ON BASKING SHARK LIVER OIL.

By Mitsumaru TSUJIMOTO.

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Basking shark (Japanese: "Ubazamé" or "Bakazamé"), *Cetorhinus maximus* (Gunner), reaches to a length of 36 feet and is the largest of all the living fish. The chemical examination of basking shark liver oil was first made by the author[1] in 1917; three commercial specimens, which were apparently prepared from adult fish, contained squalene, and in one of them the author discovered a peculiar iso-octadecane (pristane),

(1) *J. Soc. Chem. Ind. Japan*, **20** (1917), 953, 1099; *J. Ind. Eng. Chem.*, **9** (1917), 1098; **12** (1920), 65.

$C_{18}H_{38}$. Then the author[2] and also Y. Toyama[3] examined the liver oils from young basking sharks (length ca. 2.4–2.7 m.); the former found about 8% of cholesterol in the oil. In France, E. André and H. Canal[4] investigated the oils from two adult and a young basking sharks, and observed a reciprocal relation between the contents of cholesterol and squalene.

Basking shark liver oil is sometimes of peculiar properties, for example, a notable amount of pristane being present in it, so it is one of the most interesting liver oils.

For a long time it had been the author's earnest desire to obtain the liver of the adult fish and to prepare the oil in the laboratory. This was recently fulfilled by procuring the following two specimens.

(1) **Basking Shark Liver Oil No. 1.** The fish which gave this oil was a large female basking shark caught in Toyama Bay[5] on December 14, 1933. It was not dissected at the fishing district, but was sent to Kyoto, where it was exhibited as a show under a signboard of a "large monster sea dragon". As it had been known that the fish would be dissected in the city, several negotiations were made with its owner, and a part of the liver was eventually procured to the laboratory on January 12, 1934, after the lapse of nearly one month.

The fish mentioned above had a length of 775 cm.[6] and a weight of about 2000 kg. The liver had a greyish-white colour mingled with blood-red parts, and was of a very oily consistency; in spite of long keeping in the fish body, it showed a comparatively little putrefaction. A batch of 1000 g. of the liver gave, on complete exhaustion, 854 g. i.e., 85.4% of the oil. From 57 kg. of the liver, 45 kg. (ca. 79%) of the oil was obtained by careful heating.

The oil was a pale orange-yellow liquid with a not unpleasant odour; it deposited a little solid substance at room temperature of 6–14° C. With sulphuric acid it gave a brown colour with a slight violet-red tinge; nearly no blue colouration was observed by the $SbCl_3$ test.

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(2) *Repts. Tokyo Imp. Ind. Research Lab.*, **15** (1920), No. 2, 1, and No. 10, 85.

(3) *J. Soc. Chem. Ind. Japan*, **27** (1924), 601.

(4) *Ann. chim.*, (X), **7** (1927), 69; *Bull. soc. chim.*, (IV), **45** (1929), 598. The lengths of the sharks were 6m., 4.7m., and 3.4m. respectively.

(5) Toyama Bay is an inlet of the Japan Sea and lies to the north of Central Japan, being bounded by Etchu Province (Toyama Prefecture) on the east and south and by Noto Province (Ishikawa Prefecture) on the west.

(6) This figure is due to Mr. Kan-emon Kikuchi of the Toyama High School, who actually measured the fish and to whom the author wishes to express his thanks.

(2) **Basking Shark Liver Oil No. 2.** On January 25, 1934, a telegram from Higashi-Iwase Town Office, Toyama Prefecture, was received by the author, which informed that a large shark was caught again in Toyama Bay. Contrary to the case of the former shark, by easy negotiations and chiefly through the kindness of the above-mentioned office, a part of the liver was procured on January 31. According to a communication of Mr. Awata, a fish-dealer, who treated the shark, it was male in sex, had a length of 24 "shaku" (727 cm.) and a weight of 580 "kwan" (ca. 2170 kg.); the liver weighed 90 "kwan" (337.5 kg.).

The liver was mostly of a dirty, yellowish-grey colour. One kilogram of it contained 838 g., i.e., 83.8% of the oil. From 29 kg. of the liver, about 23 kg. (ca. 79%) of the oil were obtained.

The oil had a pale, orange-yellow colour and did not deposit solids even in winter. Sulphuric acid gave a yellow-brown colour; the $SbCl_3$ test nearly no colouration.

The characteristics, etc., of these oils were found as shown in Table 1.

Table 1.

	d_4^{15}	n_D^{20}	Acid value	Saponif. value	Iodine value (Wijs)	Unsaponif. matter (%)
Oil No. 1 (Female)	0.8973	1.4794	0.16	126.3	185.6	30.35
Oil No. 2 (Male)	0.8808	1.4785	0.21	94.8	191.5	45.13

The oil No. 2 had lower specific gravity and saponification value and higher iodine value. These were chiefly due to the higher proportion of squalene in the oil. The observation that the liver oil of male shark contains more squalene, has already been made in the case of "kurokozamé" (*Centroscyllium*).[7]

(3) **Fatty Acids.** After removing the unsaponifiable matter, the soap solution was decomposed with hydrochloric acid. The fatty acids thus liberated had the properties shown in Table 2.

The fatty acids from the oil No. 2, which contained more squalene, showed a far less unsaturation.

(7) Tsujimoto, *Repts. Tokyo Imp. Ind. Research Lab.*, **27** (1932), No. 15, 20.

Table 2.

Fatty acids from	Appearance	Melt. pt.	Neutr. value	Iodine value	n_D^{25}	Ether-insol. bromide (%)	Br content of the bromide (%)
Oil No. 1	Nearly white crystalline mass	Chiefly melted at 24–25°C., became clear at 27°C.	186.4	130.0	—	27.0	70.23
Oil No. 2	Mixture of white solids and a pale yellow liquid	Became clear at 20–21°C.	179.3	88.2	1.4605	9.3	69.63

(4) **Unsaponifiable Matter.** Some of the properties are given in Table 3. (Cholesterol was determined by the digitonine method.)

Table 3.

Unsaponif. matter from	Appearance	n_D^{20}	Iodine value	Cholesterol (%)
Oil No. 1	Pale yellow liquid; deposited a little solid substance in winter	1.4900	338.9	1.83
Oil No. 2	Pale yellow liquid	1.4863	302.4	0.94

The lower refractive index and iodine value of the unsaponifiable matter from the oil No. 2 were due to the notable proportion of pristane.

(5) **Determination of Hydrocarbons.** These were determined by distillation under diminished pressure.[8]

Oil No. 1 (a). The oil (50.3 g.) was distilled under 5 mm. pressure. Above the bath temperature 255°C the distillation began, the thermometer of the flask soon rising to 180°C. At the maximum temperature 247°C. (bath temp. 313°C.) the distillation ended. The distillate was a pale yellow liquid; yield 13.1 g., acid value 2.21. Subtracting the amount of free acids, the yield of hydrocarbons was 25.8%. The refractive index of the distillate, after washing off the acids, was n_D^{20} 1.4897. Its main constituent was squalene. But as an appreciable amount of pristane

(8) Tsujimoto, *J. Ind. Eng. Chem.*, **12** (1920), 71.

appeared also to be present, the lower boiling fraction was determined separately.

Oil No. 1 (b). The oil (50.5 g.) was distilled under the pressure of 5 mm. The distillation began above 250°C. of the bath temperature; the thermometer of the flask soon indicated 144°C. The temperature of the bath was gradually raised to and kept at 270°C., at which nearly no squalene distilled over. The maximum temperature of the distillation was 154°C.; then the temperature sank and the distillation ended. The distillate (colourless liquid) was 1.4 g., and had acid value 1.04. Subtracting free acids, the yield of hydrocarbons (pristane part) was 2.76%. The acid-free substance had n_D^{20} 1.4430 and iodine value 31.8.

Oil No. 2. The oil (50.2 g.) was distilled under 5 mm. pressure. The pristane and squalene parts were determined in one distillation by changing receivers.

Pristane part. Maximum bath temperature 270°C.; maximum distillation temperature 154°C.; distillate (colourless liquid) 3.4 g., acid value 0.202; yield of hydrocarbons 6.76%; the acid-free substance had n_D^{20} 1.4410 and iodine value 18.9.

Squalene part. Maximum bath temperature 320°C.; maximum distillation temperature 246°C.; distillate (nearly colourless liquid) 17.8 g., acid value 0.72; yield of the hydrocarbon 35.34%; the acid-free substance had n_D^{20} 1.4950.

The total yield of the hydrocarbons was 42.1%.

As the above experiments showed, the basking shark liver oils used in the present investigation were notably rich in pristane, especially in the oil No. 2 reaching to about 6%. With such specimens it would not be difficult to prepare pristane in kilogram units, even with ordinary apparatuses of a laboratory. If the total liver of the second shark had been utilized, about 16 kg. (ca. 20 liters) of pristane would have been obtained.

It is also to be noted that the notable occurrence of pristane in basking shark liver oil appears not to be of rare, but of rather frequent instance.

Besides pristane and squalene, there occurred in the oils a new unsaturated hydrocarbon, which is described in the next paper.

Tokyo Imperial Industrial Research Laboratory,
Hatagaya-cho, Shibuya, Tokyo.