COMMERCIAL SHARK OIL.

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My attention has been recently directed to the very anomalous characters of the oils known in commerce as shark oil, shark-liver oil, and African fish oil. African fish oil is, I believe, a name given to a variety of oil yielded by a species of shark caught off the coast of Africa, while the term "shark oil" is ordinarily a mere abbreviation of shark-liver oil, as the commercial article is presumably derived from the liver of the shark, although other parts of the fish are admittedly capable of yielding oil.

The great peculiarity commonly attributed to shark oil is its extremely low density. Thus, all the liquid glycerides known to occur naturally, have a density at the ordinary temperature ranging between 912 and 970, or if castor oil and its allies be excluded the highest observed density of a natural glyceride is about 940. These figures exclude the oils from the sperm whale and the bottle-nose whale, as these products have been shown not to be glycerides, but to consist essentially of the oleic ethers of higher monatomic alcohols.

There is a very general agreement that shark oil is a product of very low density. This statement is met with in "Spon's Encyclopædia" page 1371; and in the edition of "Muspratt's Chemistry" edited by Vincent, vol. i, page 479, shark oil is stated to be light yellow, of specific gravity ranging from 870 to 876, and to have been found by Roynolds from a partial examination to consist of glycerin, a peculiar oleic acid very rich in carbon, and another undefined liquid oil. Leading sperm oil importers of the kingdom, to whom I have applied for information on the subject, agree in stating shark oil to have a very low density, ranging from 860 to 870. The same oil of low density is known in America, for Mr. C. M. Stillwell, of New York, communicated to me the figure 864 as that of the density of shark oil.

The remarkably low density of shark oil attracted my attention some years since, and led me to imagine that the oil might have a constitution similar to that of sperm and bottle-nose oils. In a paper read by me before the Society of Chemical Industry (*Journal*, Vol. II. page 53) I stated that I was not then prepared to say anything definite respecting it, for the simple reason that it had resisted every attempt to saponify it. I tried to effect its decomposition by aqueous potash, by a solution of potash in absolute alcohol, by heating it with solid potash to 200°C, and by treatment with moderately strong sulphuric acid. In some cases, the experiments were made under the ordinary atmospheric pressure, and in other cases in sealed tubes at temperatures varying from 100° to 150°C. At that time my experience was limited to three or four samples of shark oil, and in no case did I find it to yield less than 80 per cent. of unsaponifiable matter to ether. The amount of samples at my disposal at that time did not allow of my making a satisfactory examination of the nature of the unsaponifiable matter, and the subject remained in abeyance till comparatively recently, but meanwhile I had examined a sample of shark-liver oil exhibited in the Health

Exhibition, which had a specific gravity of 869.2, and yielded after saponification 80.8 per cent, of matter soluble in ether.

The first instance in which I have noticed a record of a shark oil of a density similar to that of the ordinary glycerides occurs in a paper by Mills and Akitt (*Journal of the Society of Chemical Industry*, Vol. III, page 367) in which a density of 929.3 was observed.

I have recently examined a number of specimens of shark-liver oil, which I have every reason to believe to be genuine. Whilst throwing doubt on older statements, my results show that shark-oil is peculiar in yielding a very notable proportion of unsaponifiable matter, consisting in great part of cholesterin. If the sample be saponified with alcoholic potash in the usual way, the alcohol boiled off, and the aqueous solution of the soap agitated with ether, the separated ethereal layer leaves on evaporation a nearly colourless crystalline mass, which, if dissolved in boiling alcohol, deposits on cooling abundant crystals, which are seen under the microscope to consist of plates of cholesterin, and yield the characteristic colour-reactions of that body.

The following results were obtained in my laboratory by the analysis of six specimens of apparently genuine shark-liver oil. Samples Nos. 2 and 3, were from the same fish, a female shark caught off Norway. For these specimens, as for many other samples of fish oils, I am indebted to the Normal Company, Aberdeen, who have done much to advance the application of fish-products.

	1. Japanese	2. Crude.	3. Refined.	4.	5.	6.
Specific gravity at 15.5°C.	926.0	918.5	928.5	914.3	913.6	911.3
Percentage of KHO required	17.73	16.96	19.76	15.3	14.00	14.0
= Saponification-equivalent	316.4	330.8	283.9	366.9	400.0	400.0
Ether-residue; per cent.	2.82	8.70	0.70	10.25	17.30	10.34

With concentrated sulphuric acid, Nos. 1 and 3 samples gave a reddish-brown spot, with violet edges, the whole changing on stirring to reddish-brown. Nos. 2, 4, 5, and 6 agreed in giving a bright violet spot, changing to blood-red; on stirring, the whole became a magnificent violet colour, changing rapidly to dark red and brown.

The ether-residues from these samples, varying from 0.7 to 17.3 per cent., were highly crystalline, and undoubtedly chiefly composed of cholesterin. It is evident that the variations in the specific gravity of the samples follow closely the proportions of ether-residue. If the percentage of potash be calculated on 100 parts of the oil actually saponified, and not on 100 parts of the sample, including the unsaponifiable matter, the proportion is found to range from 17.0 to 19.6 per cent., and the corresponding saponification-equivalents from 330 to about 282.

By the courtesy of the Commissioner, Sir James Marshall, I have been supplied with several samples of shark oil exhibited in the West African Court of the Colonial and Indian Exhibition. These form part of the collection contributed by Mr. E.

Allegre, of Bathurst, River Gambia; and are quite different in appearance from the shark oils from other sources. This may be due in some measure to previous specimens having being bagged or filtered, but such treatment would not wholly account for the difference. Two typical samples of the West African shark oil have been examined. No. 73 was of a lemon-yellow colour. It contained much solid fat and had a smell like that of cod-liver oil. No. 266 was dark brown and turbid, but contained but little solid fat. The smell was of a most offensive character. On analysis, these samples gave the following results:—

	No. 73 Yellow.	No. 266 Brown.
Specific gravity at 15·5°C.	926·0	932·8
Percentage of KHO required.	19·75	17·42
= Saponification-equivalent.	284·1	322·0
Ether-residue; per cent.	2·26	12·60
„ „ characters.	Yellow, crystalline; contained cholesterine.	Brown, treacly.
Colour with strong sulphuric acid.	Dark violet, changing to reddish-brown.	Dark violet, quickly turning black, and finally dark yellowish-green.

On the other hand, the following figures have been obtained by the examination of samples of so-called shark-oil, which were presumably adulterated. Sample B was the oil exhibited in the Health Exhibition, and had been purchased by the exhibitors in consequence of my failure to effect saponification of shark oil, which property, it was considered, might render the product valuable for certain purposes:—

	A.	B.	C.	D.	E.	F.	African fish oil.
Specific gravity at 15·5°C. ..	874·6	869·2	866·1	876·1	868·4	868·4	867·2
Percentage of KHO required ..	..	4·50	5·50	—	—	—	—
Ether-residue; per cent. ..	69·9	80·8	83·5	83·5	87·0	87·0	82·8
„ specific gravity ..	..	..	..	869·8	842·5	844·2	..
„ odour on heating ..	..	pine resin	..	resinous	resinous	resinous	..
„ with sulphuric acid ..	..	reddish-brown, becoming darker on stirring	..	reddish-brown, becoming fine violet on heating; aromatic odour	greenish-brown; fluorescent	greenish-brown; fluorescent	..

An ultimate analysis of the ether-residue from sample B gave:—Carbon, 86·62; Hydrogen, 12·62; Oxygen (by difference), 0·76 per cent. No nitrogen was detected. These results approximately agree with the composition of a terpene, $C_{10}H_{16}$, which would contain 88·23 of carbon and 11·77 of hydrogen. When heated, the ether-residue gave no volatile matter till the temperature had risen about the boiling-point of mercury; but it then distilled regularly, giving a product which was colourless, or nearly

so, optically inactive, and assimilated 160 per cent. of bromine. The odour suggested that of rosin spirit.

A further examination was also made of the unsaponifiable matter from sample D which was from the same source as B, though differing somewhat in density. 50 c.c. of the ether-residue was distilled in a small fractionating flask. A single drop of liquid distilled at 320° C., but nothing further came over below the temperature at which it became necessary to remove the thermometer. On heating the contents of the flask still further, the liquid began to boil and distil with great regularity; the contents of the flask and the fractions successively collected gradually increasing in colour, density, and initial boiling-point, as shown in the following Table:—

	Volume.	Colour.	Density.	Initial Boiling Point.
1st Fraction ..	8.3 c.c. ..	Very pale yellow ..	817.0 ..	85
2nd Fraction ..	14.0 „ ..	Pale yellow ..	823.5 ..	95
3rd Fraction ..	4.0 „ ..	Lemon yellow ..	862.0 ..	124
4th Fraction ..	15.0 „ ..	Olive-green ..	895.6 ..	147
5th Fraction ..	4.0 „ ..	Reddish-brown ..	924.0 ..	249
Residue ..	4.7 „ ..	Dark brown ..	viscous.	

The odours of the fractions were in all cases more or less aromatic, some being extremely powerful. The lighter fractions had an odour resembling geranium oil or verbenas*; while the denser smelt and tasted like rosin oil. I have recorded the initial boiling points observed; but, on attempting to further fractionate the products, no distillates could be obtained till a much higher temperature was reached, and the products of this second operation appeared to have undergone considerable change. Thus, the fraction boiling below 360° C. measured 21.2 c.c., and had a density of 848.9; while that distilling above the boiling-point of mercury measured 12 c.c., and had a density of 924.0.

It did not seem worth while to carry the examination of a special sample any further, but the results obtained are not without interest. It is inconceivable that the shark can really produce a body of which upwards of 80 per cent. has all the characters of rosin oil except a high density. Ordinary rosin oil has a specific gravity always exceeding 950, and more frequently 990. A product from rosin, having a density of 870, would have the characters of a rosin spirit, and would distil with considerable facility. Polymerised products, obtained by treating terpenes with strong sulphuric acid, might have very high boiling points; but colophene is said to have a density of 940. Petroleum and shale products, having a density of 870, would distil much more readily than the ether-residues examined, and would not yield a distillate having the very high bromine-absorption observed. That the product is not natural to shark oil seems certain; but, if added as an adulterant it says much for the ingenuity of the operator.

From the results recorded it appears, therefore, that two distinct kinds of shark oil are known. One of these is an ordinary glyceride, often containing a very consider-

* It is worthy of notice that cholesterin, when subjected to dry distillation, yields a neutral oil insoluble in potash, from which a second distillation with water separates a volatile oil having an agreeable odour of geranium.

able proportion of cholesterin, or some cholesterylic ether. The other kind if actually a natural product, which seems highly improbable, contains from 70 to 80 per cent. of unsaponifiable matter, having characters which appear to connect it with the terpenes. If this variety of shark oil be factitious, it is remarkable, that the adulteration should have been conducted in so general and uniform a manner as must have been the case.

I have to acknowledge the assistance of Messrs. H. J. Hardy and W. Barraclough who have made most of the determinations recorded in the foregoing paper.

CONCLUSION OF THE SOCIETY'S PROCEEDINGS.