ON A NEW HYDROCARBON IN BASKING SHARK LIVER OIL.

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In the author's first experiments on the isolation of pristane (at that time described by the name of "iso-octadecane"),[1] the crude hydrocarbon even after alkali-washing and redistillation had iodine value 4.4. In Y. Toyama's elaborate investigation on the occurrence of pristane in various squalene-containing shark liver oils, in which the present name has been proposed for the hydrocarbon,[2] the crude substances corresponding to pristane showed always more or less iodine values (2.3–25.6). It should, however, be mentioned that the specimens of shark liver oil used by him were all meagre in the proportions of pristane, the actual yield being 0.5–0.7%, so that in order to separate the hydrocarbon from the oil a strong heating was necessitated. So Toyama judiciously took the unsaturated compounds more likely to be decomposition products rather than normal constituents of the oils. A few years ago the present author[3] got a similar result with "gonshika" liver oil. Thenceforth the author has been inclined to consider the unsaturation or at least a part of it to be due to some naturally occurring substance or substances in the oils. To decide the question it is necessary to procure a shark liver oil that contains pristane in a fairly large proportion. Advantageously the basking shark liver oils reported in the preceding paper are well suited for the purpose.

(1) **Experiment 1.** The basking shark liver oil No. 1 (1500 g.) was distilled under 4.5–5.5 mm. pressure in batches of 300 g. in a Claisen flask, the maximum temperatures of the metal bath and the distillation being 270°C. and 146–152°C. respectively. The yield of the distillate was 31.5 g. (2.1%); it had acid value 1.20. On washing off the free acids with alkali, it formed a nearly colourless liquid of n_D^{20} 1.4400 and iodine value 10.1. It (30 g.) was re-distilled under 14 mm. pressure over metallic sodium in

(1) *J. Soc. Chem. Ind. Japan*, **20** (1917), 1099; *J. Ind. Eng. Chem.*, **9** (1917), 1098.

(2) *J. Soc. Chem. Ind. Japan*, **27** (1924), 333; *Chem. Umschau*, **30** (1923), 181.

(3) *Repts. Tokyo Imp. Ind. Research Lab.*, **26** (1931), No. 10, 33. Gonshika is said to be a very large shark, but its scientific name has not yet been ascertained. The properties of its liver oil closely resemble those of basking shark liver oil.

a small flask; the distillation began at the bath temperature 210°C. Up to the distillation temperature 174°C., 28.6 g. distilled; the distillate had n_D^{20} 1.4395 and iodine value 5.2.

As may be seen from the above-mentioned, the pristane part had, even after purification, an appreciable iodine value. For the separation of unsaturated hydrocarbons from the saturated, a method was tried, which consisted in the application of the greater solubility of the former in alcohol or methanol. This method gave, however, unsatisfactory result, at least with a small quantity of the specimen. As there was no simple method applicable, a final resort was found in the so-called "Bromestermethode",(4) which has been proposed for the separation of saturated and unsaturated fatty acids. Of course, the method has a drawback that it requires energetic chemical reactions, viz., bromination and debromination.

The distillate (25.3 g.) was dissolved in 100 c.c. of ether, and with well cooling in ice, about 0.2 c.c. of bromine was added, thereby no precipitate was formed. On removing the excess of bromine with a solution of sodium thiosulphate and bicarbonate, 26 g. of the bromine addition compound was obtained. It was then distilled under 2.5–3 mm. pressure; the maximum temperature of the bath and the distillation were 188°C. and 142°C. respectively. Contrary to expectation the distillation proceeded continuously without a break, so it was stopped appropriately. The distillation residue was a brown-coloured liquid, which on washing with bicarbonate solution, weighed 1.5 g. It was treated with rasped zinc and alcoholic hydrochloric acid. The reaction went on difficulty. The yield of the debrominated product was 1.1 g., which contained still a little bromine as indicated by the CuO flame reaction. It was an orange-yellow liquid of n_D^{20} 1.4533 and iodine value 64.3. No precipitate was formed on saturating its ethereal solution with hydrogen chloride, so squalene was not present in it.

Although no definite compound was isolated by the above experiment, it has been confirmed that there occur in the pristane part of the basking shark liver oil some natural, unsaturated hydrocarbon or hydrocarbons.

(2) **Experiment 2.** The basking shark liver oil No. 2 was distilled in batches of 300 g. under 3–5 mm. pressure, the maximum temperatures of the bath and the distillation being 270°C. and 139–157°C. respectively. On the whole, 3000 g. of the oil gave 196 g. (6.5%) of the distillate. The

(4) A. Grün, "Analyse der Fette und Wachse", Vol. I, p. 223.

latter was a nearly colourless liquid of acid value 0.3; after alkali washing it had n_D^{20} 1.4400 and iodine value 9.5.

The distillate (195 g.) was redistilled under 9–10 mm. pressure in a flask with a Willstätter bulb. Up to the bath temperature 242°C. and the distillation temperature 175°C., 191 g. of the distillate was obtained. In this distillation the distillate was divided into four fractions to see if some separation of the components be effected. But they had nearly equal refractive indices (n_D^{20} 1.4390–1.4394), so they were mixed together. The distillation residue had n_D^{20} 1.4702 and produced a white precipitate with hydrogen chloride in an ethereal solution; this was probably due to the presence of squalene.

Then the distillate (187 g.) was again distilled under 10.5–11 mm. pressure over metallic sodium; the maximum temperature of the bath was 215°C. and that of the distillation 165°C.; the weight of the distillate 183 g., n_D^{20} 1.4389, iodine value 3.4. The residue also contained a small amount of squalene.(5)

Hereupon the "Bromestermethode" was tried on the refined distillate. It (182 g., 235 c.c.) was dissolved in an equal volume of ether and on cooling 1.3 c.c. of bromine was added. The solution showed a little turbidity and on standing a small amount (ca. 0.1 g.) of a white precipitate was formed, probably due to admixed squalene. The solution was filtered from the precipitate, and washed with a solution of sodium thiosulphate and bicarbonate to remove the excess of bromine. On distilling off the ether, 187 g. of the bromine addition product was obtained (a somewhat larger weight was caused by admixed solvent). It was then distilled under 2.5 mm. pressure; the distillation began at the bath temperature 200°C. Up to the bath temperature 210°C. and the distillation temperature 156°C., 227 c.c. of the distillate was obtained. At this point the distillation was interrupted.(6) The distillation residue formed a dark, brownish-yellow liquid and weighed 7.6 g., which in winter deposited a little solid substance. Debromination was effected with rasped zinc, alcoholic hydrochloric acid and petroleum ether. Difficulty was experienced as in the case of the previous experiment. The debrominated product was a dark, brownish-yellow liquid and amounted to 5.7 g.; by the flame reaction, it was found to contain a little bromine. Finally it was refined

(5) The cause why in these distillations squalene was accompanied in the low boiling fractions was not exactly known.

(6) If we assume the unsaturated hydrocarbon to be $C_{18}H_{36}$, by calculating from the iodine value (3.4), its amount is ca. 6 g. or ca. 8 c.c.; hence the amount of the saturated hydrocarbon corresponds to 235−8=227 c.c.

by distilling under 12 mm. pressure. At 175–185°C., 3.9 g. of a pale yellow liquid distilled over; it had d_4^{20} 0.7948, n_D^{20} 1.4470 and iodine value 66.2. It was free from the halogen, and squalene was not present in it.

(Found: C, 85.46; H, 14.66; Mol. wt. (in benzene), 240. Calc. for $C_{18}H_{36}$: C, 85.62; H, 14.38; Mol. wt., 252.3. Calc. for $C_{18}H_{38}$ (pristane): C, 84.94; H, 15.06; Mol. wt., 254.3.)

The substance was, therefore, recognized to be a mixture of an octadecylene, $C_{18}H_{36}$ (calculated iodine value, 100.6) and pristane, the former predominating.

On the assumption that the substance is a simple mixture of the two hydrocarbons, we get by calculation d_4^{20} 0.8006 and n_D^{20} 1.4510 for the values of the octadecylene (according to Toyama, pristane d_4^{20} 0.7835, n_D^{20} 1.4390). Adopting these values, the molecular refraction of the octadecylene is 84.82, which agrees closely with the calculated value $C_{18}H_{36}$]= 84.86.

The experiment to concentrate the unsaturated hydrocarbon by means of methanol was performed as follows: the mixture (2.105 g.) was treated with 100 c.c. of methanol. The soluble part amounted to 1.331 g. (63.2%) and had n_D^{20} 1.4480 and iodine value 70.3. It (1.209 g.) was again treated with 50 c.c. of methanol. The soluble part was 0.653 g. (54.0%) and had n_D^{20} 1.4500 and iodine value 78.4. The operation was interrupted from the want of the material, but it seemed to be possible to concentrate further the unsaturated hydrocarbon. Of course, the insoluble parts had also fairly high iodine values (1st 43.5, 2nd 51.1).

The concentrated substance (iodine value 78.4) was hydrogenated with platinum black as catalyser. The product was a liquid of n_D^{20} 1.4405 and iodine value 1.9. If hydrogenation be carried out completely, the final product appears to be pristane or a very similar compound.

By the above experiments, the occurrence of an octadecylene in the basking shark liver oil has been confirmed. Its amount was, however, far smaller than anticipated.

The objection that unsaturated hydrocarbons might be formed by the decomposition of the oil by over-heating, may be negated from the following grounds, viz., (1) the temperature of the bath was comparatively low (up to 270°C.), so that no appreciable decomposition would be expected to occur, and (2) decomposition products of the dry distillation of squalene are a mixture of hydrocarbons and not a single compound such as octadecylene. Also according to Toyama's experiments, such products, which correspond to pristane, are highly unsaturated hydrocarbons of very high iodine values.

The octadecylene appears to occur not only in basking shark liver oil, but also in other squalene-containing shark liver oils, probably in far smaller proportions.

Although the author has not yet succeeded in isolating this hydrocarbon in pure state, nevertheless as there is little doubt as to its natural occurrence, he has given the name "Zamene" to it (Japanese: "Samé" or "Zamé" = shark).

Summary.

Although small in proportion, a new octadecylene, $C_{18}H_{36}$, has been found to occur, together with pristane, in basking shark liver oil. In far smaller proportions, it probably occurs in many other, squalene-containing shark liver oils in association with pristane. The author has proposed the name "Zamene" for this new hydrocarbon.

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