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CHARACTERISTICS OF SHARK LIVER OILS FROM NORTHEASTERN BRAZIL [1]

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Shark liver oil has been important because of its high content of fat soluble vitamins and because of its importance for the oil and soap industries.

Liver oils of sharks of Japanese origin have been examined by Shimma & Shimma (1966, 1969) and the ones from South American origin were studied by Gruger *et al.* (1946), Karnovsky *et al.* (1965), Olley & Duncan (1965), Malins *et al.* (1965), Gelpi & Oró (1968), and Gershbein & Singh (1969).

The purpose of the present study was to determine the nature of the liver oil of several species of sharks caught off the coast of northeastern Brazil.

MATERIALS AND METHODS

Sharks common to the coastal areas of northeast Brazil, tiger shark = *Galeocerdo cuvier* (Le Sueur) — sample number 1 and 2 —, nurse shark = *Ginglymostoma cirratum* (Bonnaterre) — sample number 3 to 5 —, great blue shark = *Prionace glauca* (Linnaeus) — sample number 6 and 7 —, and the shark *Carcharhinus porosus* Ranzani — sample number 8 and 9 —, were caught off the coast of the State of Ceará during late 1972 or early 1973. The sharks were preserved by packing in ice and eviscerated after returning to port. The livers were removed, packed in ice overnight, and processed immediately afterward.

Extraction of the oil from the livers were according to the method of Uno & Tokunaga (1955). The entire liver was used in each case, and the amount of reagents used in extraction was based on the weight of the fresh liver. Each liver was macerated in Waring Blender with distilled water, in the amount equal to 20% of the weight of the liver. After homogenization, the slurry was placed in a stainless steel container and autolyzed for two hours at 50-55°C.

Upon the completion of this time, sodium hydroxide pellets (0.5% of weight) were added and the temperature was raised to 90°C, at which temperature it remained for one hour. Boiling water (150-200%) was then added to cause separation of the material into two layers. At times, it was necessary to use a saturated salt solution, to facilitate phase separation. The oil layer was removed, filtered, and cooled.

Procedures of the A.O.A.C. (1965) were followed for the following analyses: refractive index at 40°C, specific gravity using picnometer, iodine number (Hubl), saponification number (Koettstorfer), and unsaponifiable matter. Acid value was determined according to the method of Nippon Yukagaku Kyokai (1966).

Formation of methyl esters

For transmethylation of the shark oil, a slight modification of the method of Gammon & Whiting (1969) was used. It consisted of placing 0.2 ml of the liver oil in a 50 ml Erlenmeyer flask, adding 3 boiling beads, and drying for 10 minutes at 100°C. After this, 5 ml freshly prepared sodium methylate (0.025 g sodium to 20 ml anhydrous methanol) was added to the dried sample. The flasks were loosely stoppered with a Teflon stopper and placed in an agitating water bath at 61°C for one hour. After esterification, 2.5 ml distilled water and 2 drops of acetic acid were added with agitation. Then 1 ml of hexane was added, the mixture was agitated and transferred to a 30 ml separatory funnel,

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where the phases were allowed to separate. The lower aquous layer was discarded, and the upper layer, containing the methylated fatty acids was transferred to a screw top test tube.

Gas chromatography of fatty acid methyl esters

For this method, the following apparatus and conditions were required: Instrument — Tracor Model MT160 ; Detector — Flame Ionization, H_2 — 30 ml/min., Air — 150 ml/min.; Column — S.S. 2.0 m x ¼" ; Packing — 20% LAC 728 (DEGS) on chromosorb CWR 60/80 ; N_2 flow — 30 ml/min.; Injector temperature — 250°C ; Detector temperature — 250°C ; Column temperature — 200°C ; Atenuation — 64 x 10^2 , 4 x 10^2 ; Sample size — 1 to 2 ul .

The area of each peak was calculated by multiplying peak height by peak width at half height and the percentages of each fatty acid by normalization. Identification of each fatty acid was made by co-chromatography and/or by calculating the logarithm of the expected relative Rf , with stearic acid as a reference.

RESULTS AND DISCUSSION

Physical and chemical characteristics of the shark liver oil are shown in tables I and II . Generally, the weight of the shark liver is between 8-10% of the total weight and contains between 10 and 85% oil (Bailey, 1952) . In the present study values of 2.5 — 13.5 , for total yield of liver and values of 41.2 — 62.3% of extracted oil from the livers were observed. These values compare favorably with those obtained by Tohoku Regional Fisheries Research Laboratory (1952) , while studying the great blue shark (captured in the Pacific Ocean) and the species *Carcharinus albimarginatus.*

According to the Brazilian legislation (Decree n.° 45,502 , February 27 , 1959) , shark liver oil, particularly of the Lamidae, Galeidae, Squalidae families, extracted by expression and heating, and filtered at low temperature, must be conform with the following characteristics: refractive index — from 1.4704 to 1.4745 at 40°C ; specific gravity — from 0.908 to 0.927 at 25°C ; acid value — maximum 2.8 ; iodine value — from 170 to 195 ; saponification value — from 140 to 205 ;

TABLE I

Particulars of shark liver oil from northeastern Brazil.

Sample number	Sex	Timd of catch	Body weight (A) (kg)	Body length (cm)	Liver weight (B) (kg)	B/A x 100 (%)	Oil content (%)	Liver color
1	f	10/72	19.0	165	2.1	11.1	46.2	grey
2	f	10/72	4.0	85	0.1	2.5	47.8	clear grey
3	m	08/72	22.0	164	1.3	5.9	43.7	clear grey
4	m	10/72	12.0	128	0.6	5.0	44.5	clear grey
5	f	11/72	43.0	210	4.1	9.5	43.8	rose-violet
6	f	11/72	9.4	125	0.4	4.3	41.2	yellow-grey
7	f	02/73	99.0	—	7.2	7.3	62.3	rose-grey
8	f	09/72	59.0	180	5.0	8.5	58.6	rose-grey
9	f	02/73	62.0	205	8.4	13.5	61.4	grey-violet

TABLE II

Characteristics of shark liver oil from northeastern Brazil.

Sample number	Refractive index (n_D^{40})	Specific gravity (d_4^{20})	Acid value	Iodine value	Saponification value	Unsaponifiable metter content (%)
1	1.4725	0.9150	0.25	112.7	184.5	1.40
2	1.4800	0.9150	0.25	170.0	190.0	3.37
3	1.4760	0.9191	0.15	125.6	195.8	1.76
4	1.4740	0.9170	0.15	137.5	191.0	2.40
5	1.4740	0.9253	0.27	126.0	--	1.60
6	1.4815	0.9253	0.55	155.0	171.0	1.93
7	1.4750	0.9210	0.25	123.0	—	1.40
8	1.4705	0.9160	1.42	102.9	192.7	1.53
9	1.4735	0.9160	0	123.0	—	0.40

and unsaponifiable matter content — maximum 3% .

Specific gravity and acid value are within the range limit; saponification value and unsaponifiable matter content exceed in one oil sample each; refractive index with 4 oil samples of higher values, the remainder within the range limit; iodine value only 2 oil samples were within the range limit, the remainder presented lower values.

The distribution of fatty acids present in the shark liver oils studied is shown in table III . The two predominant fatty acids were C 16:0 (23 — 39%) and C 18:1 (10 — 26%) , compared with relatively small amounts of the polyunsaturated acids, C 20:4 (3 — 6%) and C 22.6 (4 — 17%) . The only large difference noted between species is that the great blue shark which gave a much higher percentage (11 — 17%) of the unsaturated fatty acid, C 22:6 , than the other species examined. A large percentage of C 22:6 was found in hammerhead sharks, but not in basking sharks by Shimma *et al.* (1968) . In basking sharks in the same study, as well as in deep sea sharks of Suruga Bay (Shimma & Shimma, 1966) C 18:1 predominated (17 — 43%), and C 20:1 and C 22:1 were present in large quantities (8 — 30%) .

The most frequent monoenoic acids found in common shark liver oils are 20:1 , 22:1 , and 24:1 , presented in high percentage. The samples studied in this work have comparatively shown high percentage of 22:6 , as well, which perhaps in caused by catching having been done in surface waters (Shimma, 1973) .

Gelpi & Oró (1968) in studies of bulk quantities of South American shark liver oil, found that the relative quantities of C 18:1 , C 20:1 and C 22:1 fatty acids were close to 18.5% in each case with C 14:0 , C 16:1 , and C 18:0 present in concentrations of 5.5 , 6.8 , and 3.1 respectively. The amount of palmitic acid (C 16:0) exceed all others (20.3%) , but polyunsaturated fatty acids were present only in small quantities.

In an unidentified species of shark (Ito & Fukuzumi, 1963) , and according to Klenk & Eberhagan (1962) in herring sharks *Isurus cornubicus* Gray, the predominating acid was found to be C 20:1 . Neither C 20:1 nor C 22:1 was present in large quantities in the present study (2-6%) . In addition, the relatively low iodine value, 102-170 , as compared to the 139-352 of Shimma & Shimma (1966) . In an earlier study of *Centrophorus* Müller & Henle (Atlantic) and *Seymnorhinus lichia* (Bonnaterre) — Europe, Hilditch (1934) found that C 18:1 predominated (30%) with under 20% of the acids being saturated.

The differences of saturation and unsaturation in shark liver oils is subject to large

TABLE III

Fatty acid composition of shark liver oil from northeastern Brazil.

Fatty acids	Percentages of fatty acids — sample numbers								
	1	2	3	4	5	6	7	8	9
14:0	2.5	2.5	2.7	2.9	3.7	3.7	3.7	2.6	3.3
15:0	1.1	1.2	1.0	1.1	1.2	1.4	0.9	1.2	1.1
16:0	30.5	36.7	39.1	28.6	31.3	29.7	23.6	29.4	34.9
16:1	7.6	5.7	6.7	6.1	5.7	2.8	6.1	7.4	7.5
17:0	2.9	2.2	2.6	2.3	—	2.1	—	2.9	—
17:1	1.0	0.8	0.9	1.4	—	0.4	—	1.0	—
18:0	9.4	8.1	7.0	7.8	7.1	5.9	9.3	11.0	6.9
18:1	20.9	20.3	17.6	21.7	20.6	10.9	25.6	21.0	22.7
18 2	1.9	1.7	1.2	1.1	1.7	1.9	1.4	2.0	1.0
20 0	0.4	0.3	0.4	0.2	0.3	0.7	0.2	0.4	0.3
20:1 18:3	2.7	2.7	2.0	2.2	2.3	4.7	2.4	2.9	2.1
18:4	0.4	0.5	0.4	Tr.	0.6	0.3	0.7	0.4	0.4
20:2	0.4	0 6	0.5	0.3	—	0.7	—	0.5	0.3
UK	0.1	—	—	—	0.6	0.3	0.1	0	0.1
20:3	0.4	0.3	0 3	0.2	0.7	0.3	0.3	0.3	0.2
22:1 20:4	4.1	3.6	5.4	5.5	4.5	4.2	4.5	4.6	3.6
20:4 II	0.7	0.7	0.9	0.4	0.5	0.5	0.4	0.7	0.4
20:5	1.7	1.5	1.4	1.8	1.6	2.9	2.1	1.4	2.1
UK	—	0.1	—	—	—	0.3	—	0.2	—
24:1	2.9	2.6	2 6	3.6	5.7	2.5	2.6	3.0	1.8
22:4	1.3	1.2	1.0	1.6	1.8	2.9	2.3	1.1	1.3
22:5	2.0	2.0	2.1	3.4	3.8	3.7	2.7	1.8	1.9
22:6	5.1	4.6	4.8	8.0	6.3	17.3	11.1	4.0	7.8

variation and has been attributed to differences in species, food, sexual maturity, and temperature of the sea water (Bailey, 1952) even though Blumer (1967) found that the fatty acids of basking shark liver oil were more saturated than the oils of the zooplankton, genus *Calanus,* which formed the greater part of its diet. This was especially evident in the polyunsaturated C 20 and C 22 fatty acids and indicates a saturation of the fatty acids by the digestive system of the shark.

The present study seems to be in agreement with the results of Gelpi & Oró (1968) and to support the generalization that sharks from warm waters have oils which are more saturated than those of sharks from cold waters. This in turn may be due to the fact that the vegetable oils of aquatic plants, the ultimate source of the diet of all fish, are more saturated in tropical than in temperate climate.

SUMMARY

This paper deals with the characteristics of liver oil of northeast Brazil's sharks of the species *Geleocerdo cuvier* (Le Sueur), *Ginglymostoma cirratum* (Bonnaterre), *Prionace glauca* (Linnaeus), and *Carcharhinus porosus* Ranzani.

1. The values of 2.5 — 13.5% for total yield of liver and values of 41.2 — 62.3% of extracted oil from the livers were observed.

2. Characteristics of fatty acids seem to be in agreement with the results obtained before and to support the generalization that shark from warm waters have oils which are more saturated than those of shark from cold waters.

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