HEXADECENOL AND TETRADECENOL IN SPERM HEAD OIL.*

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The higher alcohols contained in the unsaponifiable matter of sperm oil have hitherto been studied by many authors, among whom Tsujimoto,(1)

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(1) *J. Soc. Chem. Ind., Japan*, **24** (1921), 41.

André and François,(2) and Hilditch and Lovern(3) deserve a special mention. For a thorough description 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. hexadecenol $C_{16}H_{32}O$ and tetradecenol $C_{14}H_{28}O$ in sperm oil, is given below. Tsujimoto stated the possible existence of hexadecenol in sperm head oil, but he found no tetradecenol. André and François, in their studies on the unsaturated alcohols of sperm head oil, found neither hexadecenol nor tetradecenol. Hilditch and Lovern found 4% of hexadecenol in the unsaponifiable matter of sperm head oil, but no hexadecenol in sperm blubber oil. One of us (Toyama)(4) concluded in his previous study that hexadecenol could have been present, if any, only in a very minute amount in sperm blubber oil. The foregoing notes show that though the presence of hexadecenol in sperm oil has been pointed out by a few authors, it has not been isolated with certainty, and nothing is known of its constitution. Tetradecenol has so far never been found in sperm oil and other fatty oils.

In the experiments of the separation of denticetic acid ($\Delta^{5:6}$-dodecenoic acid) from sperm head oil, as described in the preceding paper,(5) the product of methanolysis consisting of the methyl esters and the free unsaponifiable matter was first fractionated. The fatty acids and the unsaponifiable matter were separated from the lowest fraction boiling below 150°/15 mm. Whilst the fatty acids were worked up further for the separation of dodecenoic acid, a comparatively high iodine value of the unsaponifiable matter pointed to the possible presence of some lower members of unsaturated alcohols, besides oleyl alcohol, in sperm head oil. Accordingly the present experiments have been carried out with the object of separating these lower members of unsaturated alcohols starting with a large quantity of sperm head oil. For these purposes, sperm head oil was converted into a mixture of methyl esters and free unsaponifiable matter by methanolysis, and the mixture was fractionally distilled. From the fraction boiling below 180°/15 mm. the unsaponifiable matter was separated and then acetylated. The acetates thus obtained were brominated, and the product was distilled so as to remove the saturated acetates as distillate, leaving the bromides of unsaturated acetates as residue. This was debrominated and reconverted into the unsaturated acetates, from which hexadecenyl acetate and tetradecenyl acetate were separated on fractionation. Saponification of the acetates yielded hexadecenol

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

(3) *J. Soc. Chem. Ind.*, **48** (1929), 365.

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

(5) This Bulletin, **10** (1935), 570.

and tetradecenol which, however, were contaminated with a small proportion of saturated alcohols. A complete removal of the latter was not attained in these experiments.

For the determination of the position of ethylenic linking in two alcohols, the acetates were oxidised with potassium permanganate in glacial acetic acid. Hexadecenyl acetate yielded *n*-heptoic acid $CH_3\cdot(CH_2)_5\cdot COOH$ and acetyl-hydroxynonoic acid $HOOC\cdot(CH_2)_7\cdot CH_2O\cdot COCH_3$; hydroxynonoic acid liberated from its acetyl ester yielded, on further oxidation, azelaic acid $HOOC\cdot(CH_2)_7\cdot COOH$. Tetradecenyl acetate yielded, on subsequent saponification of the ester in the oxidation products, *n*-nonoic acid $CH_3\cdot(CH_2)_7\cdot COOH$ and hydroxyvaleric acid $HOOC\cdot(CH_2)_3\cdot CH_2OH$; the latter yielded on further oxidation glutaric acid $HOOC\cdot(CH_2)_3\cdot COOH$. From these results the following constitutions were established:

Hexadecenol $CH_3\cdot(CH_2)_5\cdot CH{=}CH\cdot(CH_2)_7\cdot CH_2OH$,
Tetradecenol $CH_3\cdot(CH_2)_7\cdot CH{=}CH\cdot(CH_2)_3\cdot CH_2OH$.

According to the above constitutions, hexadecenol in sperm head oil corresponds to zoomaric acid ($\Delta^{9:10}$-hexadecenoic acid) which is of common occurrence in marine animal oils, and tetradecenol in sperm head oil corresponds to physeteric acid ($\Delta^{5:6}$-tetradecenoic acid) found in sperm oil. A similar relation exists between oleyl alcohol ($\Delta^{9:10}$-octadecenol) found in sperm oil and some other marine animal oils and oleic acid ($\Delta^{9:10}$-octadecenoic acid). It is, therefore, advisable to designate hexadecenol and tetradecenol in sperm head oil as zoomaryl alcohol and physeteryl alcohol respectively.

Experimental.

1. **Separation of Hexadecenol.** The same specimen of sperm head oil(6) as used for the separation of denticetic acid was employed for the present experiments. The oil was pressed at the room temperature to remove the solid portion, and the liquid portion was subjected to methanolysis by means of methanol containing sodium hydroxide. The product of methanolysis (10 kg.), consisting of the methyl esters and the free unsaponifiable matter, was distilled, the fraction boiling below 180°/15 mm. was separated and saponified, and the soap solution was treated with ether for the extraction of unsaponifiable matter. The yield of unsaponifiable matter was 357 g. It was acetylated by heating with acetic anhydride. The resulting acetates (410 g.) having saponification value 206.6 and iodine value (Wijs) 24.3 were dissolved in 4 l. of ether, and a little excess of bromine was gradually added with constant stirring under cooling with ice. The excess of bromine was removed from the ethereal solution by washing with sodium thiosulphate solution, and the ethereal solution was then washed with water and dehydrated. On removal of ether, the product of bromination was subjected to distillation. The rate of

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(6) This Bulletin, **10** (1935), 570.

the distillation of saturated acetates became very slow at about 180°/2 mm. when the distillation was discontinued, and there was obtained 160 g. of residue consisting of the bromides of unsaturated acetates. It was dissolved in 250 c c. of methanol, 160 g. of zinc powder was added, and the liquid was heated on the water-bath under a reflux condenser, while 250 c.c. of 5 N hydrogen chloride in methanol was gradually added. After heating for one hour, the insoluble residue was filtered off, the filtrate was diluted with a large quantity of water, and the debrominated product was extracted with ether. The insoluble residue was washed thoroughly with ether, and the washing was added to the main ethereal solution. After washing with water and subsequent removal of ether from the united ethereal solution, the residue was heated with acetic anhydride to regenerate acetates since it was found that the hydrolysis of acetates had taken place in the course of debromination with the formation of free alcohols. The acetates (97 g.) thus obtained was fractionally distilled up to 200°/15 mm., and the following fractions were separately collected.

Fraction	B.p. /15 mm.	Saponif. value	Iodine value	n_D^{20}	Yield (g.)
(1)	Below 160°	—	—	—	1.1
(2)	160 – 175°	215.7	91.1	1.4459	4.5
(3)	175 – 185°	209.2	87.1	1.4469	5.4
(4)	185 – 195°	200.3	84.3	1.4477	15.0
(5)	195 – 200°	195.2	82.2	1.4486	40.1
Residue and loss	—	—	—	—	30.9

The fraction (4) was subjected to a further fractionation, by which the portion boiling above 195°/15 mm. was separated. This was united with the fraction (5), and repeatedly fractionated, by which 12.2 g. of a fraction boiling at 195–198°/15 mm. and having the following constants was separated as hexadecenyl acetate $C_{18}H_{34}O_2$.

d_4^{15} 0.8760, d_4^{20} 0.8725, n_D^{15} 1.4506, n_D^{20} 1.4486, mol. refraction (based on the data at 15°) 86.70 (calc. for $C_{18}H_{34}O_2$ $\vDash_1$: 86.51), saponif. value 197.5 (calc. 198.8), iodine value 83.2 (calc. 89.9).

Hexadecenol obtained by saponification of the acetate showed the following constants (Found: C, 79.91; H, 13.45. Calc. for $C_{16}H_{32}O$: C, 79.91; H, 13.42%).

d_4^{15} 0.8537, d_4^{20} 0.8503, n_D^{15} 1.4605, n_D^{20} 1.4584, mol. refraction (based on the data at 15°) 77.15 (calc. for $C_{16}H_{32}O$ $\vDash_1$: 77.14), iodine value 98.6 (calc. 105.7).

The hydrogenation product of hexadecenol crystallised from 90% alcohol in lustrous laminae which showed acetyl value 197.1 (calc. for cetyl alcohol $C_{16}H_{34}O$: 197.4) and melted at 49.5–50° both alone or admixed with cetyl alcohol. On oxidising the hydrogenation product with chromic acid in glacial acetic acid, it yielded palmitic acid $C_{16}H_{32}O_2$; neutr. value 218.1 (calc. 219.0), m.p. and mixed m.p. 62–62.5°.

2. **Oxidation of Hexadecenyl Acetate.** Ten grams of hexadecenyl acetate was dissolved in 100 g. of glacial acetic acid, and 20 g. of powdered potassium permanganate was added in small portions. After heating for one hour on the water-bath under a reflux condenser,

the solution was diluted with water, and the oxidation products were extracted with a large quantity of ether. After a portion of the solvent had been distilled off, the ethereal solution was shaken with potassium carbonate solution which separated the acidic substances as their potassium salts from the neutral substances remaining in the ethereal solution. The aqueous solution containing potassium salts was acidified with hydrochloric acid, the liberated acidic substances were taken up with ether, and the ethereal solution was washed with water until the acidity of the washing became very faint. On removal of ether, there was obtained 6.5 g. of acidic substances. A comparatively low yield may be attributed to an incomplete oxidation with potassium permanganate or to the loss caused by washing the ethereal solution with water. These were distilled; 1.8 g. of a fraction (a) boiling below 185°/100 mm. was first separated, and then the distillation was carried out under a lower pressure, giving 3.1 g. of a fraction (b) boiling below 198°/5 mm.

The fraction (a) was redistilled, and a fraction boiling below 170°/100 mm. was collected. It was washed with a little water for the removal of the contaminated acetic acid, and the remaining liquid showed neutr. value 433.2 (calc. for $C_7H_{14}O_2$: 431.2) and n_D^{20} 1.4217, and was identified as *n*-heptoic acid by preparing its amide which, after being recrystallised from petroleum ether, melted at 94.5–95° both alone or admixed with *n*-heptoic acid amide(7) (Found: N, 10.70. Calc. for $C_7H_{15}ON$: N, 10.85%).

On subjecting the fraction (b) to a further fractionation, a fraction boiling at 200–204°/15 mm. was separated which was found to be acetyl-hydroxynonoic acid $C_{11}H_{20}O_4$.

d_4^{20} 1.0187, n_D^{20} 1.4462, mol. refraction 56.61 (calc. for $C_{11}H_{20}O_4$: 56.19), neutr. value 255.1 (calc. 259.6), saponif. value 509.4 (calc. 519.1).

Hydroxynonoic acid $C_9H_{18}O_3$ obtained by saponification of its acetyl derivative was a viscous oil having neutr. value 315.3 (calc. 322.2). Oxidation of hydroxynonoic acid with chromic acid in glacial acetic acid gave a solid product. It was taken up with ether, the ethereal solution was washed with water containing sodium chloride, and after distilling off ether from the ethereal solution the residue was recrystallised from water, yielding azelaic acid $C_9H_{16}O_4$ which had neutr. value 594.5 (calc. 596.5), m.p. 104–105°, and mixed m.p. 105–106°(8) (Found: C, 57.30; H, 8.50. Calc. for $C_9H_{16}O_4$: C, 57.41; H, 8.57%).

3. **Separation of Tetradecenol.** As described above, 97 g. of unsaturated acetates were fractionated, and five fractions (1)–(5) were separately collected. For the separation of tetradecenol, the fraction (2) and the portion boiling below 175°/15 mm. obtained by a repeated fractionation of the fraction (3) were combined and subjected to a further fractionation, and there was obtained 3.4 g. of a fraction boiling at 165–170°/15 mm. as tetradecenyl acetate $C_{16}H_{30}O_2$. It had the following constants.

d_4^{15} 0.8729, d_4^{20} 0.8694, n_D^{15} 1.4477, n_D^{20} 1.4457, mol. refraction (based on the data at 15°) 77.93 (calc. for $C_{16}H_{30}O_2$ ╒$_1$: 77.28), saponif. value 218.2 (calc. 220.7), iodine value 92.7 (calc. 99.8).

Tetradecenol $C_{14}H_{28}O$ liberated from its acetate showed the following constants (Found: C, 79.29; H, 13.23. Calc. for $C_{14}H_{28}O$: C, 79.16; H, 13.30%).

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(7) The specimen used for the mixed melting point test was prepared in the following way: castor oil was first subjected to dry distillation, and a fraction corresponding to *n*-heptyl aldehyde was separated. The latter was oxidised into *n*-heptoic acid, which was then converted into the amide; m.p. 94.5–95°.

(8) Azelaic acid used for the mixed melting point test was obtained by the ozonolysis of oleic acid.

d_4^{15} 0.8507, d_4^{20} 0.8473, n_D^{15} 1.4573, n_D^{20} 1.4553, mol. refraction (based on the data at 15°) 67.98 (calc. for $C_{14}H_{28}O\,\overline{\overline{|}}_1$: 67.91), iodine value 111.2 (calc. 119.6).

When hydrogenated, tetradecenol yielded a crystalline solid which on recrystallisation from 80% alcohol melted at 37–37.5°. The melting point is nearly the same as recorded for *n*-tetradecanol (38°).(9) On oxidising the hydrogenation product with chromic acid in glacial acetic acid, it yielded myristic acid $C_{14}H_{28}O_2$ which, after being recrystallised from 80% alcohol, showed neutr. value 244.2 (calc. 245.8), m.p. and mixed m.p. 53.5–54°.

4. **Oxidation of Tetradecenyl Acetate.** Tetradecenyl acetate (2.7 g.) was dissolved in 27 g. of glacial acetic acid, 6 g. of powdered potassium permanganate was added, and the solution was heated on the water-bath under a reflux condenser for 2 hours. Water was then added, the oxidation products were extracted with a large quantity of ether, and the ethereal solution was concentrated and shaken with potassium carbonate solution. By these treatments acidic substances were converted into their potassium salts and separated from the ethereal solution, while the neutral substances which escaped oxidation remained in the ethereal solution. The aqueous solution containing potassium salts was heated with the addition of potassium hydroxide on the water-bath in order to saponify the ester. The free acidic substances liberated on acidification with hydrochloric acid was once taken up with ether, the ethereal solution was washed with water containing sodium chloride, and then the ether was driven off. The acidic substances (2.2 g.) thus obtained were treated with a little water, yielding the aqueous solution and the insoluble portion.

The insoluble portion (1.2 g.) was distilled, and a fraction boiling below 195°/100 mm. was separated. It showed neutr. value 358.1 (calc. for $C_9H_{18}O_2$: 354.8) and n_D^{20} 1.4322. Its amide, when recrystallised from 50% alcohol, melted at 97.5–98°. The melting point was not lowered when the substance was admixed with varying proportions of a pure specimen of *n*-nonoic acid amide,(10) m.p. 98.5–99°.

Sodium chloride was added to the aqueous solution separated from the insoluble portion, and the solution was shaken with ether. On removal of ether from the ethereal solution, the residue was treated with petroleum ether, and the insoluble portion was separated which consisted of an oily liquid and had neutr. value 482.1 (calc. for hydroxyvaleric acid $C_5H_{10}O_3$: 475.2). This was subjected to oxidation with chromic acid in glacial acetic acid, and the product was collected by using ether. The residue obtained by distilling off ether was recrystallised from benzene, yielding crystals of m.p. 96–96.5°. The melting point was not lowered when the crystals were admixed with varying proportions of glutaric acid (m.p. 97.5-98°).

Summary.

Hexadecenol and tetradecenol have been isolated from the unsaponifiable matter of sperm head oil, and the acetates of these alcohols have been oxidised with potassium permanganate in glacial acetic acid. From the results of an examination of the oxidation products, the constitutions of these alcohols have been established as follows:

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(9) "Beilsteins Handbuch der organischen Chemie", 4th Ed., I, 428.

(10) Prepared from *n*-nonoic acid which was obtained by the ozonolysis of oleic acid.

$\Delta^{9:10}$-Hexadecenol (zoomaryl alcohol)	$CH_3\cdot(CH_2)_5CH{=}CH\cdot(CH_2)_7\cdot CH_2OH$
$\Delta^{5:6}$-Tetradecenol (physeteryl alcohol)	$CH_3\cdot(CH_2)_7CH{=}CH\cdot(CH_2)_3\cdot CH_2OH$

It is thus seen that hexadecenol and tetradecenol in sperm head oil are the mono-ethylenic alcohols corresponding to zoomaric acid ($\Delta^{9:10}$-hexadecenoic acid) and physeteric acid ($\Delta^{5:6}$-tetradecenoic acid) respectively.

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