ON THE OCCURRENCE OF A HYDROCARBON IN ISHINAGI LIVER OIL.

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Of hydrocarbons occurring in the liver oils of animals, the most remarkable one is the highly unsaturated hydrocarbon, squalene, $C_{30}H_{50}$, which is contained in a fairly large number of shark liver oils, and although small in proportion, the saturated hydrocarbon, pristane, $C_{18}H_{38}$, usually accompanies squalene. In recent years, H. J. Channon and G. F. Marrian[1] found a hydrocarbon probably of the formula $C_{32}H_{54}$, $C_{33}H_{56}$ or $C_{34}H_{58}$, in the livers of man, sheep, horse, and pig; the present author in conjunction with K. Kimura[2] isolated a hydrocarbon, possibly corresponding to the formula $C_{35}H_{60}$, from the liver fat of sperm whale. However, so far as fish livers are concerned, no hydrocarbon has hitherto been discovered in them besides the above two hydrocarbons in shark liver oils. Recently I found a hydrocarbon in the liver oil of ishinagi, *Stereolepis ischinagi* (Hilgendorf). This oil, first investigated by me, is distinguished by the remarkable content of a vitamin A-like substance (liver resin), which sometimes amounts up to nearly 50% of the oil.[3] The amount of the hydrocarbon in the oil was small; it was highly unsaturated. Owing to the want of material, no definite formula has yet been assigned to it, but it appeared to be of a high molecular weight. The present paper is a preliminary report on this hydrocarbon.

Experimental Part.

The ishinagi liver oil used for the present investigation was a mixture of four samples of the oil prepared in the laboratory. It was a brownish red-yellow, viscous liquid, which appeared almost black in thick layer, and deposited an appreciable amount of solid fat in winter. An intense blue colouration was observed in the antimony trichloride test. The oil showed the following numbers:

d_4^{15}	0.9358	Saponif. value	146.2
n_D^{20}	1.5070	Iodine value (Hanus)	155·5
Acid value	11.8	Unsaponif. matter	22.36%

(1) *Biochem. J.*, **20** (1926), I, 409.

(2) *Chem. Umschau.*, **35** (1928), 317.

(3) Tsujimoto, *Chem. Umschau.*, **29** (1922), 385; S. Ueno, M. Yamashita and Y. Ôta, *J. Soc. Chem. Ind. Japan*, **31** (1928), 1198.

The fatty acids contained 68.5% of liquid acids, and consisted mainly of palmitic and oleic acids, together with stearic and clupanodonic acids. Hexadecenic acid and a small proportion of saturated acids higher than stearic were probably present.[1]

The unsaponifiable matter formed a reddish-orange, very viscous liquid. In order to separate the hydrocarbon, it was treated with methanol. 35 Gr. of the substance were heated with 350 c.c. of methanol, thereby complete solution occurred, but on cooling the solution became turbid, and an oily precipitate was gradually deposited. On standing over night, the supernatant liquid was decanted off; the precipitate was repeatedly washed with a small amount of methanol. In this way about 1 gr. of a yellow-orange, viscous liquid was obtained. It had an orange-yellow colour even after treatment with a pretty large amount of animal charcoal in ethereal solution. As the liquid was difficultly soluble in methanol, ethyl alcohol, and acetic anhydride, there was little doubt that it consisted mainly of hydrocarbon, but judging from its colour and colour reaction (Liebermann's), it appeared to be still impure. Owing to the difficulty of purification of such small material, it was analysed without further treatments as follows:

d_4^{17} 0.942 Iodine value (Hanus) 290.8

n_D^{17} ca. 1.54 ,, ,, (Rosenmund and Kuhnehenn) 310.0

Solidif. pt. Not solidified at 0°

Molecular weight. (1) 0.0114 gr. subst., 0.1307 gr. camphor (m.p. 177.7°), m.p. of the mixture 172°, depression 5.7°, mol. wt. 612. (2) 0.1442 gr. subst., 10.85 gr. benzol, depression 0.103°, mol. wt. 644.

Elementary analysis: Subst. = 0.1127; CO_2 = 0.3493; H_2O = 0.1187 gr. Found: C = 84.53; H = 11.79%.

Thus the substance had high specific gravity and refractive index, and as indicated by its iodine value, it was highly unsaturated. As the percentage of carbon and hydrogen amounted only to 96.32%, it was still impure to be taken as a hydrocarbon as had been anticipated.

Bromine addition compound. 0.1152 Gr. of the substance was dissolved in 10 c.c. of ether, and on cooling the flask with ice, a little excess of bromine was added. On standing for about one hour, the precipitate was collected on a filter and washed with ether; yield 0.1950 gr. or 169.3%. A white powder; on heating it became somewhat brown at 130°C., brown at 150°C., and turned black with sintering at 170°C. The bromine content was determined to be 67.07% (Carius).

(1) Tsujimoto, *Report of the Tokyo Imperial Industrial Laboratory*, Vol. **24** (1929), No. 4, p. 1.

Hydrogen chloride addition compound. 0.3 Gr. of the substance (not treated with animal charcoal) was dissolved in 10 c.c. of ether, and on well cooling, dry hydrogen chloride gas was passed into it to saturation. The solution showed various change of colour, and finally turned blackish violet. On standing for two hours, the precipitate was collected and washed with ether; yield 0.15 gr. On recrystallising it from acetone, a nearly white powdery substance was obtained. This sintered at above 120° C., and melted at 128–129°C. with bubbling (decomposition). The chlorine content was 30.85%.

Discussion.

The results of the above experiments were yet insufficient to determine the composition of the hydrocarbon. It was even questionable whether the substance consisted of a single compound. But assuming it to be so, the following two suggestions are possible, the decision of which I should postpone to further investigation:

(1) By assuming the high values of specific gravity, refractive index, and molecular weight to be due to some admixed impurities, and taking the halogen contents and the melting point of the comparatively pure bromine and hydrogen chloride addition compounds into consideration, it appears that the hydrocarbon closely resembles to that of the liver fat of sperm whale (loc. cit.), viz. Br content of $C_{35}H_{60}Br_{12}$=66.62%; Cl content of $C_{35}H_{60}6HCl$=30.42%.

(2) If we take the values of specific gravity, refractive index, and molecular weight to be nearly correct, then the substance is a compound higher than C_{40} atoms, and the number of double bonds must be more than six. The compounds nearly corresponding to these data are $C_{45}H_{76}$ (mol. wt. 616.6, iodine value 329.4 as eight double bonds) and $C_{46}H_{78}$ (mol. wt. 630.6, iodine value 322.1). The calculated halogen contents of the addition compounds are as follows:

	Br (%)		Cl (%)
$C_{45}H_{76}Br_{16}$	67.47	$C_{45}H_{76}8HCl$	31.23
$C_{46}H_{78}Br_{16}$	66.97	$C_{46}H_{78}8HCl$	30.75

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