Component Fatty Acids of Indian Shark Liver Oil

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TSUJIMOTO (12) *et al.* had recorded some semi-quantitative data for Japanese shark liver oils. Later Pathak, Agrawal, and Mathur (9) reported a detailed quantitative data for two samples of Indian Shark *(Galeocerdo rayneri)* liver oils obtained from two different sources (Arabian Sea and Bay of Bengal). At the same time the latter have actually mentioned in their paper (9) that "any final conclusions regarding the peculiar composition of shark liver oils can be drawn only when a few more reliable and detailed data are available." Lovern (4) had earlier remarked that "it is unfortunate that out of the great range of Elasmobranch species there are only a few for which any quantitative fat analyses are available." So in order to supply some more data of this peculiar class (Elasmobranch) of fish liver oils Pathak and co-workers are trying to study as many of them as are available in Indian waters. As a result Pathak and Suwal (10) have recently communicated a paper on two samples of *(Carcharias melanopterus* and *Pristis cuspidatus)* liver oils obtained from the Bay of Bengal, and the present one is the third of a series of papers and the fifth oil.

Shark liver oil belongs to the IV group of Elasmobranch species containing a high (40-50, or even higher) percentage of saturated fatty acids. The result of the present study from a species of shark *(Carcharias melanopterus)* liver oil from the Arabian Sea only confirms the findings of previous workers.

Experimental

The shark liver oil from the Arabian Sea, supplied by the director, Department of Fisheries, Bombay, was refined and freed from phosphatides as usual.

Some 195 g. (I.V. 132.0) of the refined and phosphatide free oil was saponified, unsaponifiable matter was extracted, and fatty acids were obtained in the usual way (9). The 180 g. (I.V. 140.1) of the mixed acids thus recovered were subjected to the lead salt alcohol separation method as modified by Hilditch (1), whereupon 47 g. (I.V. 5.2) of insoluble (solid) acids (A) and 133 g. (I.V. 187.0) of soluble (liquid) acids were obtained. Unfortunately some of the liquid acids were spilled, and 70 g. were left. This quantity was then subjected to the lithium salt acetone separation method (11), when 46.7 g. (I.V. 129.1) of insoluble (mainly monoethylenic) acids (B) and 23.3 g. (I.V. 300.0) of soluble (polyethylenic acids (C) were obtained.

Each of the acids (A, B, and C) was separately methylated and fractionated as usual through E.H.P. column (3). Saponification equivalents and iodine values of each of the subfractions of all the groups of esters were determined, and the data are given in Table I.

The composition of each of the ester fractions was calculated from saponification equivalents and iodine values by the method of Hilditch (2). The mean unsaturation expressed as the fractional number of hydrogen atoms short of saturation, for example, —2.0 (monoethenoid), was determined by interpolation and extrapolation from the respective ester fractions in each of the groups from which the mean equivalent of each of the homologous ester groups (C_{18}, C_{20}, etc.) follows. The component acids in the ester fractions are given in Table II along with the composition of the original oil built up from these figures.

TABLE I

Fractionation Data of Methyl Esters of Acids of Shark Liver Oil Fractions A, B, C

No.	G.	S.E.	I.V.
Methyl Esters of A Acids			
A1	2.67	252.3	0.67
A2	2.82	263.6	0.54
A3	3.04	266.5	0.88
A4	4.07	268.8	0.66
A5	4.83	275.1	0.85
A6	4.12	281.7	1.10
A7	4.97	287.0	1.60
A8	6.08	287.8	3.80
A9	4.40	321.0[a]	25.50
Methyl Esters of B Acids			
B1	2.23	241.2	42.6
B2	3.28	255.5	66.6
B3	2.85	262.8	72.9
B4	3.10	274.0	79.5
B5	3.50	277.7	88.4
B6	3.41	279.8	95.1
B7	3.39	291.1	117.1
B8	4.27	291.2	132.3
B9	4.22	297.0	176.6
B10	3.05	303.0	200.7
B11	3.94	325.7[a]	231.4
Methyl Esters of C Acids			
C1	1.75	269.1	148.6
C2	3.28	296.4	188.8
C3	3.37	315.4	310.6
C4	3.20	319.7	332.7
C5	3.73	345.9	338.2
C6	2.10	355.3	342.4
C7	0.92	361.5	345.3
C8	3.39	363.7[a]	350.0

[a] S.E. of esters, after extracting the unsaponifiable matter with ether A9 301.6, B11 305.9, C8 346.1.

TABLE II

Component Acids in Groups A, B, and C and in the Whole Fat

Acids	A (26.1%)	B (49.4%)	C (24.5%)	Total
Lauric		Trace		Trace
Myristic	1.8	2.6		4.4
Palmitic	14.0	4.5		18.5
Stearic	7.8	1.2		9.0
Arachidic	1.8			1.8
Unsaturated				
C_{14}		2.8		2.8
C_{16}	0.2	10.8	1.8	12.8
C_{18}	0.5	15.6	3.8	19.9
C_{20}		11.8	7.2	19.0
C_{22}			7.3	7.3
C_{24}			4.3	4.3
Non-saponifiable	Trace	0.1	0.1	0.2
Mean unsaturation of				
C_{14}		—2.0		—2.0
C_{16}	—2.0	—4.0	—3.0	—2.1
C_{18}	—2.0	—6.1	—4.3	—4.0
C_{20}			—8.0	—8.0
C_{22}			—9.9	—9.9
C_{24}			—11.0	—11.0

Discussion

The fatty acid composition of the oil *(Carcharias melanopterus)* is given in the last column of Table II. It is noticed that the total saturated acid content is 33.7% (myristic acid 4.4%, palmitic acid 18.5%, stearic acid 9.0%, and arachidic acid 1.8%) of the total. The unsaturated counterpart is 66.3% (C_{14} acid 2.8%, C_{16} acid 12.8%, C_{18} acid 19.9%, C_{20} acid 19.0%, C_{22} acid 7.3%, and C_{24} acid 4.3%) of the total. This re-

TABLE III

Fatty Acid Composition of Some of the Indian Shark Liver Oils

Acids	Shark liver oil 1 (9). *Galeocerdo rayneri* from Arabian Sea	Shark liver oil 2 (9). *Galeocerdo rayneri* from Bay of Bengal	Saw fish liver oil 3 (10). *Pristis cuspidatus* from Bay of Bengal	Shark liver oil 4 (10). *Carcharias melanopterus* from Bay of Bengal	Shark liver oil 5 (author). *Carcharias melanopterus* from Arabian Sea
Lauric	0.4	.....	.....	.....	Trace
Myristic	3.3	1.5	1.2	3.1	4.4
Palmitic	24.9	23.6	22.9	18.4	18.5
Stearic	11.1	14.5	12.7	9.5	9.0
Arachidic	1.2	0.3	0.1	0.1	1.8
Unsaturated					
C_{12}	0.1	.....	.....	.....	.....
C_{14}	1.1	0.2	0.2	0.8	2.9
C_{16}	11.2	10.9	8.2	10.8	12.7
C_{18}	19.6	23.3	28.5	19.7	20.0
C_{20}	22.3	11.6	16.4	15.2	19.0
C_{22}	4.8	12.2	5.2	17.1	7.3
C_{24}	.....	1.9	4.6	5.3	4.4
Mean unsaturation of					
C_{12}	−2.0	.....	.....	.....	.....
C_{14}	−2.0	−2.0	−2.0	−2.0	−2.0
C_{16}	−2.6	−2.0	−2.0	−2.1	−2.1
C_{18}	−3.9	−2.6	−2.2	−3.6	−4.0
C_{20}	−7.0	−5.8	−5.3	−7.0	−6.8
C_{22}	−10.6	−8.4	−7.4	−9.0	−9.9
C_{24}	.....	−11.0?	−11.0?	−11.0?	−11.0?

veals clearly that the saturated acid content is on the lines as suggested by Tsujimoto (12). For the purpose of comparison and explanation the reliable quantitative fatty acid composition of other varieties of shark liver oils as well as saw fish liver oil obtained by previous workers along with the present one is summarized in Table III. It is noticed that the saturated acid content of the liver oils No. 1, 2, 3, and 4 and the present one are 40.9, 39.9, 36.9, 31.1, and 33.7%, respectively, of which the most predominating palmitic acid is 24.9, 23.6, 18.4, 22.9, and 18.5%, respectively. The unsaturated counterpart is 59.1, 60.1, 63.1, 68.9, and 66.3%, respectively. Unsaturated C_{16} acid content is very close to each other in all the cases. There are many other points of similarities, which can very easily be seen in the table. It however brings two important facts to light, *viz.*, that the saturated acid content, as observed before, is very high for a marine fish liver oil, and secondly that the composition of all the liver oils is very similar both in the contents of acids and in the unsaturation of the unsaturated acids.

On a closer examination of the oils No. 4 and 5 *(Carcharias melanopterus)* from the Bay of Bengal and the Arabian Sea it is noticed that the component fatty acids are still more similar, even though their habitats are different. Palmitic and stearic acids are remarkably close to each other (18.4 and 18.5% palmitic and 9.5 and 9.0% stearic). Myristic and arachidic acid content in No. 4 is lower by 1.3 and 1.7% than No. 5. The unsaturated acid content too is very similar, *e.g.*, C_{18} acid is 19.7 in No. 4 and 20.0% in No. 5. C_{16} acid differs by only 2 unit per cent, C_{20} acid in No. 4 is lower by 3.8 unit per cent, which is made up in the content of C_{22} acid in No. 4, *i.e.*, it is richer by 9.8 unit per cent as compared to No. 5. Unsaturations in them are also very similar.

From the statistical survey of the composition of marine and fresh water fish liver oils Lovern (5) gave the following figures as the average composition of each class.

On comparison of the present data with the average (Table IV) it is noticed that the content of C_{22} acid is akin to marine type whereas C_{20} acid falls short by 10 unit per cent and the saturated acid content is also different for a marine fish fat.

The analyses of oils summarized in Table III of the Elasmobranch species, which has been put in

TABLE IV

Average Composition of the Fats of Fish (wt. %)

Type	Total C_{16}	Unsat. C_{16}	Unsat. C_{18}	Unsat. C_{20}	Unsat. C_{22}
Fresh water	40	20	40	13	2.5
Boundary	30	15	35	17.5	9
Marine	25	10 (2.0-2.5)	25 (2.6-3.3)	25 (5.5-6.5)	15 (7.0-9.5)

the IV group of Tsujimoto, consistently shows much higher saturated acid content and strongly suggests that such peculiar compositions in marine fish liver oils are characteristic of this particular family. It is, of course, definite that the composition of oils of this class of fish also varies, which may be due to difference in species, age, and locality. It may further be said that in certain groups of zoologically related animals the synthesis of different types of fats, by different groups of organisms and/or because of a particular type of biochemical process, is possible. As for the high saturated acid content in the IV group of Elasmobranch fish, Lovern (6) has observed that there is evidence of simultaneous hydrogenation of polyethylenic and monoethylenic derivatives. The temperature of water inhabited by fish may also be responsible to some extent, a fact which has earlier found evidence in eel (7) and tunny (8) fat. So, on the whole, the findings of the present work are in conformity with earlier workers, and the high saturated acid content is only natural in this case and class of fish.

Summary

1. A sample of liver oil of an Indian shark *(Carcharias melanopterus)* from the Arabian Sea has been studied.

2. Tsujimoto's lithium salt acetone method has been adopted for the separation of the highly unsaturated acids from the mixed acids, which were further resolved into simpler groups with the help of Hilditch's modified lead salt ethanol method. The efficient column (E.H.P.) of Longenecker has been employed for fractionation in the present work.

3. The present oil is found to belong to the IV group of Tsujimoto's classification of the Elasmobranch fish liver oils.

4. The abnormal saturated acid content is discussed. The present analysis provides an additional instance of this peculiar group of Elasmobranch liver oils.

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Pilot-Plant Production, Tempering, and Evaluation of Global Edible Spreads from Vegetable Oils[1]

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A RECENT paper describes the discovery of an edible-spread composition of wide plastic range to meet the needs of Armed Forces stationed under widely differing climatic conditions (5). The composition contains vegetable oil, distilled glycerol monostearate, and other ingredients. It may be spread on bread or crackers at low temperatures and still does not melt or separate at high temperatures encountered in the tropics.

After a basic formula had been found for preparing a spread with desirable plasticity characteristics, several problems arose in the further development of the product. For example, when prepared in the laboratory, the spread usually developed small crystals which imparted an undesirable grainy "mouth feel." It was also difficult to prepare, in the laboratory, uniform material in sufficient quantities for organoleptic evaluation. Preliminary studies in the pilot plant in which a small Votator [3] unit was used for rapidly solidifying the spread demonstrated that an improved and more uniform product could be made.

Previous conceptions of a spread with suitable mouth "getaway" prescribed that it must melt readily and almost completely in the mouth (1). Undoubtedly the most difficult problem to be solved in preparing a suitable high-melting edible spread was to discover a formulation which would be emulsified readily when eaten with other food without leaving a pasty or waxy residue in the mouth. A description of pilot-plant techniques and of recent advances made toward improving getaway and physical stability of the global-spread composition is the subject of this paper.

Pilot-Plant Production

The first paper describing a global spread contained a table giving a typical formulation (4). Subsequent refinements and modifications now justify further comments regarding the composition. Since the product contains no aqueous phase, the salt is prepared by grinding sodium chloride (C.P.) in a nickel-plated hammer mill. Approximately 99% of the ground salt will pass through a 325-mesh screen. Originally, the addition of 0.2 part of butter-flavor concentrate per hundred parts of total glycerides was recommended. However subsequent evaluations indicate that a spread containing 0.04 part of this concentrate is preferred by the taste panel at the Northern Utilization Research Branch. In place of 0.2 part of butter-color concentrate, 0.0035 part of dry carotene has been used satisfactorily. Composition of the spread currently being produced is given in Table I.

TABLE I

Composition of Global Spread

Ingredients	Parts
Vegetable salad oil	83
Distilled monostearate	17
Soybean phosphatides (oil-free)	0.2
Salt	2.5
Carotene	0.0035
Butter-flavor concentrate	0.04
Propyl gallate	0.01
Citric acid	0.005
Vitamin A	1,650,000 units/100 lbs.
Vitamin D	330,000 units/100 lbs.

The equipment used for preparing global spread in the pilot plant, as shown in Figure 1, consists of a jacketed mixing kettle, a means of introducing nitrogen into the material as it is drawn to a gear pump, and a Votator cooling unit. The cylinder of the Votator is constructed of nickel, and other equipment is stainless steel.

The constituent materials for preparing a spread are added to the mixing kettle, heated to about 170°F. (77°C.) and then pumped to the Votator from which the spread issues in a fluid stream. Fifteen to 20 volume-percentage nitrogen based on the oil volume is introduced ahead of the pump. There is no pressure valve on the discharge side of the Votator, and the material flows readily and evenly into containers. The mass rather quickly "sets up" to a firm consistency.

A mixing kettle with a capacity of 2 gal. is chosen since only about 10 lbs. of material are required for various analyses and taste-panel evaluations. The Votator chamber has a diameter of 3 in. and 90 sq. in. of heat-transfer area. A gear pump with a capacity of 12 gal. per hour is used. Cooling water at 60°F. (16°C.) is adequate for chilling the spread.

Difficulties were encountered in incorporating the salt in the spread. Attempts were made to mix salt

[1] Presented at the American Oil Chemists' Society meeting, Chicago, Ill., Nov. 2-4, 1953.
[2] One of the Branches of the Agricultural Research Service, U. S. Department of Agriculture.
[3] The mention of firm names or trade products does not imply that they are endorsed or recommended by the Department of Agriculture over other firms or similar products not mentioned.