵ Twenty years later, it was still described as "reproducing closely the animal, sharp, warm and persistent odor of natural castoreum."¹⁴

Here is an example of a simple conventional synthetic castoreum formula containing castoreum absolute:

Castoreum synthetic no. 1

150 Anisyl acetate
100 Bornyl acetate
75 Dimethyl hydroquinone
50 Cinnamyl acetate
50 Ethyl anisate
50 p-Cresol
40 Methyl salicylate
30 Bouleau (birch tar oil)
20 Methyl benzoate
15 Castoreum absolute
580

Here is a more complex conventional formula that contains

no natural castoreum. It was developed before the advent of dermatological considerations of perfume materials.

Castoreum synthetic no. 2

100	Styrax resinoid
40	Cinnamyl acetate
40	p-Cresyl acetate 10%
35	Peru balsam
30	Calamus 10%
15	Labdanum resinoid
15	Creosote 5%
15	Birch tar oil
15	Geranium
15	Bornyl acetate
15	Cedarwood
10	Guaiacol 10%
8	Phenyl propyl aldehyde
8	p-Methyl quinoline
8	Valeric acid 10%
6	Benzylidene acetone
5	Geraniol
5	Musk ambrette

385

In the 1970s, Boelens and Wobben¹⁶ found that the addition of o-hydroxy benzyl ethyl ether and/or 8-allyl-8-hydroxy tricyclo[5.2.1.0^{2,6}]decane to a synthetic castoreum resulted in a very natural castoreum odor (without using any natural castoreum). The synthetic castoreum formula was given as follows:

Mixture A¹⁶

738	Benzoid acid
50	Farnesol
20	Farnesyl acetate
10	Farnesyl isobutyrate
15	o-Cresol
5	p-Cresol
4	m-Cresol
6	Salicylic acid
2	Borneol
1	Eugenyl phenyl acetate
25	Ethyl benzoate
10	Methyl benzoate
6	Methyl phenyl carbinol
4	Acetophenone
2	Pentanoic acid
2	Butanoic acid

900

Experiments showed that the best and most natural castoreum odor resulted when the two aroma chemicals were used together, and in the proportions shown in the following mixture:

Mixture D¹⁶

900	Mixture A
85	o-Hydroxy benzyl ethyl ether
15	8-Allyl-8-hydroxy tricyclo[5.2.1.0 ^{2,6}]decane

1,000

One example¹⁶ shows the addition of Mixture D (20% in benzyl alcohol) to a men's cologne in the amount of 2.5%.

Pyrazines and other nitrogen-containing compounds mentioned previously, some of which may be commercially available, may be useful in developing synthetic castoreum compounds.

Presently, various castoreum substitutes are offered by different perfume companies.

Discoloration

Natural castoreum is at a disadvantage versus synthetic castoreum, because natural castoreum turns a reddish-brown color in alkali and aged alcoholic solutions.

Dermatological Aspects

Some of the perfume materials used previously in synthetic castoreum compounds have to be eliminated or be specially processed or used in limited amounts in accordance with RIFM recommendations. Among such are:

- benzylidene acetone—eliminated
- musk ambrette—eliminated
- Peru balsam—only distillates, limited to 0.4% in consumer products
- styrax resinoid—only extracts (or distillates), limited to 0.6% in consumer products

Applications

Castoreum has found application in both medicine and perfumery. In the fifth century BC, Hippocrates mentioned the medicinal uses of castoreum. Early Indians attributed curative powers to castoreum.¹⁷

In a 17th-century volume on medico-chemical applications of the beaver, castoreum is described as a proven remedy for earache and deafness, headache, sciatica, epilepsy and the pains of gout. Applied externally, it also was said to alleviate tumors of the liver. In addition, it induced sleep and, taken up the nose, helped to clear the brain (because of induced sneezing).¹⁸

The same source reports that castoreum also kills fleas and acts as an antidote for the sting of scorpions, spiders and tarantulas. It reportedly protects against pestilence. "The doctors of Ausbourg have introduced castoreum into 30 of the best drug compositions in the Pharmacopoeia," according to this source.¹⁸

In the 18th century, castoreum was recommended as a remedy for cerebral and nervous diseases, vertigo, stomach cramps and various gynecological problems.¹⁹

As late as the 19th century, castoreum was listed in Dunglison's Medical Dictionary (1874) as an anti-spasmodic drug.²⁰

In perfumery, castoreum is used mostly as a fixative, especially in oriental-type fragrances but also in Amber, Chypre, Cuir de Russie, Jockey Club and Peau d'Espagne fragrances, to cite a few older types. Furthermore, castoreum imparts a pungent, tart, animal note to fragrances and enhances woody odors.

Castoreum is also used in florals, such as carnation, mimosa and orchid, to mention but a few.

In the past, castoreum infusions were found to be suitable in cream, face powder and hair lotion perfumes.²¹

Castoreum resinoid was used in Peau d'Espagne fragrances for sachet powder and in toilet soap fragrances such as Chypre, Cuir de Russie and Opoponax. The soaps were colored, because castoreum resinoid produces a reddish discoloration.

Today, natural castoreum is available as absolute, resinoid, rectified and incolore. Natural and synthetic castoreums are used in today's newer oriental and semi-oriental, herbal and woody fragrance types for women and men. Besides fixing fragrances, castoreum imparts a special cachet to them, and it is likely to remain a valuable ingredient of future fragrances.

References

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