CHAPTER 2

PREPARATION AND SAPONIFICATION OF SPERMACETI

§ 1. PREPARATION OF SPERMACETI

690. The spermaceti I examined was separated as follows from a yellow colored oil which commercial spermaceti always contains.

691. An amount of 50 g of spermaceti with a melting point of 44°C was comminuted without heating in 50 g alcohol with a density of 0.816[1] (g/mL). The materials were left to stand at an ambient temperature of 18 to 20°C. After twenty-four hours, the alcohol was decanted onto a filter. The undissolved residue was treated with 100 g of boiling alcohol in a round-bottomed flask in which the material was left to cool. It was then filtered. The deposit that had precipitated from the alcohol during cooling and the material that had not been dissolved were treated with boiling alcohol until the washing liquid left hardly any oily material after cooling, filtering and evaporation. The spermaceti thus prepared[2] had a melting point of 49°C.

692. This oily material was obtained by slow evaporation on a water bath of the alcohol used to macerate the commercial spermaceti and the alcohol used for the first two washings with boiling alcohol. The evaporation residue started to congeal at 32°C; at 23°C it showed many spermaceti crystals in a yellow oil. The two substances were separated by filtration.

Comments on this oil

693. It was yellow, smelled like commercial spermaceti and had no effect on colored reagents[3]. At 18°C, it was still fluid. Its solubility in alcohol with a density of 0.821 (g/mL) was markedly higher than that of spermaceti with a melting point of 49°C. It was very difficult to saponify with caustic potash but nevertheless, I succeeded in converting it into palmitic acid, oleic acid and a fatty, non-acidic material with a melting point of about 20°C that seemed to me to be akin to cetyl alcohol.

694. The small amount of oil extracted from the spermaceti did not allow me to carry out a sufficiently exact examination for me to assign it a definite place in the classification of the oils and fats, but all the evidence we have points to the likelihood that it belongs to the fourth genus. It would be interesting to know if the relationship between this oil and spermaceti[4] is the same as that between olein and the stearins.

695. The oil about which I am talking lowers the melting point of the spermaceti since the commercial product melts at 44°C; it also increases its solubility in alcohol with a density of 0.821 (g/mL) since 100 parts of this boiling liquid dissolved 2.5 parts of the pure spermaceti as against 3.5 parts of the commercial product. It is clear that the yellowish color and the unpleasant smell of the latter stem from compounds that are foreign to spermaceti and even to this oil, since I have obtained spermaceti that was perfectly colorless and almost odorless. I have also observed the presence of an oil that was colorless and had only a very slight odor. I don't know to what extent oxygen from the air and light could have an effect on commercial spermaceti[5].

§ 2. ANALYSIS OF THE SAPONIFICATION PRODUCTS OF SPERMACETI AND THE PREPARATION OF CETYL ALCOHOL

696. The saponification of spermaceti can be achieved very satisfactorily by placing 100 parts of spermaceti in a round-bottomed flask with 100 parts of potassium hydroxide[6] dissolved in 200 parts of water and allowing the materials to digest for several days at a temperature between 50 and 90°C. The flask must be shaken from time to time. I first thought that the saponification of spermaceti required a temperature in excess of 100°C and for this reason, I carried it out in my distillative autoclave[7]. However, since then I have ascertained that it is also possible to operate at lower temperatures.

697. Water is added to the soapy mass and an excess of tartaric acid or phosphoric acid is poured over it; it is heated sufficiently for the fatty matter to melt and long enough for it to collect on the surface of the liquid. On cooling, 1. *an aqueous liquid*; and 2. *a fatty material* are obtained.

Aqueous liquid

698. By evaporating the aqueous liquid together with the washing liquors of the fatty material, a residue results that is treated with alcohol with a density of 0.800[8] (g/mL). When the extract is gently evaporated, it only leaves 0.90 parts of a syrupy liquid which does not taste at all sweet and which consists of water and a very small amount of colored organic matter.

Fatty material

699. It weighs 101.6[9] parts. It has a very light canary yellow color. It starts to congeal at 45°C but it is only between 44 and 43°C that it becomes completely solid. It remains soft until 39°C[10]. When allowed to congeal from the melt floating on water, the temperature at which it congeals is 44.5 to 43.5°C. If it is cooled slowly, it displays a lamellar and shiny consistency. 100 parts of alcohol with a density of 0.817[11] (g/mL) dissolve 115 parts of fatty matter without boiling. The solution stays

clear for several hours but after twenty-four hours, it has deposited very small shiny needles. It turns litmus strongly red and the red liquid turns blue on the addition of water.

700. This fatty material consists of *cetyl alcohol* and *palmitic and oleic acid*. Analyzing this material is very simple. It is placed in a dish with baryta water and heated under constant agitation to make sure that the acids are completely neutralized. The excess of baryta water is then removed with boiling distilled water. When the material has become completely dry, it is treated with cold anhydrous alcohol which dissolves the cetyl alcohol together with small amounts of barium palmitate and barium oleate. By evaporating the alcohol and redissolving the residue in a small amount of highly concentrated alcohol or ether, the cetyl alcohol dissolves and in this way it can be separated from the barium soaps that dissolved at the same time as the cetyl alcohol. These soaps are combined with the soaps that did not dissolve in the alcohol and they are acidulated by hydrochloric acid to obtain free *palmitic and oleic acid.* The cetyl alcohol is then obtained by evaporating the alcohol or ether. If the cetyl alcohol still contains barium soaps, it must be treated with cold alcohol or ether.

701. 101.6 parts of fatty material obtained by saponifying 100 parts of spermaceti consist of:

Free palmitic and oleic acids, melting point 45°C…	60.96[12]
Cetyl alcohol……..	40.64
	101.60

Investigation of the acids

702. They consist of:

Acid anhydrides……..……	96.35
Water…….	3.65[13]

as can be ascertained by treating the free acids with lead oxide.

703. They are completely dissolved in boiling aqueous potash. When the soap is left to cool, it deposits *pearly potassium bipalmitate*. The liquid that is separated from the deposit deposits another batch of *potassium bipalmitate*[14] on cooling, after it has been concentrated and the excess of alkali neutralized by tartaric acid. Finally, by again filtering the liquid and subjecting it to the same treatment as before until it no longer deposits any or hardly any bipalmitate, a solution of potassium *oleate* is obtained.

Palmitic acid

704. The *potassium bipalmitate* in the soap from spermaceti consists of:

Palmitic acid anhydride……...……	100
Potassium oxide……	8.9

705. The palmitic acid in the spermaceti melts at 55 to 56°C. It crystallizes in small, radiating needles. It has neither taste nor color. At 60°C, it is completely miscible with alcohol with a density of 0.820 (g/mL)[15]. The solution turns litmus strongly red and the liquor becomes blue on the addition of water.

706. When the palmitic acid in the spermaceti is combined with baryta water, strontium hydroxide or lead oxide, it gives soaps consisting of[16]:

Palmitic acid……..	100
Barium oxide……	27.8
Palmitic acid……..	100
Strontium oxide……	20.26
Palmitic acid……..	100
Lead oxide……	85

707. I treated the potassium palmitate with alcohol to see if I could isolate palmitic acid with a melting point of 60°C. I therefore subjected the same sample of salt to five successive treatments and I obtained: 1. a salt sample containing an acid that melted at 45.5°C; 2. a salt sample containing an acid that melted at 56.75°C. When this sample was subjected to a further six successive treatments, it finally yielded: 1. an acid melting at 55°C; 2. an acid melting at 50°C. From this I conclude that it is palmitic acid rather than stearic acid that is released by the saponification of spermaceti.

Oleic acid

708. I did not have enough of this acid at my disposal to be able to obtain it absolutely free from palmitic acid. It was light yellow in color, liquid at 18°C, and miscible in all proportions with alcohol with a density of 0.821 (g/mL) at a temperature of 25°C.

709. The barium and strontium oleates had the following composition[17]:

Acid anhydride…….……	100
Barium oxide…….	31.01
Acid anhydride……..	100
Strontium oxide……	22.44

[1] This density corresponds to 92.5 % by weight.

[2] Some spermaceti apparently dissolves in boiling alcohol since cooling the solution leads to the formation of a precipitate. Since everything is not dissolved, the sample with the melting point of 49°C consists of recrystallized spermaceti plus material that

never dissolved. It would have been better to use more boiling alcohol, filter the alcoholic solution while still hot, allow it to cool and then collect the deposit, wash it to remove oil adhering to the crystals and finally dry it.

[3] The author refers regularly to 'colored reagents'. He means indicators like litmus and hematin.

[4] 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), more than 70% of the acids and about 60% of the alcohols in spermaceti are monounsaturated. Accordingly, more than 40% of the wax esters will have two double bonds and thus a relatively low melting point. However, some oily components may already have been discarded when the commercial spermaceti was prepared, making this product a kind of stearin.

[5] Apparently, it was already known that oxygen and light can accelerate the development of rancidity in oils.

[6] If this is indeed potassium hydroxide, it is present in a large excess. Given the average molecular formula for spermaceti of $C_{33}H_{64}O_2$, this allows an average relative molecular mass to be calculated as 492; this is high in comparison with the relative molecular mass of potassium hydroxide of 57.

[7] According to the *Dictionnaire des Sciences Naturelles* (Ed. Frédéric Georges Cuvier, Volume 13, page 233, 1819), this distillative autoclave was developed by Chevreul on the basis of the "marmite de Papin", a kind of pressure cooker. Papin used this cooker to soften bones and extract their nutritious components.

The autoclave described comprises a silver lining inside a copper vessel so that the autoclave can handle corrosive compounds, a conical valve that is pressed against its seat by a spiral spring, the tension of which can be adjusted so that the operating pressure of the autoclave can be set, a beam scale allowing the pressure inside the autoclave to be estimated, and means to condense vapors emerging from the vessel through the conical valve. Chevreul developed this piece of equipment when treating cork with all kinds of solvents under widely different conditions. He provided a more detailed description in *Annales de Chimie*, **96,** page 141.

[8] This is close to absolute alcohol.

[9] So its weight has increased on saponification and subsequent acidulation. If we assume an average molecular mass of 492 for spermaceti, hydrolysis should raise this to 510. So in theory, 100 parts of spermaceti could yield 103.7 parts of fatty matter.

[10] These observations seem to be somewhat contradictory. Presumably, the author saw that on cooling below 43°C, the material had set into a solid mass, which at 39°C was still soft to the touch.

[11] Alcohol with a density of 0.817 (g/mL) contains 92.1% ethanol by weight.

[12] 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, also provides the compositions of the fatty acids and the alcohols present in spermaceti. The average chain length of the alcohols is a bit larger than that of the fatty acids but since the free acids contain two oxygen atoms whereas the alcohols contain only one oxygen atom, the average relative molecular masses must be about the same (250 à 260). This is not reflected in this table, which shows much more acid than alcohol.

[13] Assuming an average relative molecular mass for the acids of 255, the amount of water should equal: (100 : 2 x 255) x 18 = 3.53.

[14] Amongst the saturated fatty acids in spermaceti, palmitic acid accounts for only 18%. Myristic acid (C14:0) accounts for 50%, lauric acid (C12:0) for 27% and stearic acid (C18:0) for some 5%. This leads to an average carbon number of 14 and an average relative molecular mass of 228 for the free acid. If it is then assumed that the *bipalmitate* consists of one molecule of free acid and one molecule of potassium soap, 100 parts of free acid would correspond to 8.55 parts of elemental potassium and to 10.31 parts of potassium oxide. If the acid were expressed as 'dry' acid, 100 parts of this dry acid would correspond to 8.9 parts of elemental potassium and to 10.73 parts of potassium oxide. Accordingly, the 'potasse' in the table has been translated as 'potassium' and not as 'potassium oxide.

[15] This alcohol contains 91.0% ethanol by weight or 94.0% by volume.

[16] The values in this table don't make sense since the relative molecular masses of the palmitic acid calculated on the basis of the values in the table are: 550 for barium, 508 for strontium and 262 for lead. Assuming an average carbon chain length of 14, a value of 440 would have been expected.

[17] These data again allow the relative molecular mass of the 'dry' oleic acid to be calculated. Again, there is some discrepancy between the data since for barium, they lead to a value of 493, whereas for strontium the value is 459. With an average chain length of the unsaturated fatty acids of 17.2, the average relative molecular mass of the free acid would be some 271 and that of the dry acid would be 534, a figure that is rather different from those arrived at from the experimental data.