AMBERGRIS: GOLD OF WHALES.

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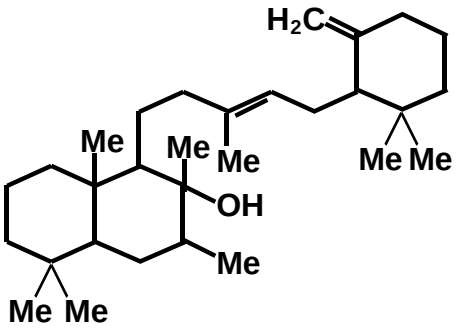
In the tales of Thousand and One Nights, Sindbad the Sailor shipwrecks on an island. He discovers a spring of ambergris, a badly smelling semi-solid that flows like wax into the sea where it is swallowed by giant fishes and vomited up again as fragrant lumps to be cast up on the shore. In Arabian society this material was named 'anbar' and from this word the European name ambergris was derived. The Arabs used ambergris as medicine for the treatment of heart and brain diseases and believed that raw ambergris emanated from springs near the sea.

The Greeks, influenced by early Arabian society, also believed that ambergris came from springs in or near the sea. They expressed an early burgundy lifestyle believing that it enhanced the effects of alcohol when smelled before drinking wine or when it was added to wine. In Chinese culture ambergris was referred to as the dragon's spittle perfume. It was thought to be the drooling of dragons while they were sleeping on the cliffs at of the seaside. In the Orient it is still used as an aphrodisiac and as a spice for food and wine. In Japanese society ambergris is named “kunsurano fuu”, literally translated “whale droppings".

These explanations are largely folkloric although the Japanese were not to far off. Ambergris is produced by the sperm whale (Physeter catodon) as an intestinal secretion product, frequently correlated to the sperm whale’s diet: cuttlefish. The beaks of cuttlefish are very sharp and may cause small wounds in the gastro-intestinal tract of the sperm whale. As a reaction to these small wounds ambrein is produced, a conversion product of cholesterol. This is not at all surprising as more and more publications in the scientific medical literature conclude that cholesterol plays a major role in wound healing in animals. The concentration of cholesterol in the affected area is statistically significantly higher compared to the non-affected area, and that may also be the case in the intestine of the sperm whale. The mechanism behind this process is still a mystery, but it becomes more and more evident that cholesterol isn’t such a bad guy at all.



AMBREIN

The structure of ambrein betrays its cholesterol origin. The biochemistry of ambrein in the scientific literature is, however, still largely on a speculative level; its no so easy to ask Moby Dick on a doctor’s consult. It has been suggested that ambergris may

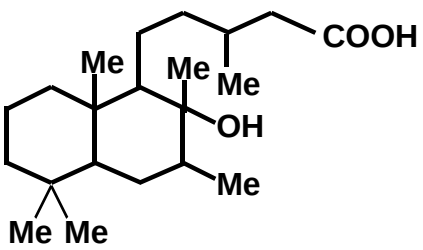
also be an indigestible residue of the cuttlefish that accumulates in the intestinal tract of the sperm whale. This explanation is, however, less likely, although the hard lumps of ambergris floating on the sea or washed ashore frequently contain the beaks of squids.

Next to ambrein two other steroids are present in significant amounts: epicoprostanol and coprostanone (Ruzicka). These are probably intermediates in the process of formation of ambrein. These products are “closer” to cholesterol, and they have outspoken fixative properties for flavours and fragrances. Being unavailable except for what is obtained from beachcombing it is difficult to do research on the reaction sequence of cholesterol to ambrein.

In the gut of the sperm whale ambergris is a black, medium viscous, off-smelling liquid, but on exposure to sunlight and oxygen from the air it is swiftly oxidised and hardens to a pleasantly smelling, wax-like solid, with a characteristic aromatic odour.
Sooner or later it ends up on the beaches of East Africa and on the western coasts of Middle-American countries as lumps of a pellucid, wax-like solid. The ambergris lumps that are found on the beaches sometimes may be huge, up to some 100 kg. The character finding such a lump would be able to retire immediately.

For a long time Zanzibar was the trading centre for ambergris. It used to be reserved for the rich and famous, including kings and nobleman, in times when these were still considered to be superior to the people who paid with hard and tedious labour for their status. Since time memorial ambergris has been used as a fixative for fragrances and flavours. It has the remarkable and unique property of being able to massively reenforce odorous products to last much longer than they would do otherwise. It is claimed that a single drop of tincture of ambergris applied to a piece of paper and placed in a book will still remain fragrant after many years and once touched again, the fingers will smell after ambrein even after several days and several washings.

Ambrein was first isolated by Pelletier & Carentou in 1820. Because of the significance of ambrein for the fragrance and flavour industry the demand has been high. Whaling is now, fortunately, banned and there is a strict prohibition on the trading of ambergris. Consequently there has been an intensive search for alternatives for ambergris. It is possible to produce ambrein synthetically, but the costs are out of perspective. The so-called labdanoid terpenoids, found widespread in nature in all kinds of plants, animals and micro-organisms, are acceptable alternatives. The starting products are resinous acids, in particular labdanolic acid.



LABDANOLIC ACID

Close family members of labdanolic acid are abietic acid, agathic acid and cativic acid, that are obtained by “milking” pine-trees. Labdanolic acid can be considered as a degradation product of ambrein, after modification of the side chain. A similar set

of oxidation reactions occur with the exudates of pine-trees: abietic acid, as it comes to the market, does not occur naturally but is formed from labile precursors upon exudation. The fixative properties of abietic acid are not to be denied (and used in hair care applications), although it does not have any fragrancing properties and will be sticky on the skin.

The decaline structure that is found in labdanolic acid is also found in ambrox (ambroxide), an oxidation product of ambrein with 4 chiral carbon atoms. Ambrox contains a tetrahydrofuran ring, and has a scent that compares to ambrein. Bee balm (INCI: Monarda didyma) is a source for labdanum extract, and comes relatively close to the odour perception of ambrein, although the fixative power is totally incomparable. Next to bee balm also other plants produce ambrein-like products such as labdanum (INCI: Cistus Ladaniferus), that is used as an alternative to ambrein, but also here the fixative properties are not so outspoken as with ambergris.

It is therefore worthwhile to consider the fixative properties of cholesterol. After all, part of the properties of ambergris must be related to cholesterol, as ambergris contains 20-60% of it. It is therefore not surprising that fragrance preparations containing cholesterol show a greatly improved fragrance retention.

In a way, this could be identified as a controlled release mechanism of the fragrance. Cholesterol behaves as a kind of gatekeeper allowing molecules to leave the skin to the outside world, reaching the olfactory organ of those sitting opposite to you, simultaneously disabling transdermal transport. An applied fragrance must be noticeable present but never be dominant and stay always on the background. A good fixative is important and characteristic for the better perfumes. It enables to reach that goal and continue the fragrance to be present for a prolonged period of time.

Some time ago we discussed the (cosmetic) chemistry of cholesterol in more detail with you, and here's another example of the versatility of this unique product. Those of you working with cholesterol in skin care preparations are very well aware, that the amount of fragrance needed when cholesterol is in the recipe can be reduced with at least 50% to get the same olfactory result. As fragrances frequently cause problems relative to emulsion stability, this can be seen as an extra bonus of using cholesterol. An absolutely exciting piece of cosmetic chemistry !