

out of Print

AMBERGRIS

Its nature and uses. - Ambergris, *ambra grisea*, or *ambra ambrosiaca*, is, as the name implies, a grey wax-like opaque substance, but a very dark-coloured viscid product is also met with in commerce. The latter variety is of an inferior quality and odour and is often subject to a considerable amount of adulteration. Ambergris is found in lumps up to 300 lbs. in weight, either floating in the tropic seas or cast upon the shore on the coasts of Madagascar, China, Japan, Sumatra, the Moluccas, and Coromandel. At various times small quantities have been found on the west coasts of Scotland and Ireland, but these have been of rare occurrence and have probably drifted long distances. The occasional appearance of lumps of ambergris on the sea shores has given rise to much Eastern tradition, and the material is used extensively as a perfume and in certain religious ceremonial rites. "La Parfumerie Moderne" (Dec. 1920), states that the origin of the ambergris is to be found in the cephaloped eledonia, the staple diet of the sperm whale. Cephaloped eledonia was used by the Romans as a perfume. Guttefosse has isolated ambergris from cephaloped eledonia moschata. Exposure of ambergris to the atmosphere and its immersion in sea water generally causes some surface oxidation to take place, producing a grey crust with a yellow interior, a freshly cut surface often showing a very beautiful speckled and streaked appearance, with concentric layers of dark and light colours. Pieces of ambergris are occasionally caught in the nets during fishing operations, and often contain the decayed remains of marine animals. Ambergris has a characteristic odour and striae, which are extremely difficult to counterfeit with any degree of success.

A morbid product of the sperm whale.- Ambergris is an organic substance formed in the bladder and the intestinal tract of the cachalot or sperm whale (Physeter macrocephalus). Though various theories have been propounded, its formation is still a matter of considerable speculation. It is generally considered to be an intestinal calculus or gall stone of the sperm whale of normal or accidental formation. Biologists have found that the formation of ambergris is due to acute and chronic biliary conditions in the whale, its accumulation being the direct outcome of a diseased state. Observations of whalers over a large number of years have shown that the largest quantities of ambergris are obtained from the whales caught in an emaciated condition. Under normal conditions the ambergris is excreted, but the sperm whale appears to be subject

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to a peculiar disease causing the ambergris to collect in the intestinal canal usually near the ventral aperture. It has been suggested that the formation of the ambergris is the result of imperfectly digested food much of which originates from the cephalopoda consumed by the whale. The presence of the undigested horny gills of the cuttlefish in ambergris is often claimed to indicate the genuineness of the product. Another theory proposed to account for the formation of ambergris is that the swallowing by the whale of indigestible horny fish materials sets up local intestinal irritation producing a secretion (Perfume and Essential Oil Record, 1911, Vol. 2, pp. 252-253).

Properties of genuine ambergris.- Genuine ambergris varies in colour from black to white, and when newly extracted is a soft mass possessing a highly disagreeable odour due to the presence of volatile and oxidizable organic sulphur compounds in a state of decomposition. These latter constituents are eliminated on exposure to the atmosphere, giving place to a pleasant musk-like odour, recalling that of benzoin, and the mass assumes a highly polished waxy surface. Microscopic examination of ambergris shows it to consist of a conglomeration of an acicular crystalline body. Ambergris varies in density from 0.780 to 0.980, Brande gives 0.780 to 0.896, and Pareura 0.908 to 0.920. It is insoluble in water, soluble in organic solvents, oils and alkalis. It is optically inactive. It can be kneaded between the fingers when it becomes a plastic mass emitting an agreeable and lingering odour. When warm and dry ambergris becomes electrified by friction.

The chemical analysis and the properties of a specimen of genuine ambergris taken from a sperm whale caught off the coast of New England in 1916 were examined by Lund (Tidskrift Kem. Farm. Terapi, 1917, Vol. 14, pp. 254-255). It was found to consist of 74 percent organic matter soluble in ether, 20 percent organic nitrogenous matter insoluble in ether and 6 percent inorganic matter consisting mainly of silica, alumina, and calcium carbonate. The ether-soluble portion was found to possess the following constants, M.P. 52° C., Refractive index N. 50-D 1.5028, Saponification value 24, Iodine value 78, Acetyl value 45, Free fatty acids 3.0 percent. Bruff (Tids. f. Kem. Farmaci Terapi, 1915, p. 125), and Schweiz (Apoth. Zeit., 1915, Vol. 53, p. 729), examined specimens of ambergris with the following results:

Spec. gravity.....	Up to 0.950
Saponification value.....	17.2 to 35.0
Ash.....	Traces
Melting point.....	Becomes ointment-like in appearance at 60° C., but melts at higher temperatures. At 100° C. it volatilizes as a white vapour.

A remarkable property of ambergris is that with bromine in carbon tetrachloride an octo-brom derivative of ambreine is produced $C_{23}H_{32}OBr_8$, a white solid. With chlorine, the ambergris is decomposed.

Chemical composition of the wax.- Ambergris consists mainly of the glycerides of highly complex fatty acids, with a small percentage of inorganic matter containing calcium phosphate and carbonate with traces of iron, alumina, silica, sodium and potassium chloride. Some investigators have established the presence of iodides in ambergris, this being due probably to particular specimens having been contaminated with seaweed. Ambergris contains 85 percent of fatty matter, generally regarded as ambreine. When ambergris is distilled in the presence of steam, 13 percent is volatile and consists of an oil of highly aromatic odour. Some authorities claim that ambergris contains up to 2.5

percent of benzoic acid, but recent investigations have failed to confirm this statement. On treating ambergris with phosphorus pentachloride, a white amorphous mass is produced consisting mainly of penta-chlorambreine $C_{23}H_{35}OCl_5$ (Riban, Comp. rend., 1912, Vol. 154, p. 1729).

The whole of the constituents of ambergris, being of a highly complicated character, have not yet been identified and isolated. The much prized aroma of ambergris is known to be due to the blending of a large number of glycerides and esters of the higher fatty acids, all present individually in minute amounts. The main chemical constituent of ambergris is ambreine, an unsaponifiable fat which crystallizes out from saturated alcoholic solutions of ambergris in the form of elongated needles. Ambreine was isolated by Pelletier and Caventon, who found it to be of alcoholiform character and somewhat related to the cholesterol series. Cholesterol itself is known to be a normal bile constituent of animal life, and the higher alcohols, such as cotic alcohol, are known to be present in the free state in marine cetacean oils. Pelletier gave the melting-point of the extracted substance ambreine as $37^{\circ} C.$, but Reban in 1912, on further examination, prepared the chlorine and the bromine derivatives, together with the acetic and benzoic compound ethers, and found that the substance called ambreine by Pelletier really consisted of a mixture of substances, one of which crystallized well at $82^{\circ} C.$, and boiled with decomposition at $182^{\circ} C.$ Pure ambreine $C_{23}H_{40}O$ has now been established as consisting of a white crystalline solid of M.P. $82^{\circ} C.$, which exhibits a remarkable superfusion for a considerable time even when seeded. Cole (Philippine Jour. Science, 1922, Vol. 20, pp. 105-111), states that true ambergris melts at $65^{\circ} C.$, and the ether-soluble portion ambreine at $82^{\circ}-85^{\circ} C.$

Uses in high-grade perfumery.- Ambergris was known from very early times, and was reputed to possess highly curative properties for certain diseases and ailments. Modern medical research has failed to substantiate any of the claims for its therapeutic value. The present high cost of ambergris is due entirely to the uncertainty of the supplies, to its use in perfumery as a remarkable "fixative", and to its highly pleasant and delicate musk-like odour. Ambergris is finding increased application as a perfume fixative, and is destined to become the base par excellence in first-class perfumes and cosmetics. As a perfume base it has great durability. Ambergris is not successfully used alone, but it possesses the remarkable property of attaching and blending minute quantities of other highly delicate and expensive essential oils and perfumery agents.

Deite gives the following method for the manufacture of tincture of ambergris:- Ten grammes of the grey variety of ambergris is cut into thin slices and then pulverized with an equal quantity of sugar of milk, the whole being then dissolved in a litre of spirits of wine. Deite claims that this alcoholic solution of ambergris passes through a process of "ageing" and should only be used after twelve months' storage, when it has considerably improved from a perfumery standpoint.

Identification and detection of adulteration:- The high market prices and the erratic supplies of genuine ambergris have both tended towards adulteration and the production of ambergris substitutes. The genuine product is slowly soluble in cold alcohol, takes a high polish, and should possess a low saponification value. The melting-point of the commercial product varies over a wide

range, and is of little value in detecting adulteration. Artificial ambergris which has appeared on some of the Continental markets consisted mainly of benzoin, frankincense, musk, and wax, with a variety of other substances to give body and appearance to the product. Other substitutes have consisted of perfumed vegetable fats, although bearing a marked resemblance to the genuine ambergris. Cole (Philippine Journ. Science, 1922, Vol. 20, pp. 105-110), states that a microscopic examination of the structure of a specimen of ambergris is more valuable in detecting adulteration than a determination of the physical and chemical constants. Cole found that genuine ambergris showed the presence of finely-divided and opaque-channelled pieces of chitinous material up to 0.1 mm. in thickness, originating from the inner shell of the cuttle fish. A cheap specimen of ambergris of Continental origin was found to contain ground fragments of moss and bark - to produce the speckled appearance, - and consisted principally of the latex of Artocarpus elastica. Other adulterations found inter-mixed with the genuine substance were tallow, gum, benzoin, and olibanum.

In examining a suspected specimen of ambergris, the following features should be noted: Colour and appearance with special reference to speckling, microscopic appearance and structure, nature of fracture, solubility in cold and hot alcohol, and the amount and composition of the inorganic residue. The newly exposed surface of genuine ambergris should exhibit a fine grain structure in the form of thin layers. A crude test for the heavy adulteration of ambergris is to pierce with a needle. The genuine product allows the needle on withdrawing to show a perfectly clear surface; when heavily adulterated, particles adhere to the needle. The Chinese test for genuine ambergris is to scrape on to the surface of a quantity of boiling tea, in which it should dissolve. Thorpe (Dictionary of Chemistry, Vol. 1, p. 85) states that genuine ambergris adheres like wax to the edge of a knife with which it is scraped, retains the impression made by the finger nails, is generally brittle, and takes a high polish.

Need for synthetic ambergris:- The present position of synthetic ambergris and the ambergris market is shown in the following extract taken from the perfumery report of Gehe and Co., Ltd., of Leipzig:

"It is but natural that the excessive prices demanded for this article should have had the effect of diminishing the demand, but however dear it may be there are always perfumers who will not do without this favourite article. If we consider, however, that by a suitable treatment of the compounds belonging to the aromatic acid series it has been possible to obtain a substitute for musk, it does not seem beyond the reach of possibility to manufacture synthetic ambergris also, the natural product consisting principally of a peculiar non-saponifiable fat. Such a discovery would have the result of putting an effectual limit to such exorbitant quotations as are now made, while the discoverer would be sure to reap a material reward from the constant demand of this article, which does not depend upon fashion."

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