HEXADECENOL IN SPERM BLUBBER OIL.*

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In a previous study on the unsaponifiable matter of sperm blubber oil by one of us (Toyama),(1) oleyl alcohol, cetyl alcohol and octadecyl alcohol were separated, and the presence of cholesterol in a small proportion was also indicated. Other minor components were, however, not closely studied; hexadecenol was not separated and it was thought that this alcohol could have been present, if any, only in an extremely small amount. We have now made a closer examination of the minor components of the unsaponifiable matter of sperm blubber oil. The present paper deals with the experimental results concerning hexadecenol.

The higher aliphatic alcohols are now being produced on industrial scale by the high pressure hydrogenation of the corresponding fatty acids or their esters, and find a wide application in the industrial field. On the other hand, sperm oil has recently attracted much interest owing to its high content of higher alcohols, and the methods of the separation of these higher alcohols from sperm oil have been much studied. A method is now being carried out on industrial scale in this country. Furthermore, it should be noted that the unsaturated higher alcohols, such as oleyl alcohol which is contained in sperm blubber oil in a large proportion, appear not to have been obtained as yet by the high pressure hydrogenation of the corresponding fatty acids or their

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

esters, and consequently sperm blubber oil seems to be the only important raw material of the unsaturated alcohols. Under these circumstances, it is desirable, also from the industrial point of view, to gain a fuller information on the unsaturated alcohols in sperm blubber oil.

In these experiments, the unsaponifiable matter was first prepared by heating the sperm blubber oil with barium hydroxide and water under pressure and by subsequent extraction of the product consisting of barium soaps and free unsaponifiable matter with acetone. The acetone extract thus obtained was, however, contaminated with a small amount of barium soaps and unsaponified oil. It was, therefore, refluxed with alcoholic potash to effect a complete saponification of the contaminated oil, after which the product was acidified with hydrochloric acid. The resulting unsaponifiable matter which was contaminated with free fatty acids was taken up with ether, the ethereal solution was washed with an aqueous solution of potassium hydroxide containing a little alcohol in order to remove the free fatty acids as their potassium soaps, and the unsaponifiable matter was obtained from the ethereal solution. The unsaponifiable matter (10 kg.) thus obtained was fractionally distilled, the fraction boiling below 188°/ca. 5 mm. was separated, and the solid portion was removed by cooling the fraction dissolved in acetone. The liquid portion was converted into acetates and fractionated. The higher fraction was removed, and the lower fraction was saponified to yield free alcohols, from which a further quantity of solid portion was removed on cooling the acetone solution. The liquid portion was subjected to a further fractional distillation, by which the fraction boiling below 200°/15 mm. was separately collected. This fraction still contained a considerable amount of saturated alcohols. For a further removal of saturated alcohols, it was converted into acetates and then brominated. The product was distilled so as to remove the saturated acetates as distillate, leaving the bromides of unsaturated acetates as residue which was then debrominated to regenerate the unsaturated acetates. These were saponified, and the free alcohols were subjected to a further distillation in order to remove the high boiling portions. Since the lower fraction was suspected to be contaminated with some hydrocarbons, it was treated with 85% methanol, the insoluble portion removed, and the soluble portion separated. After repeated fractionation there was obtained a fraction corresponding to hexadecenol. The actual yield was only 16 g., but the total quantity contained in the unsaponifiable matter used for these experiments would be far larger than the actual yield. The presence of tetradecenol was not ascertained in these experiments; it could have been present, if any, in a far smaller amount than hexadecenol.

The acetate of hexadecenol was oxidised with potassium permanganate in acetone. Among the oxidation products, *n*-heptoic acid $CH_3\cdot(CH_2)_5\cdot COOH$ and acetyl-hydroxynonoic acid $HOOC\cdot(CH_2)_7\cdot CH_2O\cdot COCH_3$ were identified. Further oxidation of hydroxynonoic acid, obtained by saponification of its acetate, with chromic acid in acetic acid yielded azelaic acid $HOOC\cdot(CH_2)_7\cdot COOH$. Hence, the constitution of hexadecenol is represented by the formula $CH_3\cdot(CH_2)_5\cdot CH{=}CH\cdot(CH_2)_7\cdot CH_2OH$. It is thus seen that hexadecenol in sperm blubber oil is identical with zoomaryl alcohol ($\Delta^{9:10}$-hexadecenol) in sperm head oil.

Experimental.

1. **Separation of Unsaponifiable Matter.** Sperm blubber oil used for these experiments was procured from the Nihon Hogei K. K. (Japan Whaling Co., Ltd.) and had d_4^{25} 0.8735, n_D^{25} 1.4635, acid value 0.85, saponification value 123.8, iodine value (Wijs) 82.6 and unsaponifiable matter 38.98%. It deposited a large amount of crystalline solid at the room temperature. The unsaponifiable matter was separated in the following way: every 1 kg. of the oil was mixed with 400 g. of crystalline barium hydroxide (corresponding to an excess of 12%) and 1 l. of water, and the mixture was heated for one hour under 5–6 atm. in an autoclave. The product was taken out from the autoclave, squeezed for the removal of water as far as possible, then mixed with anhydrous sodium sulphate, cut into small pieces and extracted with acetone in an extractor. The acetone extract containing unsaponifiable matter was contaminated with a small amount of barium soaps and unsaponified oil, and on removal of acetone the residue was refluxed with an excess of alcoholic potash in order to effect a complete saponification. The product was then acidified with hydrochloric acid, and the unsaponifiable matter together with a small proportion of free fatty acids were taken up with ether. The ethereal solution was washed with an aqueous solution of potassium hydroxide containing a little alcohol, and the free fatty acids were converted into potassium soaps which were separated from the ethereal solution. The latter was thoroughly washed with water, and the solvent was removed by distillation. The yield of unsaponifiable matter was 10,120 g. (or 36.1%) from 28 kg. of the oil. It had d_4^{25} 0.8443, n_D^{25} 1.4572, acetyl value 186.8 and iodine value 73.9, and deposited a large amount of crystalline solid at the room temperature so that it was not mobile.

2. **Fractionation of Unsaponifiable Matter and Removal of Solid Portion.** The unsaponifiable matter obtained above was subjected to a fractional distillation. A batch of 530 g. was taken in each distillation, and 5 fractions were separately collected; fractions (1) and (2) were collected in an amount of 100 c.c. by volume, fraction (3) 200 c.c., fraction (4) 100 c.c., and fraction (5) consisted of the remainder of the distillate which was obtained by continuing the distillation until nearly nothing distilled further. The pressure was not maintained exactly at 5 mm. in each run, and consequently the boiling points given below were not estimated exactly in the same way in each run. The following results were obtained from 10,070 g. in total.

Fraction	B.p. / 5 mm.	Iodine value	Yield (g.)
(1)	Below 188°	51.8	1,600
(2)	188 – 190°	57.5	1,600
(3)	190 – 192°	68.4	3,190
(4)	192 – 195°	80.6	1,580
(5)	195 – 198°	96.8	1,680
Residue and loss	—	—	420

Fraction (1) was dissolved in 16 l. of 95% acetone, kept at 5–7° over a night, and the crystalline deposit formed was filtered off. It had iodine value 11.5, while the liquid portion (1,140 g.) obtained from the filtrate had iodine value 68.1. The latter was acetylated by heating with acetic anhydride, and the acetates having saponif. value 185.6 were distilled, yielding 829 g. of a fraction boiling below 212°/15 mm. This was saponified, and the free alcohols liberated were dissolved in 95% acetone as before and kept at 0° over a night. The solid portion was removed by filtration, and there was obtained 610 g. of the liquid portion from the filtrate which was then distilled, yielding 338 g. of a fraction boiling below 200°/15 mm. For a further removal of solid portion from this fraction it was dissolved in 95% acetone, cooled down to —10°, and the solid deposit was filtered off. The liquid portion (238 g.) obtained from the filtrate was then dissolved in 90% acetone, cooled down to —12°, and on removal of a further quantity of solid deposit, there was obtained 208 g. of liquid portion from the filtrate. It was distilled once more, and 160 g. of a fraction boiling below 200°/15 mm. and having iodine value 71.2 was separately collected.

3. **Separation of Hexadecenol.** The fraction described above, boiling below 200°/15 mm., was converted into the acetates. These (188 g.) were dissolved in 1.9 l. of ether, cooled down to —10°, and bromine (80 g.) in a slight excess was gradually added with constant stirring in the course of two hours. After standing for a short time, the excess of bromine was removed by washing with sodium thiosulphate solution, and then the ether was distilled off from the solution, giving 257 g. of the product of bromination which consisted of the unchanged saturated acetates and the bromides derived from unsaturated acetates. It was then subjected to distillation in order to drive off the saturated acetates. The distillation was continued up to 160°/2 mm., when the rate of distillation became very slow, and the operation was discontinued. Yield of the residual bromides 198 g. These were mixed with 200 g. of zinc powder, and 300 c.c. of methanol was added. The mixture was heated on the water-bath under a reflux condenser with the addition of 300 c.c. of 5 N hydrogen chloride in methanol in the course of 30 minutes, and after heating for 30 minutes more, the mixture was diluted with water. The oily substances separated were taken up with ether, and the ethereal solution was washed with water and then distilled. The debrominated products thus obtained were found to consist largely of free alcohols formed by the hydrolysis of acetates. They were reconverted into acetates by heating with acetic anhydride, and the latter distilled giving 116 g. of a fraction boiling below 215°/15 mm. The free alcohols obtained by saponifying this

fraction was distilled once more, giving 84 g. of a fraction boiling below 200°/15 mm. By these distillations, there was an indication of contamination of hydrocarbons in the fraction boiling below 200°/15 mm., especially in the lowest boiling portion. In an attempt to remove hydrocarbons the fraction boiling below 200°/15 mm. was shaken out with 900 c.c. of 85% methanol, kept at the room temperature over a night, and separated into the soluble and the insoluble portions. Each portion had the following constants, and the hydrocarbons seemed to be concentrated in the insoluble portion to a certain extent.

	Yield (g)	Iodine value	Acetyl value
Insoluble portion	17.4	95.1	192.4
Soluble portion	64.6	96.7	196.0

The soluble portion was distilled once more, giving 51 g. of a fraction boiling below 197°/15 mm. It was still contaminated with a small proportion of saturated compounds. It was dissolved in 370 c.c. of 90% acetone and cooled down to $-20°$, by which a small amount of solid deposit was formed. The liquid portion obtained from the filtrate was then subjected to a repeated fractionation, and 16 g. of a fraction boiling at 187–190°/15 mm. was finally separated as hexadecenol $C_{16}H_{32}O$.(2)

d_4^{15} 0.8534, n_D^{15} 1.4600, mol. refraction 77.11 (calc. for $C_{16}H_{32}O \models_1$: 77.14), iodine value 98.0 (calc. 105.7).

Hydrogenation of hexadecenol yielded cetyl alcohol $C_{16}H_{34}O$ which showed acetyl value 197.2 (calc. 197.4), m.p. and mixed m.p. 49.5° after recrystallisation from 95% alcohol. Hexadecenyl acetate $C_{18}H_{34}O_2$ obtained by heating hexadecenol with acetic anhydride had the following constants.

d_4^{15} 0.8760, n_D^{15} 1.4508, mol. refraction 86.73 (calc. for $C_{18}H_{34}O_2 \models_1$: 86.51), saponif. value 196.8 (calc. 198.8), iodine value 83.5 (calc. 89.9).

4. **Oxidation of Hexadecenyl Acetate.** Ten grams of hexadecenyl acetate was dissolved in 100 c.c. of acetone, and the solution was heated on the water-bath under reflux condenser with the addition of 30 g. of powdered potassium permanganate in the course of 40 minutes, and the heating was continued for 30 minutes more. Water (250 c.c.) was then added, 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 1 l. of ether in order to extract the oxidation products, and the ethereal solution was then treated with potassium carbonate solution which dissolved out the acidic oxidation products as their potassium salts, leaving the neutral substances in ethereal solution. On removal of ether, there remained 3.2 g. of neutral substances. The aqueous solution containing potassium salts was acidified with hydrochloric acid, the acidic substances liberated were taken up with ether, the ethereal solution

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(2) The fraction boiling below 187°/15 mm. was obtained with a yield of 15 g., and had acetyl value 196.1. Though the comparatively low acetyl value might be attributed to a contamination of hydrocarbons, tetradecenol was considered to be present, if any, only in a far smaller amount than hexadecenol in sperm blubber oil.

was washed with water containing sodium chloride, and on distilling off ether from the solution, there was obtained 7.7 g. of acidic substances as an orange yellow liquid. It was fractionated; the fraction (a) boiling below 160°/100 mm., 1.6 g., was first separated, then the fractionation was continued under a lower pressure, and after the fraction boiling below 160°/5 mm., 2.0 g., was set apart, the fraction (b) boiling at 160–190°/5 mm., 2.0 g., was separated. On refractionation of the fraction (a), the portion boiling below 160°/100 mm. was separated which had neutr. value 431.5 (calc. for $C_7H_{14}O_2$: 431.2). The amide prepared from it melted at 94-94.5° after recrystallisation from petroleum ether and no depression of melting point was observed when the substance was admixed with a pure specimen of *n*-heptoic acid amide.(3)

The fraction (b) had neutr. value 269.0 and saponif. value 507.5, and was thought to consist mainly of acetyl-hydroxynonoic acid $C_{11}H_{20}O_4$ (neutr. value 259.6 and saponif. value 519.1). The free hydroxy-acid obtained on saponification of the acetate was purified by washing with petroleum ether, yielding hydroxynonoic acid $C_9H_{18}O_3$ as a faintly yellow, viscous oil having neutr. value 329.2 (calc. 322.2). Acetyl-hydroxynonoic acid regenerated by heating the free hydroxynonoic acid with acetic anhydride showed neutr. value 261.2 and saponif. value 513.5. For a further oxidation of hydroxynonoic acid, 0.8 g. of the substance was dissolved in 30 c.c. of glacial acetic acid, and the solution was heated with the addition of 5 g. of chromic acid on the water-bath under reflux condenser for two hours. The oxidation products were once taken up with 400 c.c. of ether, and after the ethereal solution being washed with water, the ether was removed by distillation, yielding a crystalline residue from which azelaic acid $C_9H_{16}O_4$ was obtained on recrystallising from water; neutr. value 591.2 (calc. 596.5), m.p. and mixed m.p. 105-106°.(4)

Summary.

Hexadecenol has been separated, in a very small yield, from the unsaponifiable matter of sperm blubber oil, and its constitution has been established as $CH_3\cdot(CH_2)_5\cdot CH{=}CH\cdot(CH_2)_7\cdot CH_2OH$. Hence, hexadecenol in sperm blubber oil is proved to be identical with zoomaryl alcohol ($\Delta^{9:10}$-hexadecenol) previously found in sperm head oil.

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(3) *n*-Heptyl aldehyde was separated from the product of dry distillation of castor oil. It was then oxidised into *n*-heptoic acid, from which the amide was prepared; m.p. 94.5–95°.

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