# TETRADECENOIC AND DODECENOIC ACIDS IN SPERM OIL.

## II. DODECENOIC ACID IN SPERM HEAD OIL.*

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As described in the preceding paper,(1) tetradecenoic and dodecenoic acids were separated from sperm blubber oil, and their constitutions were determined with the results that tetradecenoic acid was proved to be identical with physeteric acid ($\Delta^{5:6}$-tetradecenoic acid) found by Tsujimoto in sperm head oil, whilst dodecenoic acid, named denticetic acid, was found to be $\Delta^{5:6}$-dodecenoic acid and not $\Delta^{3:4}$-dodecenoic acid which was stated by Hilditch and Lovern(2) to occur in sperm head oil. We have now separated dodecenoic acid from sperm head oil, and examined whether its constitution is really $\Delta^{3:4}$-dodecenoic acid as stated by Hilditch and Lovern or not.

In these experiments, the head oil was first subjected to methanolysis, and the product consisting of the methyl esters and the free unsaponifiable matter (chiefly higher alcohols) was fractionated. The fraction boiling below 150°/15 mm. was separately collected, the unsaponifiable matter was removed from it, and the fatty acids were separated. These were treated with lead acetate in 90% alcoholic solution at the room temperature. However, the lead soaps of saturated acids were not precipitated to a sufficient extent; the liquid acids obtained from the filtrate appeared from their iodine value (41.6) to contain still more than 50% of saturated acids. The liquid acids were then fractionated, and a fraction corresponding to $C_{12}$-acids was separated. It was then subjected to the bromo-ester method of Grün and Janko;(3) i.e. it was converted into the methyl esters and then brominated, the product was distilled so as to remove the saturated methyl esters, leaving the bromides of unsaturated methyl esters as the residue which was debrominated afterward to regenerate unsaturated methyl esters. These were saponified to obtain free fatty acids which had iodine value 98.2 and contained still saturated acids in not insignificant amount. In order to remove the saturated acids as far as possible, the fatty acids obtained above were treated with lead acetate in 90% alcohol, the solution was cooled down to −15°, and the precipitate of

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(1) This Bulletin, **10** (1935), 563.

(2) *J. Soc. Chem. Ind.*, **47** (1928), 105T.

(3) *Z. deuts. Oel- u. Fett-Ind.*, **41** (1921), 553, 572.

lead soaps was filtered off. The liquid acids obtained from the filtrate consisted essentially of dodecenoic acid. For the determination of the position of ethylenic linking in dodecenoic acid, it was first converted into dihydroxylauric acid by Hazura's method, and the methyl ester of this hydroxy-derivative was oxidised with potassium permanganate in acetone. Among the oxidation products, after saponification of the acid ester, *n*-heptoic acid and glutaric acid were identified. Accordingly the constitution of dihydroxylauric acid was found to be expressed by 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 is $\Delta^{5:6}$-dodecenoic acid which is expressed by the formula $CH_3\cdot(CH_2)_5\cdot CH{=}CH\cdot(CH_2)_3\cdot COOH$. It is seen from these results that dodecenoic acid in sperm head oil is nothing else than denticetic acid ($\Delta^{5:6}$-dodecenoic acid) found in sperm blubber oil. $\Delta^{3:4}$-Dodecenoic acid described by Hilditch and Lovern is not found.

## Experimental.

1. **Separation of Dodecenoic Acid.** Sperm head oil used for the present experiments deposited a considerable amount of crystalline solid at the room temperature, and had the following characteristics: $d_4^{40}$ 0.8654, $n_D^{40}$ 1.4523, acid value 3.1, saponification value 147.7, iodine value (Wijs) 53.4, unsaponifiable matter 36.52%. It was first pressed at the room temperature, the solid portion was removed, and the clear oil was obtained with about 80% yield. An equal amount of methanol containing 3% of sodium hydroxide was added to the clear oil, and the mixture was well shaken for 40 minutes at about 40°, when it became homogeneous due to the formation of methyl esters and free unsaponifiable matter. A large quantity of water was then added to the solution, and the oily layer separated was washed with water to remove the contaminated soaps which had been formed to a slight extent in the course of methanolysis. The product of methanolysis thus obtained consisted of the methyl esters and the free unsaponifiable matter (mainly higher alcohols). It was distilled, and the fraction boiling below 150°/15 mm. was separated, the yield of this fraction being 139 g. from 4 kg. of the product of methanolysis. This fraction was saponified, and the unsaponifiable matter was removed by extraction with ether in the usual way. The fatty acids liberated from the soap solution was dissolved in 90% alcohol, lead acetate (approximately the theoretical quantity) dissolved in 90% alcohol was added, and the solution was kept at the room temperature over a night. The precipitated lead soaps were filtered, and the fatty acids were regenerated from the filtrate; yield 91 g., neutr. value 298.9 and iodine value 41.6. These were distilled, and a fraction boiling at 170–180°/15 mm. and having neutr. value 285.8 and iodine value 50.2 was separately collected in a yield of 31 g. It was converted into the methyl esters, and the latter were brominated in ethereal solution. The product of bromination was then distilled until the rate of distillation became very slow at about 110°/5 mm., when the distillation was discontinued. The residue was treated with zinc powder and sulphuric acid in methanol,(4) the debrominated methyl esters were converted into the free fatty acids which were then distilled, yielding 8.5 g. of a fraction

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(4) Kimura, *J. Soc. Chem. Ind., Japan*, **34** (1931), 958.

having b.p. 172–177°/15 mm., neutr. value 283.1 and iodine value 98.2. This fraction was then dissolved in 90% alcohol, and lead acetate (approximately the theoretical quantity) dissolved in 90% alcohol was added, the total quantity of 90% alcohol being about 10 times the quantity of the fatty acid fraction. The solution was cooled down to –15°, the precipitate of lead soaps was removed by filtration, and there was obtained from the filtrate 4.5 g. of fatty acids which were found to consist mainly of dodecenoic acid (Found: C, 72.71; H, 11.22. Calc. for $C_{12}H_{22}O_2$: C, 72.67; H, 11.19%).

$d_4^{15}$ 0.9132, $d_4^{20}$ 0.9097, $n_D^{15}$ 1.4538, $n_D^{20}$ 1.4519, mol. refraction (based on the data at 15°) 58.74 (calc. for $C_{12}H_{22}O_2\models_1$: 58.69), neutr. value 283.0 (calc. 283.1), iodine value 122.5 (calc. 128.1).

Hydrogenation of dodecenoic acid yielded lauric acid $C_{12}H_{24}O_2$, which after recrystallisation from 80% alcohol, showed neutr. value 280.4 (calc. 280.3), m.p. and mixed m.p. 43.5–44°. On oxidising dodecenoic acid by Hazura's method there was obtained dihydroxylauric acid $C_{12}H_{24}O_4$ which showed neutr. value 241.0 (calc. 241.6) and m.p. 106–107° when recrystallised from ether (Found: C, 61.93; H, 10.51. Calc. for $C_{12}H_{24}O_4$: C, 62.02; H, 10.42%). The melting point was unaltered when it was admixed with dihydroxylauric acid prepared from dodecenoic acid which was isolated from sperm blubber oil, but it melted at about 90° when admixed with dihydroxylauric acid(5) prepared from linderic acid.(6)

The precipitate of lead soaps, which was removed by the final separative operation for dodecenoic acid, contained a considerable proportion of lead dodecenoate besides the lead soaps of saturated acids, and the fatty acids regenerated from the precipitate of lead soaps yielded a crystalline product by Hazura's method, from which dihydroxylauric acid having neutr. value 241.1 and m.p. 106–107° was easily obtained by a single recrystallisation from ether.

2. **Oxidation of Methyl Dihydroxylaurate**, Dihydroxylauric acid obtained above was converted into its methyl ester by means of hydrogen chloride in methanol. The methyl ester (3.2 g.) was dissolved in 30 c.c. of acetone, and 6 g. of potassium permanganate was added in small portions. The mixture was gently boiled on the water-bath under a reflux condenser for one hour, and then acetone was removed by distillation. The residue was mixed with 60 c.c. of water, and a current of sulphur dioxide was passed into the mixture, until the excess of permanganate and the insoluble oxides of manganese disappeared completely. The oxidation products were extracted by shaking the solution with 300 c.c. of ether, and the ethereal solution was separated and washed with potassium carbonate solution, by which the acidic substances were dissolved out as their potassium salts. On distilling off ether from the ethereal solution there remained 0.2 g. of neutral substances which escaped oxidation. The aqueous solution containing potassium salts was heated on the water-bath with the addition of potassium hydroxide to

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(5) The methyl esters of the mixed fatty acids prepared from the seed oil of *Lindera obtusiloba* were fractionated, a fraction boiling at 136–142°/15 mm. was separately collected, and the fatty acids liberated from this fraction were oxidised by Hazura's method. The product was recrystallised from ether, yielding dihydroxylauric acid melting at 100–101° (Iwamoto gave m.p. 102°). Its methyl ester was subjected to permanganate oxidation in acetone. Caprylic acid and methyl hydrogen succinate were identified among the oxidation products, and consequently the constitution of linderic acid was confirmed to be $\Delta^{4:5}$-dodecenoic acid which had been established by Iwamoto.

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

saponify the acid ester. After acidification with hydrochloric acid, sodium chloride was added to the solution, and the liberated acidic substances were extracted with 300 c.c. of ether. The ethereal solution was washed with water containing sodium chloride, and on removal of ether by distillation there was obtained 2.9 g. of acidic substances. These were further treated with 50 c.c. of petroleum ether, and the insoluble portion was separated from the petroleum ether solution. On removal of the solvent from the petroleum ether solution by heating on the water-bath, the residue was then subjected to distillation by which about 1 g. of colourless distillate boiling below 170°/100 mm. was separately collected. It had neutr. value 437.5 (calc. for heptoic acid $C_7H_{14}O_2$: 431.2) and $n_D^{20}$ 1.4222, and the amide prepared from it crystallised from petroleum ether in lustrous laminae; it melted at 94.5–95° both alone or admixed with a pure specimen of *n* heptoic acid amide (Found: N, 10.83. Calc. for $C_7H_{15}ON$: N, 10.85%).

The portion insoluble in petroleum ether (0.4 g.) consisted of a white crystalline solid. Recrystallisation from benzene yielded needle-shaped crystals of glutaric acid $C_5H_8O_4$; neutr. value 851.2 (calc. 849.7), m.p. and mixed m.p. 97.5–98° (Found: C, 45.40; H, 6.05. Calc. for $C_5H_8O_4$: C, 45.43; H, 6.10%).

## Summary.

Dodecenoic acid $C_{12}H_{22}O_2$ has been isolated from sperm head oil, and methyl dihydroxylaurate $C_{13}H_{26}O_4$ prepared from it has been subjected to permanganate oxidation in acetone. On examining the oxidation products the constitution of dodecenoic acid has been proved to be $CH_3\cdot(CH_2)_5\cdot CH{=}CH\cdot(CH_2)_3\cdot COOH$. It is thus seen that dodecenoic acid in sperm head oil is identical with denticetic acid ($\Delta^{5:6}$-dodecenoic acid) in sperm blubber oil described in the preceding paper.

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