THE HIGHLY UNSATURATED ALCOHOLS IN SPERM BLUBBER OIL.*

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

In a former study on the unsaponifiable matter of sperm blubber oil, one of the authors[1] separated and identified oleyl alcohol as the chief constituent together with such substances as cetyl alcohol, octadecanol and cholesterol, but other unsaponifiable constituents present in a minor proportion were not closely examined. Later, we[2] have attempted to separate and investigate these minor constituents, and recently described the results of our experi-

* Translated from the Japanese text published in *J. Chem. Soc. Japan*, **56** (1935), 1316.

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

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

ments in which zoomaryl alcohol ($\Delta^{9:10}$-hexadecenol) was separated and its constitution was established. The present paper deals with the highly unsaturated alcohols which are present as minor constituents in the unsaponifiable matter of this oil. A review of the literature shows that the following facts have hitherto been reported in connection with the highly unsaturated alcohols in sperm oil. One of the authors, in his previous study on the unsaponifiable matter of sperm blubber oil, indicated the presence of some highly unsaturated alcohols by the fact that bromination of a fraction of the unsaponifiable matter of this oil yielded a small amount of ether insoluble bromides and also petroleum ether insoluble bromides having high Br-contents. Also Hilditch and Lovern[3] stated the presence of some highly unsaturated alcohols (mainly di-ethylenic) among C_{18}- and C_{20}-unsaturated alcohols in sperm blubber oil. According to André and François[4] the liquid fraction of the unsaponifiable matter of sperm oil contains, in addition to oleyl alcohol, alcohols of higher molecular weight and higher unsaturation than oleyl alcohol, and yields a petroleum ether insoluble bromide having the formula $C_{22}H_{42}OBr_4$. It is thus seen that, although the presence of some highly unsaturated alcohols has already been pointed out by several authors, our knowledge of the individual constituents of these highly unsaturated alcohols has hitherto been scanty.

In the previous experiment of the separation of zoomaryl alcohol in sperm blubber oil, the unsaponifiable matter of this oil was separated into 5 fractions by fractional distillation, and the lowest fraction boiling below 188°/5 mm. was worked up further for the isolation of zoomaryl alcohol. Since the highly unsaturated alcohols originally present in the unsaponifiable matter in a small proportion were deemed to have been concentrated in the highest fraction, the latter was used for the present experiment. A small amount of solid saturated alcohols was removed from this fraction, and the liquid alcohols were brominated. The ether insoluble bromides were separated and then debrominated to regenerate the highly unsaturated alcohols. These were then converted into acetates, and the latter were separated into 12 fractions by fractional distillation. The 3rd fraction had saponification and iodine values which agreed with those calculated for the acetate ($C_{22}H_{36}O_2$) of a highly unsaturated alcohol $C_{20}H_{34}O$. The free alcohol obtained on saponification of this fraction showed an elementary composition which corresponded to the formula $C_{20}H_{34}O$, and yielded on bromination an ether insoluble bromide of the formula $C_{20}H_{34}OBr_8$. The 1st and 2nd fractions showed saponification values which were a little higher than the value calculated for $C_{22}H_{36}O_2$, and

(3) *J. Soc. Chem. Ind.*, **48** (1929), 365 T.
(4) *Compt. rend.*, **185** (1927), 279.

consequently these fractions were thought to contain, in addition to the acetate of $C_{20}H_{34}O$, the acetates of some highly unsaturated alcohols of lower molecular weight (possibly the acetates of $C_{18}H_{32}O$ and $C_{18}H_{30}O$). A saturated alcohol $C_{20}H_{42}O$ was separated from the hydrogenation product of the free alcohols from the 1st–3rd fractions, and it was oxidised with chromic acid, yielding arachidic acid $C_{20}H_{40}O_2$. Accordingly the highly unsaturated alcohol $C_{20}H_{34}O$, which is present as its acetate in these fractions, is a primary alcohol having no branched chain of carbon atoms. The 12th fraction showed a saponification value which was a little higher than that calculated for the acetate ($C_{24}H_{38}O_2$) of an alcohol $C_{22}H_{36}O$, but the iodine value of this fraction agreed with the value calculated for $C_{24}H_{38}O_2$. The free alcohol yielded an ether insoluble bromide having the formula $C_{22}H_{36}OBr_{10}$. Hence the alcohol, which was present as its acetate in the 12th fraction, was deemed to consist mainly of $C_{22}H_{36}O$. The fact that the saponification value of the 12th fraction was higher than the value calculated for $C_{24}H_{38}O_2$ is presumably ascribed to the contamination of the acetates of some polyvalent alcohols (possibly some highly unsaturated alcohols belonging to the selachyl alcohol group). A further investigation is yet wanted to confirm these postulations. The hydrogenation product of the free alcohol yielded, after repeated recrystallisation, a saturated alcohol which showed an acetyl value corresponding to $C_{22}H_{46}O$.

It is thus seen from the results of the present experiment that the highly unsaturated alcohols in the unsaponifiable matter of sperm blubber oil contain two alcohols $C_{20}H_{34}O$ and $C_{22}H_{36}O$ as chief constituents. These two alcohols have the formula just corresponding to eicosatetraenoic acid $C_{20}H_{32}O_2$ and clupanodonic acid $C_{22}H_{34}O_2$ which occur in sperm blubber and other marine animal oils as chief constituents of highly unsaturated acids. Although no individual constituents of highly unsaturated alcohols other than $C_{20}H_{34}O$ and $C_{22}H_{36}O$ have been found with certainty in the present experiment, it is very probable that a further investigation, starting with a large quantity of material, may bring out a sufficient evidence for the presence of several individual constituents of highly unsaturated alcohols corresponding to those of highly unsaturated acids in marine animal oils. Postulating from the relations of the constitutions of physeteryl and zoomaryl alcohols[5] and the corresponding fatty acids in marine animal oils, two highly unsaturated alcohols $C_{20}H_{34}O$ and $C_{22}H_{36}O$ in sperm blubber oil may have ethylenic linkings in the same positions as eicosatetraenoic[6] and clupanodonic acids,[7] i.e., these

(5) Toyama and Tsuchiya, this Bulletin, **10** (1935), 573; Toyama and Akiyama, this Bulletin, **10** (1935), 579.

(6) Toyama and Tsuchiya, this Bulletin, **10** (1935), 296.

(7) Toyama and Tsuchiya, this Bulletin, **10** (1935), 441.

alcohols may possibly be identified as the alcohols obtained on reducing the carboxyl group of the corresponding highly unsaturated acids. We are intended to confirm this by subsequent experiments. Whilst the alcohol $C_{20}H_{34}O$ (eicosatetraenol), for which we propose the name catadonyl alcohol,[8] has never been recorded in the literature, the docosapentenol (clupanodonyl alcohol) $C_{22}H_{36}O$ was prepared by Tsujimoto and Kimura[9] by the reduction of methyl clupanodonate, but its occurrence in natural oils has never been reported before our experiment.

Experimental.

1. **The Preparation of Ether Insoluble Bromides from High Boiling Fraction and the Regeneration of Highly Unsaturated Alcohols by Debromination.** A specimen of sperm blubber oil having saponification value 126.8, iodine value (Wijs) 82.6 and unsaponifiable matter 38.98% was heated with barium hydroxide solution under pressure, and a mixture of barium soaps and free unsaponifiable matter was obtained, from which the latter was extracted with acetone. The unsaponifiable matter was separated into 5 fractions by fractional distillation, the yield of the highest fraction boiling at 195–198°/5 mm. being 1,680 g. from 10,070 g. of unsaponifiable matter. For the details of the above experiment the previous paper[2] should be consulted.

The highest fraction obtained above showed acetyl value 182.6 and iodine value 96.8. This fraction (1,670 g.) was divided into three batches, and each of them was dissolved in about 10 times its quantity of acetone. The solution was cooled down to about -10°, the separated solid (yield 70 g. in total, iodine value 14.5) was filtered, and on distilling off the solvent from the filtrate there was obtained the liquid portion having iodine value 100.9. The liquid portion (1,570 g. in total) was brominated in the following manner: this was divided into 3 batches consisting of 520–530 g., and each of them was dissolved in about 10 times its quantity of ether. The solution was cooled down to about -10°, and an excess of bromine (about 400 g.) was added in the course of 5 hours under constant stirring. After the completion of the addition of bromine, the solution was allowed to stand in the cold for 2 hours more and then the precipitate of insoluble bromides (53.5 g. in total) was filtered and washed with cold ether until the precipitate became white. The filtrate together with the washings was washed with sodium thiosulphate solution to remove the excess of bromine, and after subsequent washing with water and dehydration over anhydrous sodium sulphate, the solvent was distilled. The residue was then dissolved in about 10 times its quantity of petroleum ether, the solution was cooled down to about -10°, and the precipitated bromides (35 g. in total) were filtered off. The ether insoluble bromides had Br-content 69.50% and melted to a tar-like matter at about 240°. The petroleum ether insoluble bromides had Br-content 64.40% and turned black at about 150°. Fifty-three g. of ether insoluble bromides were mixed with 27 g. of zinc powder, and 80 c.c. of ethyl alcohol was added to the mixture. The liquid was heated on the water-bath under a reflux condenser, and 80 c.c. of 5 N hydrochloric acid in ethyl alcohol was added in the course of 1.5 hours. After heating 1 hour more, the supernatant solution was decanted off. The residue was again treated with 27 g. of zinc powder, 80 c.c. of ethyl alcohol and 80 c.c. of 5 N hydrochloric acid in

(8) Derived from Catadontidae.
(9) *J. Soc. Chem. Ind., Japan*, **28** (1925), 390.

ethyl alcohol as before, and then the solution was separated from the insoluble substances which were thoroughly washed with ethyl alcohol. The united solutions and the washings were diluted with a large quantity of water, and the debrominated product, which separated as an oily layer, was collected by using ether. The highly unsaturated alcohols (15.3 g.) thus obtained by debromination of ether insoluble bromides had acetyl value 166.7, iodine value 383.9[10] and n_D^{20} 1.4926. They showed a drying power and had a peculiar smell like the highly unsaturated acids in marine animal oils. A portion of the highly unsaturated alcohols was subjected to hydrogenation, and the product was recrystallised from 90% ethyl alcohol, yielding the recrystallised product and the portion recovered from the mother liquor (Table 1). The latter was, however, suspected to contain more or less unsaturated alcohols which escaped a complete hydrogenation. The acetyl values (saponification values of the corresponding acetates) calculated for $C_{18}H_{38}O$, $C_{20}H_{42}O$, and $C_{22}H_{46}O$ are shown in Table 2.

Table 1.

	M.p.	Acetyl value
Recrystallised product	64°	156.8
Portion recovered from the mother liquor	57°	171.5

Table 2.

	$C_{18}H_{38}O$	$C_{20}H_{42}O$	$C_{22}H_{46}O$
Acetyl value	179.6	164.9	152.3

2. **Fractionation of Highly Unsaturated Acetates.** The highly unsaturated alcohols were heated with acetic anhydride, and 15.8 g. of the resulting acetates were fractionally distilled with the results shown in Table 3.

Table 3.

Fraction	B.p. (°C./5 mm.)	Saponif. value	Iodine value	n_D^{20}	Yield (g.)
1	185-202	173.2	296.4	1.4798	0.8
2	202-207	171.6	303.0	1.4800	1.0
3	207-211	169.1	308.3	1.4804	1.3
4	211-213	168.3	309.9	1.4808	1.0
5	213-215	168.1	310.8	1.4809	1.2
6	215-217	167.9	312.0	1.4810	1.2
7	217-218	167.5	313.6	1.4817	1.3
8	218-219	166.1	315.9	1.4828	1.7
9	219-220	165.8	318.1	1.4835	1.4
10	220-221	164.2	325.5	1.4839	1.5
11	221	163.7	333.0	1.4843	1.3
12	221-225	165.1	349.9	1.4868	1.5
Residue and loss	—	—	—	—	0.6

The saponification and iodine values of the fraction (3) are close to the corresponding values (saponification value 168.8, iodine value 305.6) for the acetate $C_{22}H_{36}O_2$ of a highly unsaturated alcohol $C_{20}H_{34}O$. The free alcohol obtained on saponification of this fraction was found to have the formula $C_{20}H_{34}O$ by elementary analysis (Found: C, 82.31;

(10) This value is thought to be a little too high.

H, 11.89. Calc. for $C_{20}H_{40}O$: C, 82.68; H, 11.80%).[11] The hydrogenated product of the free alcohol showed acetyl value 164.4 (calc. for $C_{20}H_{42}O$: 164.9) and m.p. 62.5–63° after recrystallisation from 90% ethyl alcohol (Found: C, 80.19; H, 14.20. Calc. for $C_{20}H_{42}O$: C, 80.45; H, 14.19%). The melting point of *n*-eicosanol is recorded as 65–65.5°.[12] On brominating the free alcohol in ethereal solution, there was obtained 56% of an ether insoluble bromide which showed Br-content 68.82% (calc. for $C_{20}H_{34}OBr_8$: 68.77%) and turned black at about 240°.

The saponification values of the fractions (1) and (2) are a little higher than the value calculated for the acetate $C_{22}H_{36}O_2$ of an alcohol $C_{20}H_{34}O$, but on hydrogenating the free alcohol liberated from the fractions (1) and (2), there was obtained the same product having acetyl value 164.3 and m.p. 62.5–63° as that described in the case of the fraction (3).

The saturated alcohol (0.8 g.) described above, m.p. 62.5–63°, was dissolved in 30 c.c. of glacial acetic acid, and 3.5 g. of chromic acid was added. The solution was heated on the water-bath under a reflux condenser for 2 hours. On cooling it was diluted with water, and the oxidation products were extracted with 500 c.c. of ether. The ethereal solution was washed with water and then with potassium hydroxide solution by which the acidic oxidation products were converted into the potassium salts and separated from the ethereal solution. The aqueous solution containing the potassium salts was decomposed with hydrochloric acid, and the insoluble acidic substances were separated and recrystallised from 95% ethyl alcohol. The product showed neutralisation value 181.5 (calc. for $C_{20}H_{40}O_2$: 179.6) and m.p. 73.5–74°. No depression of melting point was observed when the product was admixed with a pure specimen of arachidic acid $C_{20}H_{40}O_2$ (m.p. 74.5–75°).

The highest fraction (12) showed a saponification value which is considerably higher than the value calculated for the acetate $C_{24}H_{38}O_2$ of a highly unsaturated alcohol $C_{22}H_{36}O$, but the free alcohol obtained on saponification of this fraction showed an elementary composition corresponding to the formula $C_{22}H_{36}O$ (Found: C, 83.28; H, 11.38. Calc. for $C_{22}H_{36}O$: C, 83.47; H, 11.47%). On brominating the free alcohol in ethereal solution, there was obtained 57% of an ether insoluble bromide which had Br-content 71.45% (calc. for $C_{22}H_{36}OBr_{10}$: 71.65%) and turned black at about 240°. The hydrogenation product showed acetyl value 152.2 (calc. for $C_{22}H_{46}O$: 152.3) and m.p. 67–67.5° after repeated recrystallisation from 90% ethyl alcohol. The melting point of *n*-docosanol $C_{22}H_{46}O$ is recorded as 70–70.5°.[13]

Summary.

The high boiling fraction of the unsaponifiable matter of sperm blubber oil was brominated in ethereal solution, and the ether insoluble bromide was separated and then debrominated to regenerate the highly unsaturated alcohols. These were converted into acetates, and the latter were fractionated. An examination of the resulting fractions showed that the highly unsaturated alcohols of sperm blubber oil contained two individual alcohols $C_{20}H_{34}O$ and $C_{22}H_{36}O$ as chief components.

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(11) For the elementary analyses we are indebted to Mr. Tsuchiya.
(12) Adam and Dyer, *J. Chem. Soc.*, **127** (1925), 70.
(13) Bleyberg and Ulrich, *Ber.*, **64** (1931), 2504.