CHAPTER 3

EXAMINATION OF SEVERAL CETACEAN[1] OILS

SECTION 1

EXAMINATION OF THE OIL OF THE HARBOR PORPOISE *(DELPHINUS PHOCOENA)*

§ 1. PREPARATION

869. Put the porpoise fat in water and heat on a water bath. The oil that collects in the upper part of the vessel is withdrawn with a pipette. The fat is then placed on a sloping surface and pressed for several days. A large amount of oil oozes out and this is combined with the oil from the vessel.

§ 2. PROPERTIES OF THE OIL

870. The oil that I examined had the following properties.

871. It was colored slightly yellow and smelled like fresh sardines. It had a density of 0.937 (g/mL) at 16°C.

872. It did not turn litmus red. When exposed to air and light, it lost its sardine aroma. Its color first became more intense but later disappeared almost entirely. At the same time, it developed a noticeable acidity and an aroma that showed some similarity with that of certain seed oils.

873. An amount of 5 g of boiling alcohol with a density of 0.821[2] (g/mL) dissolved 1 g of oil. The solution became cloudy as soon as it was removed from the fire. After the addition of 4 g of oil, the solution became more stable and it seemed to me that it could be mixed with the oil in all proportions[3].

874. 100 parts of oil were heated with 60 parts of potassium hydroxide dissolved in 100 parts of water. During saponification, a leathery smell evolved. When the soap was diluted with warm water, it dissolved completely. The addition of a solution of tartaric acid yielded an *aqueous liquid* and an *acidulated soapstock*[4] from which I obtained:

A.	A volatile, acid product having an odor of fish, leather and isovaleric acid; when this product was neutralized by barium hydroxide, it gave dry isovalerate……….	16.00
B.	Pure glycerin………………………………….	14.00
C.	Free fatty acids with a leathery odor………	82.20

875. When the acidulated soapstock was allowed to react with aqueous potash, the mixture separated into beautiful potassium bipalmitate[5] and a colored oleate. The biplamitate yielded a beautifully white acid, crystallized in flat needles that melted at 56°C.

§ 3. ANALYSIS OF THE OIL WITH ALCOHOL AND PREPARATION OF PHOCENIN

876. 200 g of oil was added to 180 g of alcohol with a density of 0.797[6] (g/mL). Everything dissolved after gentle heating. After twenty-four hours, the alcohol floating on the oil was decanted and then distilled. The residue is *oil no. 1*. More alcohol was mixed with this oily residue and this yielded *oil no. 2,* which had been dissolved in the alcohol, and *oil no. 3* which is the extraction residue.

The aqueous liquids from which the oils had been separated contained an *orangey coloring principle*, some *isovaleric acid* and a *principle that smelled like fish* (895).

877 OIL No. 1	OIL No. 2	OIL No. 3
It was acid; its density at 16°C was 0.931 (g/mL). When 100 parts of this oil were treated with milk of magnesium carbonate, 1.61 parts of magnesium isovalerate mixed with an oily, yellow, bitter material were released into the water. When the oil was separated from the magnesia, it weighed 96.13 parts. It was not acid and left barely 1 cm of ashes. On saponification, 100 parts of neutral oil yielded:	*Idem.* Analogous result except that there was less magnesium isovalerate and it was less colored. 100 parts of neutral oil yielded on saponification:	It was only very slightly acid; its density was 0.926 (g/mL). 100 parts of saponified oil released an odor of leather; the oil became brown and yielded:
A. Isovaleric acid corresponding to 27.71% of dry barium isovalerate.	*A.* Isovaleric acid corresponding to 26.67 parts of dry barium isovalerate.	*A.* Isovaleric acid corresponding to 12.92% of dry barium isovalerate.
B. 14.59 parts of colored, slightly bitter glycerin	*B.* 14.40 parts of brown, slightly bitter glycerin with almost no fishy odor	*B.* 12%of glycerin with a sweetish and very slightly bitter taste.
C. 79 parts of constituent fatty acids: palmitic acid and oleic acid.	*C.* 78.37% of constituent fatty acids; *idem*	*C.* 86.4 % of constituent fatty acids; *idem.*

878. These results are completely analogous to those I obtained when analyzing the oily part of butterfat and led me to conclude that there were two substances in porpoise oil. Accordingly, I treated the neutralized oil no. 1 with cold, weak alcohol and obtained the phocenin described in Book II, Chapter 15; this is much closer to the pure state than oil no. 1. I have no doubt that if oil no. 3 had been treated with alcohol, this would have separated some phocenin while leaving a substance very similar to the olein.

SECTION 2

EXAMINATION OF THE OIL OF *DELPHINUS GLOBICEPS*[7]

§ 1. PREPARATION

879. It is prepared like the previous one.

§ 2. PROPERTIES OF THE OIL

880. It was colored slightly citrine yellow. Its smell was reminiscent of fish and greased leather. Its density at 20°C was 0.918 (g/mL).

881. 100 parts of alcohol with a density of 0.812[8] (g/mL) dissolved 110 parts of oil at a temperature of 70°C. The solution did not start to become cloudy until 52°C. 100 parts of alcohol with a density of 0.795 (g/mL) dissolved 123 parts of oil at a temperature of 20°C.

882. The oil and its solutions had no effect on litmus paper or tincture of litmus.

883. When 100 parts of oil were digested with concentrated aqueous potassium hydroxide for twenty-four hours, they did not dissolve entirely. After the soapy mass had been acidulated with tartaric acid, it gave:

(A) *Isovaleric acid*

(B) 12.6 parts of red-brown glycerin that tasted both sweet and very unpleasant.

(C) 66.8 parts of a *fat* that smelled like fish and tasted rancid. It contained *oleic acid and palmitic acid* and a *non-acid material.*

884. This result made me suspect that the oil contained a substance analogous to spermaceti.

§ 3. CHEMICAL ANALYSIS OF THE *DELPHINUS GLOBICEPS* OIL BY EXPOSING IT TO THE COLD

885. When the oil was left to stand at a temperature varying between 5 and 10°C, it deposited crystals that were separated by filtration. When the filtered oil was exposed to a temperature between zero and 3°C it yielded more crystals and these were also separated from the liquid part.

ARTICLE 1

EXAMINATION OF THE CRYSTALLIZED SUBSTANCE

886. This material was drained on filter paper and then dissolved in boiling alcohol; on cooling it deposited a precipitate in the form of beautiful lamellar crystals. These crystals were separated from their mother liquor, redissolved, allowed to crystallize again and drained well. This is the material that has been studied and compared with spermaceti[9] with same melting point. From now onwards I shall call this material *dolphin spermaceti.*

887. The two spermaceti crystallized in the same way, whether they were melted and allowed to cool slowly on the surface of water, or precipitated from alcohol.

888. A thermometer immersed in the dolphin spermaceti gave a reading of 44.5°C when it started to solidify and 43.5°C when it was completely solidified.

889. 100 parts of boiling alcohol with a density of 0.834[10] (g/mL) dissolved 2.9 parts of dolphin spermaceti and 3.0 parts of standard spermaceti. Both solutions were neutral towards colored tinctures.

890. Equal weights (of about 0.9 g) of both spermaceti were boiled for thirty hours in glass retorts with 2 g of caustic potash dissolved in water. The standard spermaceti thickened before the dolphin spermaceti. Since a part of the latter seemed not to have reacted with the alkali, it was subjected to a further caustic potash treatment. The two soapy masses were then acidulated with tartaric acid. The fatty matter of the saponified *dolphin spermaceti* weighed 0.82 g and melted at 40°C. The fatty matter of the saponified *standard spermaceti* weighed 0.76 g and had a melting point of 38°C. Both materials were treated with baryta water and then with alcohol. This yielded:

DOLPHIN SPERMACETI	STANDARD SPERMACETI
(A) *Cetyl alcohol* melting at 47°C, 151 mg (B) *Acid material* melting at 45°C, 552 mg. It consisted of palmitic acid and oleic acid	(A) *Cetyl alcohol* melting at 48°C, 227 mg. (B) *Acid material* melting at 37°C, 385 mg. It consisted of palmitic acid and oleic acid

891. Even if these experiments do not demonstrate the materials to be perfectly identical, they do prove that they are very, very similar.

ARTICLE 2

EXAMINATION OF THE DOLPHIN OIL FROM WHICH THE SPERMACETI CRYSTALS HAD BEEN REMOVED

892. Its color was a bit more pronounced than that of the oil from which the spermaceti had not been separated and its odor was also stronger. It was perfectly liquid at 20°C. At that temperature, its density was 0.924 instead of 0.917 (g/mL), the density of the oil containing spermaceti.

893. 100 parts of alcohol with a density of 0.820 (g/mL) dissolved 149.4 parts of oil before it reached boiling point. The solution only started to become cloudy at 53°C. It was slightly acid towards litmus and the red color turned blue on addition of water. This acidity was due to a small amount of isovaleric acid since it could be made to disappear by treating the oil with milk of magnesium oxide[11]. 300 parts of oil released 1 part of orange colored magnesium isovalerate into the water.

The oil that was separated from the excess magnesium oxide by means of concentrated alcohol was not acid. It burned without leaving a residue. At 15°C, it congealed into a soft mass.

894. 100 parts of neutral oil were allowed to digest with 60 parts of caustic potash dissolved in 100 parts of water for a period of fifteen hours. When the soapy mass was brought to the boil in water, it did not produce a perfectly clear liquid. The following were isolated from this soapy mass:

(A) An amount of isovaleric acid corresponding to 34.6 parts of barium isovalerate.

(B) 15.00 parts of glycerin that contained a small amount of the *principle with the leather smell,* as well as an *orange coloring principle* all or most of which must have already been in the oil before it was saponified since when the aqueous potassium hydroxide was brought into contact with the oil, the color of the latter immediately turned to an orangey brown before saponification could have started. From this I conclude that the coloring principle is not produced by the alkali but liberated by the caustic potash which then reacts with it and makes its presence much more noticeable by forming a compound with a deep color. Most of this principle stayed in the aqueous liquid formed during the acidulation of the soap by tartaric acid, since the acidulation product had hardly any color.

(C) 66 parts of *saponified oil.* At 20°C, this material had a density of 0.892 (g/mL) and only a fraction had solidified. At 10°C, most of it was present in the form of small lamellae while the rest was perfectly liquid. It was slightly yellow and it did not smell of fish or leather since the water that had been mixed with it had removed this aroma; all that remained was the rancid smell of saponified fats. When 100 parts of this oil were boiled with water that contained 13.53 parts of pure potassium hydroxide and water containing 9.5 parts of pure sodium hydroxide, they did not dissolve completely.

When the oil was treated with baryta water and alcohol, it yielded:

(A) 51.7 parts of an acid fatty material that only partially congealed at 22°C. Its solidification was only complete at 15°C. Analysis of this material indicated that it was composed of palmitic acid with a melting point of 54°C and oleic acid that melted at 15°C[12] and had only a very slight odor.

(B) 14.30 parts of a non-acid fatty material that seemed to me to be similar to cetyl alcohol but differed in that it had a much lower melting point and because it seemed to be composed of two substances, both of which were non-acid but one of which had a melting point of 27°C and the other of 35°C. However, I am rather inclined to believe that these two substances were not pure and that both of them contained some higher melting[13] cetyl alcohol, one in a higher proportion than the other.

895. To me it is clear that the dolphin oil I analyzed contained: 1. some *phocenin*; 2. some *spermaceti*; 3. some *olein*; 4. an *odoriferous principle* that smells like fish and that seemed to me to be identical to the odoriferous principle that I found in the cartilage of *Squalus peregrinus*[14]; 5. an *orange principle,* but part of the amount found in the analysis stems from a change that the oil, or rather one of its principles, undergoes by the simultaneous action of atmospheric oxygen and heat. The *principle that smells like leather dressed with grease* stems from the change in the isovaleric acid (277).

SECTION 3

EXAMINATION OF FISH OIL[15]

Properties

896. It had a yellowish orangey brown color and its odor was that of fish and greased leather. It had a density of 0.927 (g/mL) at 20°C. At zero degrees centigrade, it remained fluid for several hours but after having been exposed to this temperature for several days, it deposited a very small amount of *solid fatty material* that was separated by filtration.

ARTICLE 1.

EXAMINATION OF THE LIQUID PART OF FISH OIL

897. It was not acid towards litmus paper.

898. At 75°C[16], 100 parts of alcohol with a density of 0.795 (g/mL) dissolved 122 parts of oil. The solution did not start to become cloudy until 63°C; it was not at all acid.

899. 200 g of oil saponified readily when heated with 120 g caustic potash dissolved in 400 g water. The soapy mass was brown and completely soluble in cold water. The solution was acidulated with tartaric acid and yielded an *aqueous liquid* and *constituent fatty acids.*

A. Aqueous liquid

900. It had a strong yellowish brown color and smelled like leather. It was distilled.

Distillation residue

901. It released some yellow colored glycerin with a very pleasant taste into the alcohol.

902. It was acid and had a leathery smell. After neutralization with baryta water, it yielded only 0.3 g of dry isovalerate. This is a very different amount from that isolated from *Delphinus globiceps.*

B. Constituent fatty acids

903. They had a greater tendency to crystallize than the natural oil. They were completely miscible with alcohol with a density of 0.821 (g/mL): the solution contained palmitic acid and oleic acid[17].

904. 100 parts of the constituent fatty acids dissolved completely in water containing 13.45 parts of potash and 9.17 parts of soda ash.

905. When 100 parts of these acids were treated with baryta water and alcohol, they yielded only 0.6 parts of strongly colored, non-acid fatty matter.

906. When the solution of these acids in aqueous potash was left to stand, it divided into a *pearly material*, which precipitated, and an oleate, which remained in solution.

Pearly material

907. Successive treatments with weak aqueous caustic potash solutions and alcohol demonstrated that the water retained appreciable amounts of potassium peroleate. It was purified by dissolving it in aqueous caustic potash. When left to stand, it formed a precipitate of *potassium bipalmitate*, the acid of which crystallized into, small, radiating needles that melted at 56°C.

Potassium oleate

908. It was acidulated with tartaric acid. When the acid originating from this acidulation was exposed to the cold, it deposited a small amount of palmitic acid, which was removed. After this treatment, the oleic acid had the following properties: its color was much deeper than that of the oleic acid from lard, mutton and beef tallow, etc. I ascribe the cause of this color to a body foreign to the true oil; this body may originate from the decomposition of part of the oil as a result of the extraction process, or it may have a completely different origin. The oleic acid had an odor of fish, which it transferred to its barium, strontium and lead soaps.

ARTICLE 2

EXAMINATION OF THE SOLID PART OF FISH OIL

909. After having been drained on filter paper, it was treated with boiling alcohol, which removed a large amount of olein. When I noticed that the solid material became colored during this treatment, I stopped the alcohol treatment. It was melted in this state. When a thermometer was immersed, its reading dropped to 21°C and then rose to 27°C when it solidified. The heat caused it to lose its leathery odor.

910. An amount of 9 g of alcohol with a density of 0.795 (g/mL) dissolved 5 g of this solid material. On cooling, the solution gave: 1. small, radiating needles of the most beautiful white; 2. small, yellow needles. The mother liquor was viscous and brown.

During this operation it seemed to me that the brown coloring principle became more abundant; either it was actually formed from the fatty material during the treatment or it was isolated from a material that had masked the color. The coloring principle became especially noticeable through the action of potassium hydroxide. I also observed that saponification generated the odor of leather, which was lost on heating.

911. An amount of 3.6 g of colored fatty material was saponified by an equal weight of caustic potash to yield a soap that was acidulated with tartaric acid.

A. Aqueous liquid

912. The aqueous liquid was distilled.

Distillation residue

913. When alcohol was applied to the distillation residue, it dissolved about 0.25 g of a yellow syrup which first tasted bitter and astringent and then slightly sweet.

Distillation product

914. The distillation product had a light odor of leather and was also slightly acid. Neutralization with baryta water yielded 30 mg of a salt with an odor of isovaleric acid rather than leather but there was too little of it to reach a verdict on its nature.

B. Saponified fatty material

915. The saponified fatty material contained two substances that I separated mechanically from each other. The most abundant one weighed 3.06 g; it was orangey yellow in color. When a thermometer was immersed in the melted material, its reading dropped to 26.5°C and then rose to 28°C. This material, which was highly soluble in aqueous caustic potash, seemed to me to be entirely made up of palmitic acid and oleic acid. The other substance weighed only 140 mg; it was brown and at 100°C, it was still not molten but dissolved completely in boiling alcohol. It left no solid residue after incineration.

916, According to these experiments, 100 parts of solid fatty matter yielded:

Saponified fatty material……………..……………	88.9

917. These are the properties I found in the solid material separated from the fish oil. This means that this material is more similar to a stearin than to spermaceti. However, it is possible that this material was foreign to the nature of fish oil and since there was only a very small amount of it, which prevented me from carrying out a large number of experiments, I do not consider this opinion to be sufficiently well founded.

918. From all the above it can be concluded that the fish oil I investigated was quite like dolphin oil with respect to its odor but differs in that: 1. it only yielded traces of volatile fatty acids on saponification; 2. it did not yield a crystallized substance like cetyl alcohol; 3. it could be saponified much more easily and did not produce appreciable amounts

of non-acid substances; 4° it contained a much larger amount of coloring principles.

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[1] The *Cetacea* are an order of marine mammals that comprises the whales, dolphins, and porpoises. The harbor porpoise *(Delphinus Phocoena)* belongs to this order via the sub-order of the *Odontoceti,* the family of the *Phocoenidæ* and the genus of the *Phocoena.*

[2] This corresponds to 90.7% ethanol by weight or 93.7% by volume.

[3] When the alcoholic solution of 1 g of oil in 5 g of alcohol was cooled, it formed two phases: an alcohol phase in which slightly less oil was dissolved and a dispersed oil phase with a relatively high alcohol content. When 4 g of oil were added, this formed more of the dispersed phase by dissolving the alcoholic phase until none was left. Thus a single phase, a solution of alcohol in oil, was obtained that could be mixed with further oil without forming a two-phase system.

[4] This time, 'graisse acidifié' has not been translated by *constituent fatty acids* (*cf.* endnote 5, Book II Chapter 1) since the products listed comprise glycerin; *acidulated soapstock* has been used instead. However, in the table below, the author refers to: "graisse entièrement acidifié' (totally acidified fat). Since the table also lists glycerin, 'this totally acidified fat' has therefore been translated as *free fatty acids.*

[5] The author must mean bipalmitate crystals.

[6] This alcohol is almost absolute. Accordingly, it should be more miscible with the oil. Nevertheless, the mixture of 200 g of oil and 180 g of alcohol separated into two phases, whereas (873) a mixture of 200 g of oil and 200 g of alcohol containing more water formed a single phase. Perhaps the temperatures in the two experiments were different.

[7] *Delphinus globiceps* (Cuvier 1812) is now referred to as *Globicephalus melas* (Traill,1809); it has a wide range of English names but the 'common pilot whale' ('whale' for short) has been selected as the name to be used in this translation since the Italian and French names also refer to this 'pilot' aspect. See also:
http://uio.mbl.edu/apps/Hershkovitz/index.php?func=t&ID=69&page=&t=t

[8] The alcohol with a density of 0.812 (g/mL) contained 93.9% alcohol by weight, or 96.1% by volume. In the same sub-section, alcohol with a density of 0.795 (g/mL) is used and this can be considered to be absolute alcohol.

[9] This is the cetyl alcohol derived from porpoise oil. If it is necessary to avoid confusion, it will be referred to as 'standard cetyl alcohol'

[10] This corresponds to 85.7% alcohol by weight or 90.0% by volume.

[11] On previous occasions, the author used magnesium carbonate. Both compounds have the property of being almost insoluble in water with a neutral pH but dissolve readily if the water is even slightly acid.

[12] This analysis did not reduce the oil to pure components since the melting point of palmitic acid is 62.9°C and that of oleic acid is 13.4°C.

[13] The melting point of pure cetyl alcohol is 49.3°C.

[14] This one of the many Latin names for the basking shark *(Cetorhinus maximus*, Gunnerus 1765).

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[15] The original refers to: 'oil from fish of commerce' but since this description covers a wide range of oil compositions and since these are likely to overlap with the compositions of the fish oil produced industrially, translating the original into just 'fish oil' is justified on chemical grounds.

[16] The alcohol is almost absolute and this temperature is very close to the atmospheric boiling point of absolute alcohol of 78.32°C.

[17] When studying lard and other mammalian fats, the author did not realise that his oleic acid was a mixture and contained also linoleic acid. In fact, linoleic acid was only identified by Hazura and Friedrich in 1887 (Monatshefte, **8**, 156). Consequently, it is not surprising that the author also calls the mixture of unsaturated fatty acids in fish oil just 'oleic acid'.