

CHAPTER 11

CETINE¹

§ 1. COMPOSITION

510.

	BY WEIGHT		BY VOLUME ²
Oxygen.....	5.478	100	1.00
Carbon.....	81.660	1490.7	19.48
Hydrogen.....	12.862	234.8	37.70

§ 2. PHYSICAL PROPERTIES

511. It melts at 49°C. On cooling it sets as a colorless, glossy, lamellate mass. At a temperature of around 360°C, it volatilizes without decomposition. It has a weak odor and is tasteless.

§ 3 CHEMICAL PROPERTIES THAT ARE
OBSERVED WITHOUT THE SPERMACETI BEING ALTERED

512. It is insoluble in water.

513. 100 parts of boiling alcohol with a density of 0.821 (g/mL)³ dissolve 2.5 parts of spermaceti. On cooling, the solution deposits a large part of the spermaceti as glossy, lamellar crystals with a pearly sheen.

514. Spermaceti exerts no effect whatsoever on litmus or hematin.

§ 4. CHEMICAL PROPERTIES THAT ARE
OBSERVED WHEN THE SPERMACETI IS ALTERED

Effect of
potassium
hydroxide on
spermaceti

515. When potassium hydroxide reacted with spermaceti at a temperature of 50 to 90°C, it converted it into cetyl alcohol and palmitic and stearic acid. (For a detailed description of the procedure, see § 2, Chapter 2, Book III.)

Effect of a
solution of
potassium
hydroxide and
potassium
palmitate on
spermaceti

516. Take 11 g of palmitic acid melting at 54°C and 7 g of spermaceti melting at 48°C. Put these in a round bottomed glass flask with a capacity of 13 dL and add 16 g of water and 18 g of pure potassium hydroxide and heat. The material forms a gelatinous magma. Pour 100 g

of water over the magma and boil for half an hour. Allow the material to macerate for two days and then heat and allow to react for two hours. The liquid does not become transparent. Add 300 g of water and boil for several minutes. Immerse a thermometer in the flask and as it cools, observe the phenomena I am going to describe.

At 100°C, the liquid is milky but no flakes are formed. At 66°C, it starts to become noticeably clearer and semi-transparent flakes become visible in the interior. At 60°C, it is so clear that a book with letters in small print positioned under the flask can be easily read. On cooling, the liquid retains its clarity until 56°C but then gradually starts to lose it. At 54°C, reading is not as easy as at 56°C. At 52°C it is difficult and at 50°C it is totally impossible: at this point, all that could be distinguished was the black of the letters and the white of the paper. Afterwards, white flakes are formed in the zones that have cooled the most and at 46°C, the white liquid is so viscous that it seems to form a pearly gel. At 45°C, it is totally opaque. Finally, the zones that cool first lose their viscosity and what is most remarkable is that if the liquid is left for several days, it forms a solid mass floating in a totally transparent liquid, just as is the case with blood.

517. In the experiment which I have just described, not all the spermaceti had undergone the reaction that can occur when it is exposed to potassium hydroxide because the ratio of the weight of acid fatty material to the weight of non-acid fatty material was 474 : 526 instead of 60 : 40⁴, which is the ratio I have found for the products when spermaceti was treated directly with potassium hydroxide .

518. I will make some remarks concerning the above results:

1. It is not necessary for all spermaceti that is brought into contact with the potassium hydroxide and the potassium palmitate to be saponified to observe the phenomena I described (516) and I can add that they also appeared in an experiment in which the spermaceti gave 37.87 parts of acid fatty material and 62.13 parts of non-acid fatty material[†]. However, in this experiment the liquid was only transparent from 59°C to about 57°C whereas in the first experiment it was from 60°C to 56°C.

2. The presence of the potassium palmitate greatly facilitates the action of the caustic potash on the spermaceti since in the experiment described in (516), the weight of the acidified spermaceti was 3.095 g, whereas in a comparative experiment without the potassium palmitate

^{*} When treating the non-acid fatty material once more with potassium hydroxide, I acidified part of this. When I combined the acid formed in this experiment with that formed previously, I found a ratio of 59.9 : 40.1; the non-acid fatty material was pure cetyl alcohol.

[†] The spermaceti used melted at 44°C and the palmitic acid originating from beef tallow had a melting point of 57°C and contained stearic acid.

but otherwise under absolutely the same circumstances, an amount of 7 g of spermaceti with a melting point of 48°C was allowed to react with 11 g of aqueous caustic potash, and the weight of the acidified spermaceti was found to be only 576 mg. If this result can be generalized, it is clear that the presence of a soap greatly favors the saponification of a fatty substance that is in contact with an alkali. It is likely that this influence stems from the ability that soap has to disperse the fatty matter that has not yet been saponified and to trigger the beginning of its dissolution. This observation will be useful to the art of soap-making.

3. The phenomenon of transparency that the liquor (516) shows over a temperature range that covers barely 6°C is remarkable in that it provides hope that the cause of several phenomena that are observed in liquids in living animals and that are generally regarded as independent of physical and chemical forces, will eventually be discovered to be governed by these forces after all.

Effect of heat
and air

519. When 5 g of spermaceti were heated in a retort, the material melted. The melt released a vapor that condensed as a yellow liquid in a flask attached to the retort. After the distillation, the liquid set in lamellar crystals that weighed about 4.5 g and melted at 23.5°C. Subsequently, a brown material was produced that only differed from the previous one by its color; it weighed 0.2 g. In addition, an aqueous acid and an empyreumatic oil were produced. The carbon weighed 50 mg.

520. When spermaceti is heated sufficiently in the presence of air, it burns like wax.

Effect of
sulfuric acid of
60 degrees in
the presence of
air

521. When 0.2 g of spermaceti in small pieces was put into a glass tube with an internal diameter of 10 mm together with 2 g of sulfuric acid at a temperature of 27°C, it gradually dissolved. After two hours, the dissolution was complete. The resulting liquid is very slightly citrine-colored and viscous; it releases a slight odor of sulfur dioxide. Twenty-four hours later, the liquid has divided into two layers: the upper layer is about 2/7 of the total volume. It is orange yellow whereas the bottom layer is yellow. After a week, the first layer is dark reddish brown except for the surface that is in contact with air, which is bluish. It should also be noted that this surface layer is in the form of a solid film, underneath which there is a liquid. The gas in the tube comprises an amount of sulfur dioxide that can be easily detected by the sense of smell and litmus paper. By continuously exposing the materials to a temperature of 100°C, the first layer is gradually converted into carbon and there is a noticeable, effervescence-free evolution of sulfur dioxide which I have the impression is accompanied by a little hydrogen sulfide. Above 100°C, there is a lively effervescence and the spermaceti is reduced to carbon.

522. When 2 g of spermaceti are heated with 200 g of aqueous nitric acid reading 32 degrees on a hydrometer, they require a much longer period of time than stearic acid to dissolve completely. By following the procedure in (46), a residue weighing 1.82 g is obtained. It is colorless, viscous and partially crystallized. It is separated into an *aqueous extract A* and an *alcoholic extract B*. Effect of nitric acid
523. It yields *acid crystals* and a mother liquor that is slightly colored, not at all astringent and does not form a precipitate with limewater. A. Aqueous extract
524. These are no different from the acid crystals prepared from stearic acid (48). Acid crystals
525. After evaporation to dryness, it weighs 0.300 g. It looks crystalline but as soon as it is mixed with water, it looks like an oil. When this oil is dissolved in alcohol, the addition of water results in an oil and an aqueous liquid. B. Alcoholic extract
526. It is similar to the oil obtained with stearic acid; it does not color dry litmus paper red but colors the wet paper. It is soluble in aqueous potassium carbonate and forms insoluble compounds with barium and calcium oxides. Oil
527. It contains the same substances as extract A. Aqueous liquid

§ 5. PREPARATION

528. (See Book III, Chapter 2, paragraph 1.)

§ 6. HISTORY AND NOMENCLATURE

529. In the trade, spermaceti has been known for very many years under this name. Fourcroy⁵ confused it with cholesterol and the fatty substance in cadavers that have been buried in the earth. I made a distinction between those two substances in 1814 and consequently I proposed the name of *cétine*, derived from κήτος, "whale", to describe the *Sperma ceti*.

¹ The substance for which the author introduced the word *cétine*, is now called spermaceti, a white waxy substance produced by the sperm whale, formerly used in candles and ointments. It is present in a rounded organ in the head where it focuses acoustic signals and aids in the control of buoyancy. Its name stems from the belief that it was whale spawn: σπέρμα (seed, sperm) and κήτος (large marine animal), from which *cétine* has also been derived.

² Spermaceti is a wax, an ester of a fatty alcohol and a fatty acid. According to Table 3.240 in *The Lipid Handbook*, 2nd edition (Eds. F.R. Gunstone, J.L. Harwood and F.B. Padley, Chapman & Hall, London, UK, 1994), the average carbon number of spermaceti can be calculated to equal 33.1. This means that 1 oxygen atom should correspond to 16.5 carbon atoms, which means that the 19.48 could be an overestimate. On the other hand, if the medium-chain, di-unsaturated wax esters were to be underrepresented in the sample concerned, the average carbon number would increase but not to a value of 19.48.

Table 3.241 (*loc. cit.*) gives the compositions of the fatty acids and alcohols in spermaceti and these show large contents of monounsaturated moieties. Accordingly, the average number of hydrogen atoms should be around 64; this means that the hydrogen to carbon ratio given by the author (1.9353) is close to the value of 1.9394 that can be calculated on the basis of the data in Table 3.241.

³ This corresponds to 90.7 % (w/w).

⁴ Table 3.241 (*loc. cit.*) also shows that the average chain length of the alcohols is almost the same as the average chain length of the fatty acids. So the average relative molecular mass of the alcohols can be estimated to be 247 whereas for the acids, this value is 263. Their ratio is therefore 484 : 516 rather than 474 : 526, let alone 600 : 400. Too high a value of the non-acidic material may indicate incomplete saponification.

⁵ Antoine-François de Fourcroy (1755-1809) was a pupil of Lavoisier but apparently did not try to save his master from the guillotine. In 1803, when Chevreul went to the Museum of Natural History in Paris to study chemistry under Vauquelin, the latter was assistant to Fourcroy, famous author of *Système des Connaissances Chimique*, a ten-volume work published between 1782 and 1800. According to Costa, Chevreul did not like Fourcroy.