# Animal Notes in Perfumery

# **Civet and Civet Compounds**

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Only a few perfume materials of animal origin are used in perfumery. Among them are musk, ambergris, civet and castoreum.

Musk<sup>1</sup> and ambergris<sup>2,3</sup> were discussed previously in this magazine. Civet is the subject of this article.

The term *civet* (French *civette*, German Zibeth) is derived from the Arabic word zabad. The glandular secretion of the animal called civet cat has been used as perfume and medicine for centuries.

#### Origin

*Civettictis civetta*, a carnivorous animal of the Viverridae family, inhabits the tropical regions of Africa (particularly Ethiopia). *Viverra zibetha* is found in eastern and southern Asia. The animals spend most of the time burrowed beneath ground. They hunt at night. The adult civet cat is approximately two feet long, about 12 to 14 inches high, and has a long tail. Its fur is whitish gray with black spots.

In eastern and southern China, the main variety of civet cat is *Viverricula indica* Desmarest. It has a long, thin body and a narrow forehead. In the wild, the civet cats mainly hunt rats, frogs, lizards, birds, snails and fish. Since 1962, wild civet cats have been tamed, and more than 500 of these cats are in Hangzhou Zoological Garden in China. They breed twice yearly. They are fed fish, rice, cornmeal mush or internal organs of chicken.<sup>4</sup>

#### Yield and Mode of Production

Both the female and male civet cats have sacs under their tails, located near the genitalia of both sexes. A glandular secretion is obtained from these pouches. The commercial civet product is gathered primarily from male cats. In ancient times, civet was collected from rocks and trees on which it was deposited. Later, civet secretion was obtained from cats held in captivity, and kept in individual portable cages.

The secretion is removed from the sac with a hand-held scoop. The yield from each cat is about 20 to 30 grams per month.<sup>5</sup> It is reported that about 30 grams of civet secretion is collected from the Chinese adult civet cat annually. The cage temperature, noise and feeding influence the secretion yield.<sup>6</sup>

The quality of the civet secretion depends on the food fed to the cat and on the methods used to store the secretion (it oxidizes rapidly under poor storage conditions and loses its odor value).  $^7$ 

Using organoleptic evaluation, the quality of the secretion obtained from the walls of the cage seems better than that of the squeezed product.<sup>8</sup>

The color of the freshly removed civet is light yellow. It becomes dark brown on exposure to air. The color also depends on the cat's diet.<sup>9</sup> Civet secretions often are adulterated by substances such as potatoes, brilliantine, butter, bananas, beans, mango, flour and honey. Starch can be detected by a simple iodine test that turns the civet blue. To detect some fats, freezing tests are used, and such adulteration can be judged by the increased amount of the absolute. The Pasteur Institute in Addis Ababa uses the percentage of the absolute as a guideline. Finding more than 60% absolute is considered to indicate adulteration; more than 50% but under 60% is export Grade I; and between 40% and 50% is Grade II.<sup>10</sup>

In the earlier part of the 20th century, natural civet was available in form of alcoholic infusions. Later, civet absolute and civet resinoid were commercially available.

## **Civet Infusions**

The term *infusion* was originally applied to preparations obtained by immersing leaves, flowers or roots in boiling water. Musk, ambergris and civet infusions were prepared by infusing these perfume materials in, usually, cold alcohol 85-95%.

Here is an example of a civet infusion.<sup>11</sup>

#### Ingredients

1 liter	Alcohol 95%
50 grams	Civet
50 grams	Potassium hydroxide 36% or 38%
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#### Procedure

Civet and half of the potassium hydroxide are pounded with a pestle in a mortar until a homogeneous paste is obtained. Then a quarter liter of the alcohol is added to obtain a liquid mixture, which is decanted into a glass container. The remainder of the potassium hydroxide is added to the residue in the mortar and pounded with the pestle. Then half a liter of the alcohol is added, and the triturated liquid is transferred to the bottle. The remain-

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ing alcohol is used to wash the mortar and the pestle, after which it is added to the bottle. The hermetically closed bottle is then kept at room temperature in a cabinet. The container is shaken once a week. The infusion is aged for at least five or six months.

These infusions were usually prepared at 5%, but higher concentration infusions of 50% were also prepared.<sup>12</sup>

Another method of preparing infusions was to mix civet with three times its weight of pulverized silica and dissolve the mixture in 90-95% alcohol, the amount of alcohol depending on the desired strength of the infusion.

# **Civet Absolute**

Civet absolute is prepared by extracting the civet secretion in a volatile solvent, removing the insoluble matter by filtering, freezing out the dissolved fat and concentrating the solution in vacuum. The absolute is a viscous, dark brown liquid.<sup>13</sup> It is used mostly as a 3% alcoholic solution.

## **Chemical Composition**

In 1900, Waldbaum identified 3-methyl indole (skatole) in civet, and said that it possessed the fecal odor of natural civet.<sup>14</sup>

In 1912, Sack isolated from natural civet an odoriferous ketone, civetone ( $C_{17}H_{30}O$ ), present in civet from 2.5% to 3.5%. Civetol also occurs in civet.<sup>15</sup>

In the early 1920s, Ruzicka and collaborators found that civetone was an unsaturated monocyclic compound and established its structure. Hydrogenation of civetone resulted in dihydrocivetone.<sup>16</sup>

The synthesis of dihydrocivetone was achieved by two different methods. The first was reported by Ruzicka and collaborators in 1926, and the second by Ziegler et al. in 1933 and 1934.

Dihydrocivetone also occurs in the scent glands of the male and female Louisiana muskrat (*Ondatra zibethicus rivalicius*). It possesses a musk-like odor. Stevens and Erickson isolated dihydrocivetone from muskrat scent glands and reported their findings in 1942.<sup>17</sup>

Civetone was later synthesized by Hunsdiecker, who also indicated that the natural civetone was the cis form.<sup>18</sup>

In 1948, Stoll and collaborators reported the synthesis of natural civetone ( $\alpha$  isomer). The  $\beta$ -civetone possesses a trans configuration, but it can be converted into the natural  $\alpha$  isomer.<sup>19</sup>

In 1973, Van Drop and collaborators reported the following constituents in an African civet extraction:<sup>20</sup>

> cyclohexadecanone cycloheptadecanone 6-cis-cycloheptadecenone 9-cis-cycloheptadecenone (civetone) 9-cis-cyclononadecenone

In 1968, Ding and Fu published results of studies done in China on the volatile components in secretions from both the female and male civet cats.<sup>21</sup> The volatile components were separated by micro steam distillation-extraction. Using capillary gas chromatography and GC/MS techniques, the researchers found the following:

- 3 indoles in the basic fraction.
- $48 C_6 C_{20}$  saturated and unsaturated fatty acids in the acidic fraction.
- 14 C<sub>14</sub>-C<sub>19</sub> macrocyclic ketones in the neutral fraction.
- 1 macrocyclic lactone in the neutral fraction.

The indoles were:

indole skatole 1,3-dimethyl indole

The macrocyclic compounds were:

cyclotetradecanone cyclotetradecenone cyclopentadecanone 3-methyl-cyclopentadecanone (muscone) cyclopentadecenone cyclohexadecenone cycloheptadecenone 6-cis-cycloheptadecenone 9-cis-cycloheptadecenone (civetone) cyclooctadecenone cyclooctadecenone cyclononadecenone cyclononadecenone cyclononadecenone cyclopentadecenone It was established that civetone, cyclopentadecanone and cyclohexadecanone were the main constituents of Chinese civet. It was also noted that the saturated and unsaturated homologues of macrocyclic ketones from  $C_{14}$  to  $C_{19}$  occur in pairs. Muscone has been found only in the secretions of *Viverrazibetha* and the female Chinese civet cat.

#### Civet Compounds

In perfumes of the 19th century and the earlier 20th century, natural civet was used in the form of infusions. Later it was typically used as a 3% solution in alcohol or other solvents.

Here is an example of a civet extract:

Civet Extract No. 1 for Furs <sup>22</sup>		
Civet infusion 1%	250	
Musk infusion 1%	100	
Ambergris infusion 1%	50	
Vetiverol	5	
Musk ambrette	5	
Nerol	2	
Methylionone pure	5	
Rose Otto	5	
Ylang ylang	5	
Rhodinol	25	
Bergamot	10	
Jasmin absolute	2	
Rose absolute	5	
1 liter Alcohol 90%	qs	

Until more recent research work in the 1970s and 1980s revealed additional civet components, the musky-smoky odor of civetone or dihydrocivetone with an intermediary amber-musk odor, and the fecal odors of indole and skatole were considered the dominant notes of civet.

Civet has common odor points with musk, flowers such as orchids (which often contain large amounts of indole) and, to a lesser extent, jasmin and lilac (some types of which also are rich in indole).<sup>23</sup>

Indole is chemically 2,3-benzopyrrole. Indole can originate from animal as well as vegetable sources. The fecal odor of indole becomes floral upon dilution.

Skatole is chemically beta- or 3-methylindole. The name is derived from the Greek *skatos* or manure, which explains its fecal odor. Skatole is also present in vegetable sources: its fecal odor occurs in certain species of shrubs and trees.<sup>21</sup>

It is difficult to imitate the complex odor of natural civet. Before civetone was discovered and synthesized, absolute civet—diluted with solvents and adjusted with a few added aromatics—served as a less expensive version of natural civet. Here is an example.

# Civet Synthetic No. 37

Civet absolute	100
Musk ketone	35
Amyl salicylate	40
Solvent	275
	450

In other types, p-cresyl phenylacetate was used.

Attempts were also made to develop entirely synthetic civet compounds. They were based on indole, skatole and

Civettal (tetrahydro p-methylquinoline, a yellowish crystalline material having a smoky skatolic odor). Here is an example.

Civet Synthetic No.	17
Tetrahydro p-methylquinoline	100
Skatole	50
Indole	25
Phenylacetic acid	175
Musk ambrette	150
Myristic acid	<u>500</u>
	1.000

A more complex conventional formula is:

Civet Synthetic No.	6
Skatole 10%	130
Tetrahydro p-methylquinoline	60
Sandalwood E.I.	50
Butyric aldehyde	35
p-Methylquinoline	20
Butyl phenylacetate	20
Musk ambrette	20
Bouleau (birch tar oil) 10%	20
Ethyl amyl ketone 10%	10
Phenyl ethyl alcohol	10
Linalyl propionate	10
p-Cresyl phenylacetate	10
Phenylacetic acid	5
Solvent	<u>600</u>
	1 000

To obtain a closer likeness, Cerbelaud recommended that synthetic compounds be passed through the exhausted civet fat, which would add the natural fatty odor of civet, difficult to achieve by any other means.<sup>25</sup>

Another suggestion was to add to a base (made from castor oil and cocoa butter) myristic acid or alcohol and a proportional mixture of tetrahydro p-methylquinoline, indole, skatole, phenylacetic acid and p-toluidine. Further addition of a larger amount of p-tertiary butyl phenol will give a leather note. p-Cresyl valerianate and m-cresyl phenylacetate will contribute the "equinine hippurate" note (a strong undertone of the natural civet). From cinnamyl butyrate and p-cresyl octoate, "sour-tawny" top notes may be obtained.<sup>26</sup>

When civetone first became available, it was expensive and was included only in small amounts in civet compounds, as this simple formula illustrates:

Civet Synthetic No. 469<sup>27</sup>

Vanillin	150
Benzoin resinoid	660
Phenylacetic acid	150
Tetrahydro p-methylquinoline	20
Civetone 10% N	10
Ethyl methyl phenyl glycidate	
(aldehyde C-16)	<u>10</u>
-	1,000

Other components used in civet compounds include the following:

Modifiers

p-cresyl caprylate p-cresyl valerianate (traces) guaiacyl butyrate patchouli vetiver

Sweeteners

butyl phenylacetate isopropyl phenylacetic acid rosacetol (trichloromethyl phenyl carbinyl acetate) vanillin yara yara (β-naphthyl methyl ether)

Fixatives

synthetic amber compounds macrocyclic or other synthetic musk types

#### Incompatibility

Civet infusions prepared with silica did not present any incompatibility problems in fragrances. But civet infusions prepared with potassium hydroxide caused discoloration and modified the odor of extracts, especially if the extracts contained aldehydes or ketones.

The same can be said for synthetic civet compounds which contain indole or skatole.

Indole discolors when synthetic civet is used in perfume compounds containing methyl anthranilate, nitro musks, vanillin and other perfume materials prone to oxidation. Indole also changes or completely destroys the odors of ionone, methylionone or irone. Indole is incompatible with alkalies, and in the presence of acids, indole resinifies, discolors and unfavorably modifies the odor of perfume compounds.<sup>28</sup>

Skatole—even if considered somewhat more stable in alkalies—should not be used in perfume compounds for cream, soap or other cosmetic preparations on the alkali or acid side. Moreover, it should not be used in perfume extracts containing vanillin and higher aldehydes. Skatole is oxidized in an acid medium to acetyl aminobenzoic acid, which is odorless.<sup>29</sup>

#### **Dermatological Aspect**

Use of musk ambrette in conventional civet compounds has been eliminated according to IFRA's guidelines.

Today's civet substitutes, offered by many perfume houses, contain civet ketones and macrocyclic or other types of synthetic musks instead of the previously used nitro musks.

#### Application

Natural civet has been used in perfumery for centuries. The secretion has a strong, pungent, animal odor, but also a musky note. It is a good fixative, has good diffusion and brings mellowing and rounding-out effects to perfume compounds.

During the 10th to 13th centuries, Chinese merchants exchanged silk, brocades and weapons for civet from Africa.<sup>30</sup>

In the 15th century, a powder made of powdered egg shells, civet and flower waters was popular. A combination of lemon peel and civet was considered a room deodorant (used by way of fumigation) and also was used to perfume items such as garments and bed linens belonging to nobility. The same ingredients rolled into a ball were used, like modern sachets, in linen drawers.<sup>31</sup>

During the Renaissance, pomades and perfumed gloves were introduced from Italy to France and Spain. Civet was a favorite perfume for gloves because its strong scent disguised the leather odor.

During the second half of the 16th century, the most pungent scents, among them civet, were apparently preferred. One reason was probably the lack of proper sanitation.

Civet was also popular in England during the 16th to 17th centuries, and was still used by gentlemen in the 18th century.

Another application of civet in the 17th century was in pomanders, a ball-shaped mixture of aromatic materials. Such a mixture might include labdanum, Damask powder, cloves, mace, nutmeg, camphor, musk and civet. Usually, the finely powdered mixture was first anointed with civet and then rolled by hand.<sup>32</sup>

Many single floral and fantasy bouquets include a civet note. Until the early part of the 20th century, civet infusions were used, later yielding to natural and synthetic civet solutions.

Among the florals are carnation, gardenia, honeysuckle, jasmine, jonquil, lilac, magnolia, mimosa, narcissus, neroli, lily of the valley, rose, tuberose and violet.

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Among traditional and classical fantasy bouquets are Chanel No. 5, Chypre, Jockey Club, Cuir de Russie, Peau d'Espagne, Trèfle Incarnat, Parma Violet and various eau de cologne types. Civet is also included in amber perfumes.

A few examples of later fragrances are Anais Anais, Azzaro, Balestra, Cabochard, Lauren and Oleg Cassini. Of the men's fragrances, Kouros, Polor, Gucci and Quorum may be cited.

In the 1970s, civet tried to make a comeback as a fragrance for men, along with musk and ambergris. Of the three, only musk was successful.

Civet resinoid was used in small amounts as a fixative or to add nuances to toilet soap perfumes, such as musk, Cuir de Russie, fougère, jasmine and sandalwood.

Civet also was used in medicine and was viewed as an aphrodisiac.

In the 10th century, in Arabia, a distillate of civet was recommended for the treatment of tumors, epilepsy, rheumatism and heart condition.<sup>33</sup>

For centuries civet has been used in traditional drugs in China. A 16th century Compendium of Material Medica attributed medicinal properties to civet that were similar to those attributed to musk.<sup>34</sup>

In Ethiopia, civet is used by some natives for the relief of headaches and as a laxative.  $^{35}$ 

#### Conclusion

Civet is an important animal fixative in perfumery.

Traditionally, civet secretion was obtained commercially from wild male cats held in captivity. In the early 1960s, the Chinese succeeded in taming Chinese civet cats, breeding them in captivity and collecting the secretion.

In 1973, a furor arose when the Society for Animal Rights called for a boycott of Chanel No. 5 perfume to protest the use of civet obtained from animals supposedly treated cruelly. Investigations in Ethiopia by two academicians and a mammologist from the U.S. showed that the alleged torture of the civet cats could not be substantiated.<sup>36</sup>

Natural civet is available as absolute and is used mostly in 3% solutions in deluxe fragrances.

The synthesis of civetone and more recent discoveries of other macrocyclic ketones in civet secretion has provided the possibility of developing civet substitutes. Suppliers now offer various specialties whose odors are close to the odors of the natural product, though not always as complex and diffuse. Natural civet is being replaced to a great extent in perfumery by these specialties.

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