# TETRADECENOIC AND DODECENOIC ACIDS IN SPERM OIL. I. TETRADECENOIC AND DODECENOIC ACIDS IN SPERM BLUBBER OIL.*

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Sperm oil is obtained from the sperm whale, *Physeter macrocephalus* L., and the oil obtained from the body blubber is generally kept separate from that of the head cavities. Sperm blubber (or body) oil and sperm head oil are, therefore, known in the foreign market. In this country, however, four kinds of oils are differentiated, i.e. head oil, blubber oil (skin oil), intestine oil and bone oil; the blubber oil is obtained exclusively from the blubber under the skin and has the largest yield, while the intestine oil is obtained from the intestines and the surrounding flesh. Sperm oil is frequently allowed to crys-

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tallise at a low temperature and subjected to pressure, by which the solid portion is removed and the oil having a low cold-test is obtained. The solid portion is used for further preparation of spermaceti. However, these separative operations are not generally carried out in this country. The constituents of sperm oil have been studied since a very earlier date. Far back in about 1820, Chevreul in his classic studies found cetyl alcohol in spermaceti, and also pointed out the presence of some peculiar constituents in sperm head oil. Afterwards there have appeared many studies, among which those of Hofstädter,(1) Bull,(2) Fendler,(3) Walker and Warburton,(4) Procter and Bennet,(5) Dunlop,(6) Lewkowitsch,(7) Allen,(8) and Nakajima(9) may be mentioned. Much contributions have been made recently to the knowledge of the constituents of sperm oil by the closer studies of Tsujimoto(10) on the fatty acids and the alcohols of sperm head oil, André and François(11) on the alcohols of sperm head oil and spermaceti, and Hilditch and Lovern(12) on the fatty acids, the alcohols as well as the component esters of sperm blubber and head oils. One of the present authors (Toyama)(13) also examined the fatty acids and the alcohols of sperm blubber oil. For a thorough account of the results set forth by these authors the original papers should be consulted. Only a short review on the literature relating to the theme of the present paper, i.e. tetradecenoic acid $C_{14}H_{26}O_2$ and dodecenoic acid $C_{12}H_{22}O_2$ in sperm oil, is given below. Tsujimoto(14) isolated a tetradecenoic acid from sperm head oil and established its constitution as $\Delta^{5:6}$-tetradecenoic acid. He inferred the presence of a tetradecenoic acid also in sperm blubber oil. The same author(15) found a tetradecenoic acid also in Tsuzu oil (seed oil of *Tetradenia glauca* Matsum.), the constitution of which was, however, proved to be $\Delta^{4:5}$-tetradecenoic acid. He assigned the name physeteric acid to $\Delta^{5:6}$-acid in sperm head oil and the name tsuzuic acid to $\Delta^{4:5}$-acid in Tsuzu oil. According to Hilditch and Lovern,(16) on the other hand, the fatty acids of sperm head oil contain 14% of tetradecenoic acid and 4% of dodecenoic acid, whilst the fatty acids of sperm blubber oil contain 4% of tetradecenoic acid, but no dodecenoic acid.

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(1), (2), (3), (4), (5), (6), (7) Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes", Vol. II (6th Edition), 875–876.

(8) "Commercial Organic Analysis", Vol. II (3rd Edition), Part I, 204–205.

(9) Dissertation, College of Engineering, Tokyo Imperial University (1917).

(10) *J. Soc. Chem. Ind., Japan,* **24** (1921), 41; **26** (1923), 608; **29** (1926), 102.

(11) *Compt. rend.,* **183** (1926), 663; **185** (1927), 279.

(12) *J. Soc. Chem. Ind.,* **47** (1928), 105 T; **48** (1929), 359 T; **48** (1929), 365 T.

(13) *J. Soc. Chem. Ind., Japan,* **30** (1927), 519, 527.

(14) *Loc. cit.,* (10).

(15) *J. Soc. Chem. Ind., Japan,* **29** (1926), 105; *Reports of the Tokyo Imperial Industrial Research Laboratory,* **23** (1928), No. 3.

(16) *Loc. cit.,* (12).

As for the constitutions of these acids, they stated that tetradecenoic acid in head oil is identical with physeteric acid ($\Delta^{5:6}$-acid) discovered by Tsujimoto, whereas tetradecenoic acid in blubber oil is $\Delta^{9:10}$-acid which is identical with the acid found in South Georgia whale oil by Armstrong and Hilditch.(17) The constitution of dodecenoic acid in head oil was stated to be $\Delta^{3:4}$-acid. However, Hilditch and Lovern did not separate the individual acids. In their experiments the mixed fatty acids were treated by the lead-soap-alcohol method, the methyl esters of the liquid fatty acids were fractionated, and the fractions corresponding to $C_{14}$- and $C_{12}$-acids respectively were separately collected. The constitutions of tetradecenoic and dodecenoic acids were derived from the results of the permanganate oxidation of these fractions which, however, were still contaminated with a large proportion of the methyl esters of saturated acids. In this connection it may be noted here that a dodecenoic acid, named linderic acid, was first isolated by Iwamoto(18) from the seed oil of *Lindera obtusiloba*, and its constitution was established by him as $\Delta^{4:5}$-acid.(19) Toyama(20) in his previous work on the sperm blubber oil, obtained some indications of the presence, though in a small proportion, of tetradecenoic acid, but the separation of this acid could not be attained. In a continuation of the previous work, we have undertaken the present experiments with a view to separate tetradecenoic acid starting with a large quantity of sperm blubber oil, and to ascertain by a closer examination of its constitution whether it differs from physeteric acid, as stated by Hilditch and Lovern, or not. Furthermore we have separated a dodecenoic acid from sperm blubber oil as well as from head oil, and examined its constitution. In this paper the experimental results concerning tetradecenoic and dodecenoic acids in blubber oil are described, while those of dodecenoic acid in head oil will be given in a succeeding paper.

In dealing with the unsaponifiable matter of sperm blubber oil, as described in a separate communication, a fatty acid fraction was obtained, mainly from the barium soaps soluble in acetone, in the course of the operations carried out for the separation of unsaponifiable matter. It contained large proportions of highly unsaturated acids and lower members of monoethylenic acids. The greater part of tetradecenoic and dodecenoic acids originally present in sperm blubber oil was thought to have entered into this fraction. For the present experiments this fraction was used as the starting

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(17) *J. Soc. Chem. Ind.*, **44** (1925), 180 T.

(18) *J. Soc. Chem. Ind., Japan*, **24** (1921), 1143; **26** (1923), 708.

(19) It is also reported that Grün and his co-workers found dodecenoic ($\Delta^{11:12}$?) and tetradecenoic ($\Delta^{13:14}$?) acids together with $\Delta^{9:10}$-decenoic acid in butter fat. Cp. *Z. angew. Chem.*, **37** (1924), 228.

(20) *Loc. cit.*, (13).

material. It was first converted into the methyl esters, and the latter fractionated, by which the fraction boiling below 170°/15 mm. was separately collected. This was saponified, the free fatty acids obtained was further fractionally distilled, and two fractions, (a) 192–197°/15 mm. and (b) 172–177°/15 mm., were separated. The fraction (a) was treated with lead acetate in 90% alcoholic solution under strong cooling, the precipitate of the lead soaps of saturated acids were filtered off, and the filtrate yielded tetradecenoic acid. The same treatment of the fraction (b) yielded dodecenoic acid. Tetradecenoic acid thus obtained was then converted into dihydroxymyristic acid by Hazura's method, and its methyl ester was subjected to the permanganate oxidation in acetone. After saponification of the ester contained in the oxidation products, *n*-nonoic acid $CH_3{\cdot}(CH_2)_7{\cdot}COOH$ and glutaric acid $HOOC{\cdot}(CH_2)_3{\cdot}COOH$ were identified, and consequently the constitution of dihydroxymyristic acid was shown to be $CH_3{\cdot}(CH_2)_7{\cdot}CHOH{\cdot}CHOH{\cdot}(CH_2)_3{\cdot}COOH$. Hence, the constitution of tetradecenoic acid is $\Delta^{5:6}$-tetradecenoic acid which is expressed by the formula $CH_3{\cdot}(CH_2)_7{\cdot}CH{=}CH{\cdot}(CH_2)_3{\cdot}COOH$. Tetradecenoic acid in sperm blubber oil was thus proved to be identical with physeteric acid in sperm head oil; no evidence was obtained to indicate the presence of $\Delta^{9:10}$-tetradecenoic acid which was stated by Hilditch and Lovern to occur in sperm blubber oil. Methyl dihydroxylaurate prepared from dodecenoic acid was subjected to oxidation in the same manner as methyl dihydroxymyristate, and *n*-heptoic acid $CH_3{\cdot}(CH_2)_5{\cdot}COOH$ and glutaric acid $HOOC{\cdot}(CH_2)_3{\cdot}COOH$ were identified after saponification of the ester in the oxidation products. From these results dihydroxylauric acid was found to have the formula $CH_3{\cdot}(CH_2)_5{\cdot}CHOH{\cdot}CHOH{\cdot}(CH_2)_3{\cdot}COOH$, and consequently the constitution of dodecenoic acid was shown to be $\Delta^{5:6}$-dodecenoic acid which is expressed by the formula $CH_3{\cdot}(CH_2)_5CH{=}CH{\cdot}(CH_2)_3{\cdot}COOH$. $\Delta^{3:4}$-Dodecenoic acid, which was stated by Hilditch and Lovern to occur in sperm head oil, could not be detected. We propose to assign to $\Delta^{5:6}$-decenoic acid the name denticetic acid(21) in order to distinguish it from its isomer linderic acid ($\Delta^{4:5}$-dodecenoic acid).

## Experimental.

1. **Separation of Tetradecenoic Acid.** As described in a succeeding paper(22) dealing with the unsaponifiable constituents of sperm blubber oil, a specimen of sperm blubber oil having $d_4^{25}$ 0.8735, $n_D^{25}$ 1.4635, acid value 0.85, saponification value 126.8, iodine value (Wijs) 82.6 and unsaponifiable matter 38.98% was heated with a little excess of barium hydroxide and water in an autoclave under 5–6 atm. for one hour, and the reaction products

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(21) Derived from *Denticete*.

(22) This Bulletin, **10** (1935), 579.

consisting of barium soaps and free unsaponifiable matter were extracted with acetone. The substances obtained on distilling off the solvent from the acetone solution were, however, contaminated with a small proportion of barium soaps and neutral oil which escaped saponification. They were heated with an excess of alcoholic potash to effect a complete saponification of the remaining neutral oil, the soaps were decomposed with hydrochloric acid, and the unsaponifiable matter contaminated with a small amount of free fatty acids was taken up with ether. The ethereal solution was then washed with potassium hydroxide solution which dissolved out free fatty acids as their potassium soaps. For the present experiments the fatty acids regenerated from the potassium soaps thus obtained were used as the starting material. They were obtained in a yield of 2.4% of the oil, and showed neutralisation value 199.1 and iodine value 133.0. Five hundred grams of these fatty acids, corresponding to 21 kg. of the oil, were refluxed with an equal amount of methanol containing 2.5% of hydrogen chloride for 30 minutes, and the resulting methyl esters were separated from excess of methanol and some unchanged fatty acids. These were distilled, and there was obtained 26 g. of a fraction boiling below 170°/15 mm. and having saponif. value 234.8 and iodine value 78.3. This fraction was converted into free fatty acids, and the latter were fractionated. Two fractions were separately collected; (a) b. p. 192–197°/15 mm., 8.4 g. and (b) b. p. 172–177°/15 mm., 1.9 g. The fraction (a) showed neutr. value 249.8 and iodine value 84.9, and was used for further separation of tetradecenoic acid, whilst the fraction (b) was used for the separation of dodecenoic acid.

The fraction (a) was dissolved in 90% alcohol, and a solution of lead acetate (about half the theoretical quantity) in 90% alcohol was added, the total quantity of 90% alcohol being about 10 times the quantity of the fraction (a). The solution was cooled down to −15°, the precipitate of lead soaps were filtered off, and the filtrate yielded tetradecenoic acid $C_{14}H_{26}O_2$ having the following constants (Found: C, 74.39; H, 11.49. Calc. for $C_{14}H_{26}O_2$: C, 74.27; H, 11.58%).

$d_4^{15}$ 0.9081, $d_4^{20}$ 0.9046, $n_D^{15}$ 1.4571, $n_D^{20}$ 1.4552, mol. refraction (based on the data at 15°) 67.86 (calc. for $C_{14}H_{26}O_2\ \digamma_1$: 67.92), neutr. value 248.8 (calc. 248.0), iodine value 107.8 (calc. 112.2).

The hydrogenation product of tetradecenoic acid gave myristic acid $C_{14}H_{28}O_2$ which showed neutr. value 244.9 (calc. 245.8), m.p. and mixed m.p. 53.5–54° after recrystallisation from 80% alcohol. On oxidising tetradecenoic acid by Hazura's method, it yielded dihydroxymyristic acid $C_{14}H_{28}O_4$ which showed neutr. value 215.0 (calc. 215.6) and m.p. 118.5–119° after recrystallisation from 75% alcohol.

2. **Oxidation of Methyl Dihydroxymyristate.** Dihydroxymyristic acid described above was converted into its methyl ester by using hydrogen chloride in methanol. The methyl ester (3.5 g.) thus obtained was dissolved in 35 c.c. of acetone, and 7 g. of powdered potassium permanganate was added in small portions. The liquid was refluxed on the water-bath for one hour, and then acetone was removed by distillation. The residue was mixed with 70 c.c. of water, and a current of sulphur dioxide was passed into the mixture until the excess of potassium permanganate and the insoluble oxides of manganese disappeared completely. The oxidation products were extracted by using 400 c.c. of ether, and after the ethereal solution was concentrated to less than half its original volume, it was then shaken with potassium carbonate solution by which the acidic substances were dissolved out as their potassium salts, while the neutral substances were left in ethereal solution. The aqueous solution containing the potassium salts was separated, and after addition of 2 g. of potassium hydroxide, the solution was heated on

the water-bath so as to saponify the acid ester contained in the oxidation products. After acidification with hydrochloric acid, the acidic substances liberated were taken up with ether. The ethereal solution was washed with water, and on removal of ether by distillation, there remained 2.3 g. of acidic substances. The low yield is thought to be due either to an incomplete oxidation with potassium permanganate or to the loss caused by washing the ethereal solution with water. The acidic substances were treated with 60 c.c. of petroleum ether (b.p. below 60°) to effect a separation into petroleum ether solution and insoluble portion. On removal of the solvent from the petroleum ether solution by heating on the water-bath, the residue was then distilled by heating in the oil-bath and there was obtained about 1 g. of colourless distillate boiling below 193°/100 mm. and having neutr. value 353.1 (calc. for $C_9H_{18}O_2$: 354.8) and $n_D^{20}$ 1.4318. The amide prepared from the distillate was found to be *n*-nonoic acid amide which showed m.p. and mixed m.p. 98.5–99°(23) when recrystallised from 50% alcohol (Found: N, 9.00. Calc. for $C_9H_{19}ON$: N, 8.91%).

The portion insoluble in petroleum ether (0.8 g.) consisted of a crystalline solid. It crystallised from benzene in lustrous needles which showed neutr. value 845.8 (calc. for $C_5H_8O_4$: 849.7) and m.p. 97–97.5° (Found: C, 45.49; H, 6.21. Calc. for $C_5H_8O_4$: C, 45.43; H, 6.11%). The melting point was not lowered when the substance was admixed with a pure specimen of glutaric acid, m.p. 97.5–98°.

3. **Separation of Dodecenoic Acid.** The fraction (b) described above had neutr. value 282.4 and iodine value 83.5. It was dissolved in 90% alcohol, and a solution of lead acetate (approximately theoretical quantity) in 90% alcohol was added, the total quantity of 90% alcohol used being about 10 times the quantity of the fraction (b). The solution was cooled down to −15°, the precipitated lead soaps were filtered, and there was obtained dodecenoic acid $C_{12}H_{22}O_2$ having the following constants from the filtrate (Found: C, 72.99; H, 11.30. Calc. for $C_{12}H_{22}O_2$: C, 72.67; H, 11.19%).

$d_4^{15}$ 0.9130, $n_D^{15}$ 1.4535, mol. refraction 58.72 (calc. for $C_{12}H_{22}O_2\ |\overline{=}_1$: 58.69), neutr. value 232.0 (calc. 283.1), iodine value 118.7 (calc. 128.1).

Oxidation of dodecenoic acid by Hazura's method gave dihydroxylauric acid $C_{12}H_{24}O_4$ which had neutr. value 240.9 (calc. 241.6) and m.p. 106–107° after recrystallisation from ether. Since the precipitate of lead soaps obtained in the final separative operation for dodecenoic acid was thought to contain a considerable amount of lead dodecenoate besides the lead soaps of saturated acids, the fatty acids liberated from the precipitate on acidification were subjected to Hazura's oxidation method so as to separate dihydroxylauric acid which showed neutr. value 241.0 (calc. 241.6) and m.p. 105–106° after recrystallisation from ether.

4. **Oxidation of Methyl Dihydroxylaurate.** The specimens of dihydroxylauric acid were combined, and converted into the methyl ester by using hydrogen chloride in methanol. The methyl ester (1.1 g.) was dissolved in 10 c.c. of acetone, and 2 g. of powdered potassium permanganate was added in small portions. After the liquid had been heated on the water-bath under a reflux condenser for one hour, acetone was removed by distillation, 20 c.c. of water was added to the residue, and a current of sulphur dioxide was passed into the solution, until the excess of permanganate and the insoluble oxides of manganese disappeared completely. The solution was shaken with ether in order to extract the oxidation products. The ethereal solution was treated with potassium carbo-

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(23) The specimen of *n*-nonoic acid amide used for the mixed melting point test was prepared from *n*-nonoic acid which was obtained by the ozonolysis of oleic acid.

nate solution, and the acidic substances were dissolved out as their potassium salts. The aqueous solution containing potassium salts were separated from the ethereal solution, a little potassium hydroxide was added, and the solution was heated on the water-bath to effect the saponification of the acid ester contained in the oxidation products. The free acidic substances obtained on acidification with hydrochloric acid were once taken up with ether, the ethereal solution was washed with water, and after removal of ether by distillation the residue was treated with petroleum ether, yielding the petroleum ether solution and the insoluble portion.

The petroleum ether solution was heated on the water-bath to distill off the solvent, and there was obtained a residue (0.5 g.) which, after being washed with a little water, showed neutr. value 439.8 (calc. for $C_7H_{14}O_2$: 431.5) and $n_D^{20}$ 1.4235, and appeared to be *n*-heptoic acid. The amide prepared from it melted at 91–92° after recrystallisation from petroleum ether, and no depression of melting point was observed when the amide was admixed with various proportions of a pure specimen of *n*-heptoic acid, m.p. 94.5–95°.(24)

The portion insoluble in petroleum ether (0.2 g.) was recrystallised from benzene in needles which had neutr. value 846.2 (calc. for $C_5H_8O_4$: 849.7) and melted at 95–96°. The melting point was not lowered when the substance was admixed with various proportions of a pure specimen of glutaric acid $C_5H_8O_4$, m.p. 97.5–98°.

## Summary.

Tetradecenoic acid $C_{14}H_{26}O_2$ and dodecenoic acid $C_{12}H_{22}O_2$ have been separated from sperm blubber oil. They are converted into dihydroxymyristic acid $C_{14}H_{28}O_4$ and dihydroxylauric acid $C_{12}H_{24}O_4$ respectively, and the methyl esters of these hydroxy-derivatives are subjected to the permanganate oxidation in acetone. From the results of an examination of the oxidation products, the following constitutions have been established:

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| Tetradecenoic acid | $CH_3\cdot(CH_2)_7\cdot CH{=}CH\cdot(CH_2)_3\cdot COOH$, |
| Dodecenoic acid | $CH_3\cdot(CH_2)_5\cdot CH{=}CH\cdot(CH_2)_3\cdot COOH$. |

It is thus seen that tetradecenoic acid in sperm blubber oil is identical with physeteric acid ($\Delta^{5:6}$-tetradecenoic acid) in sperm head oil, whilst dodecenoic acid in sperm blubber oil, to which the name denticetic acid is assigned, is $\Delta^{5:6}$-acid and is an isomer of linderic acid ($\Delta^{4:5}$-dodecenoic acid) in the seed oil of *Lindera obtusiloba*.

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(24) For the preparation of *n*-heptoic acid amide used for the mixed melting point test, castor oil was subjected to dry distillation, and a fraction consisting of *n*-heptyl aldehyde (b.p. 153–154°) was separated. This was oxidised with potassium bichromate and sulphuric acid, the product was fractionated, and a fraction of *n*-heptoic acid (b.p. 220–224°) was separated and then converted into its amide.