# DECENOIC ACID $C_{10}H_{18}O_2$ IN SPERM HEAD OIL.*

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Received October 14th, 1935. Published January 28th, 1936.

Whilst in preceding papers⑴ the separation of denticetic acid ($\Delta^{5:6}$-dodecenoic acid) from sperm blubber and head oils was described, the present paper deals with the separation of a decenoic acid—a lower homologue of denticetic acid—from sperm head oil. The only one decenoic acid in natural fats recorded in the literature is $\Delta^{9:10}$-decenoic acid discovered by Grün and Wirth⑵ as an extremely minor constituent of butter fat; the presence of decenoic acid in sperm head oil has so far never been known before the present experiment.

In a previous experiment⑶ of the separation of hexadecenol and tetradecenol in the unsaponifiable matter of sperm head oil, the liquid oil obtained by removing the crystalline solid was first subjected to the methanolysis, and

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* Translated from the Japanese text published in *J. Chem. Soc. Japan*, **56** (1935), 1313.

(1) This Bulletin, **10** (1935), 563, 570.

(2) *Ber.*, **55** (1922), 2197.

(3) This Bulletin, **10** (1935), 573.

the resulting mixture of methyl esters and free unsaponifiable matter was fractionated, by which a fraction boiling below 180°/15 mm. was separately collected. This fraction was saponified, and the fatty acids and the unsaponifiable matter were separated in the usual way.

Whilst the unsaponifiable matter was worked up further in the previous experiment, the fatty acids obtained above were used in the present experiment. They were fractionated, and a fatty acid fraction boiling below 160°/15 mm. was separated. For the separation of unsaturated acids, this fraction was treated by the bromo-ester distillation method of Grün and Janko.(4) In this method the fatty acid fraction was converted into the methyl esters, and then brominated in ethereal solution. The product was distilled under reduced pressure, by which the saturated methyl esters were removed as distillate. The residue containing the bromides derived from the unsaturated methyl esters was debrominated, and the product was saponified to regenerate the unsaturated acids, which were then fractionated to yield decenoic acid.

The decenoic acid thus obtained was converted into the methyl ester, and the latter was oxidised with potassium permanganate in acetone. After the oxidation products were saponified to liberate the free acid from the acid ester, azelaic acid $HOOC\cdot(CH_2)_7\cdot COOH$ was identified, and formic acid $H\cdot COOH$ was also detected. Accordingly the constitution of decenoic acid is to be represented by the formula $CH_2{=}CH\cdot(CH_2)_7\cdot COOH$. It is thus seen that decenoic acid in sperm head oil is identical with $\Delta^{9:10}$-decenoic acid which was found by Grün and Wirth in butter fat.(5)

## Experimental.

1. **Separation of Decenoic Acid.** In a previous experiment(3) of the separation of hexadecenol and tetradecenol, the sperm head oil having saponification value 147.7, iodine value (Wijs) 53.4 and unsaponifiable matter 36.52% was first pressed to remove the solid portion, and the liquid portion obtained in a yield of about 80% was subjected to the methanolysis. The product (10 kg.) consisting of the methyl esters and the free unsaponifiable matter was fractionated, and a fraction boiling below 180°/15 mm. was separately collected. This fraction was saponified, the resulting soap solution was extracted with

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(4) *Z. Deuts. Oel-u. Fett-Ind.*, **41** (1921), 553, 572.

(5) Grün stated that he and his co-workers found dodecenoic ($\Delta^{11:12}$-?) and tetradecenoic ($\Delta^{13:14}$-?) acids besides $\Delta^{9:10}$-decenoic acid in butter fat (*Z. angew. Chem.*, **37** (1924), 228). It should be noted that whilst decenoic acid in sperm head oil is found to be identical with that in butter fat, dodecenoic and tetradecenoic acids in sperm head oil were confirmed to be $\Delta^{5:6}$-dodecenoic (denticetic) and $\Delta^{5:6}$-tetradecenoic (physeteric) acids, respectively; neither $\Delta^{11:12}$-dodecenoic nor $\Delta^{13:14}$-tetradecenoic acid was found in sperm head oil.

ether, and the fatty acids and the unsaponifiable matter were separated in the usual way. Whilst the unsaponifiable matter was used for the isolation of hexadecenol and tetradecenol, the fatty acids were used for the present experiment. These were fractionated, and there was obtained 282 g. of a fraction boiling below 180°/15 mm. and having neutralisation value 301.9 and iodine value 26.2. This fatty acid fraction was refractionated, giving 61 g. of a fraction which distilled below 160°/15 mm. and had neutralisation value 338.2 and iodine value 18.3. This was converted into methyl esters, and the latter were brominated in ethereal solution under cooling with ice. After the ethereal solution had been freed from the excess of bromine by washing with sodium thiosulphate solution, it was washed with water and then dehydrated over anhydrous sodium sulphate. On distilling off the solvent from the ethereal solution, the product of bromination was distilled under 5 mm. When the distillation was continued up to 120°/5 mm., the rate of the distillation of saturated esters became very slow, and the operation was stopped. The residue containing the bromides derived from unsaturated esters was debrominated with zinc powder and sulphuric acid in methanol solution, and the product was saponified, yielding 9 g. of unsaturated acids. These were subjected to a further fractionation, by which the distillation began at 141°/15 mm., and 1.5 g. of a fraction boiling at 143–148°/15 mm. was separately collected as decenoic acid $C_{10}H_{18}O_2$ (Found: C, 70.47; H, 10.70. Calc. for $C_{10}H_{18}O_2$: C, 70.53; H, 10.66%). It had the following constants: $d_4^{15}$ 0.9238, $d_4^{20}$ 0.9203, $n_D^{15}$ 1.4507, $n_D^{20}$ 1.4488, molecular refraction (based on the data at 15°) 49.56 (calc. for $C_{10}H_{18}O_2 \models_1$: 49.45), neutralisation value 328.3 (calc. 329.7), iodine value 134.0 (calc. 149.2).

Hydrogenation of the decenoic acid yielded capric acid $C_{10}H_{20}O_2$ which, after being recrystallised from 70% alcohol, showed neutralisation value 325.1 (calc. 325.9), m.p. 30–30.5° and mixed m.p. 30.5–31°.(6) Unlike other mono-ethylenic acids, the decenoic acid yielded no crystalline dihydroxy derivative by oxidation with a dilute alkaline solution of potassium permanganate.

2. **Oxidation of Methyl Decenoate.** The decenoic acid obtained above was converted into the methyl ester by means of hydrogen chloride in methanol solution. The methyl ester (1.0 g.) was dissolved in 10 c.c. of acetone, and 4 g. of finely powdered potassium permanganate was added in small portions. After heating for 4 hours on the water-bath under reflux condenser the acetone was removed by distillation, and 30 c.c. of water was added to the residue. 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 with 300 c.c. of ether, and the ethereal solution was treated with potassium carbonate solution in order to dissolve out the acidic oxidation products as their potassium salts. The aqueous solution containing the potassium salts was heated on the water-bath with the addition of a little potassium hydroxide to saponify the acid ester. On decomposing the potassium salts with hydrochloric acid, the acidic substances liberated were taken up with ether. The ethereal solution was washed with brine, and ether was removed by distillation. The residue consisted mainly of a crystalline solid having a strong penetrating odour; yield 0.7 g. It was treated with petroleum ether, and the petroleum ether solution was separated from the insoluble portion. On distilling off the solvent from the petroleum ether solution, there was obtained a small amount of residue which had a smell of

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(6) The specimen of capric acid used for the mixed melting point test was separated from the seed oil of *Cinnamomum pedunculatum*; m.p. 30.5–31°.

formic acid and was soluble in water. The distillate of petroleum ether had also a smell of formic acid. On warming the aqueous solution of the residue with solutions of silver nitrate, metallic silver was deposited. When reduced with hydrochloric acid and metallic magnesium, the aqueous solution gave a smell of formaldehyde, the presence of which was confirmed by the violet colouration when the mixture of this solution, fresh milk and hydrochloric acid containing a trace of ferric chloride were heated gently.

The portion insoluble in petroleum ether yielded azelaic acid $C_9H_{16}O_4$ on recrystallisation from benzene; neutralisation value 594.2 (calc. 596.5), m.p. and mixed m.p. 105–106°(7) (Found: C, 57.28; H, 8.69. Calc. for $C_9H_{16}O_4$: C, 57.41; H, 8.57%).

## Summary.

A decenoic acid has been separated from sperm head oil. Its methyl ester was oxidised with potassium permanganate in acetone, and after the saponification of the acid ester contained in the oxidation products, azelaic acid was identified. The presence of formic acid in the oxidation products was also indicated. Accordingly the decenoic acid in sperm head oil is proved to be $\Delta^{9:10}$-decenoic acid, having the formula $CH_2{=}CH{\cdot}(CH_2)_7{\cdot}COOH$.

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7) The specimen of azelaic acid used for the mixed melting point test was prepared by the ozonolysis of oleic acid; m.p. 105–106°.