STUDIES ON THE EXTRACTION OF FISH LIVER OIL.

III. THE EXTRACTION OF OIL FROM FISH LIVERS CONTAINING LOW VITAMIN A UNIT.

By

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With 5 tables

Introduction

The following report is an account of the authors efforts to find by what method or treatment is it possible to extract from low-vitamin-A-unit-content fish livers, such as those of codfish, shark, and bonito, a possibly higher vitamin-A-unit liver oil and in larger quantity. The authors used the alkaline method on an industrial scale with the above mentioned fish livers. They hope their report may be of some reference value at least.

I. Cod Liver and Its Internal Organs.

METHODS OF EXTRACTION OF OIL:-

Liver oils extracted from codfish livers and that from codfish liver together with the other internal organs, the so-called "whole internal organs", are quite different in their vitamin A unit, their odor, and their color. Generally, these raw materials were bought separately and used separately according to the purpose of their uses. The oil extraction operation was the same as the one described for extracting oil from high-vitamin-A-unit-content fishes in the authors' former report, namely, raw materials freed from impurities after weighing were chopped finely and placed in a tank for extraction.

Methods of extraction used were (A) Method of separating the upper layer, and (B) Method of separating the whole liquor.

(A) Method..... Quantity of water used was approximately 1 to 2 times the raw material used. When oil content is large, after emulsification, the milky white liquor will be quite abundant and will make the decantation difficult, the container inconvenient for use, and, moreover, its centrifugal separation will require much more time. However, codfish liver is soft in character and easy to

be dissolved. Add NaOH of 20° to 30° Bé to adjust pH of the material about 8.0 and heat it. When at 50°C., the raw material starts to decompose, if the operation is in a fair condition its temperature may be raised directly to 80°C., at which temperature water is added to lower the temperature to 50°–30°C. while the stirring also is stopped. Cover it and decant the upper oil layer the next morning. By centrifugal separation crude oil is obtained.

(**B**) **Method**.....Use as small a quantity of water as possible and use some more NaOH than that used in Method A to adjust pH of material to 9 approximately. Then heat it. At 85°C., stop the stirring, transfer to a tank and separate either immediately or after being let stand quietly for several hours, to obtain crude oil centrifugally.

RESULTS:–

In Table I A, data cover a period from February 1948 to October 1950 during which period livers of pollack and that of codfish caught in all months excepting January and April were used for monthly tests. In February, September, October and November, 1950 fish were taken every day during a certain period. The results of daily tests with daily caught fish as samples are presented in Table I B.

From those results it is clear that when a great quantity of raw material is used and extracted with industrial equipment, the operation is convenient when

Table I A

Date	Species of fish	Liver quantity kg.	NaOH quantity of addition kg.	NaOH/ Liver %	Oil quantity kg.	Ratio of oil extracted %	Vitamin A unit U.S.P.U.	Total vitamin A quantity per gr. of liver G.U.S.P.U.	Remarks
Feb., 1948	Pollack	343.0	5.0	1.4	103.0	30.0	3750	1125.0	
〃 , 1949	〃	2078.0	45.0	2.1	670.0	32.2	——	——	
〃 , 1950	Codfish	3578.0	45.2	1.2	1125.0	31.4	11480	3604.7	
Mar., 1949	〃	2894.0	55.2	1.9	716.0	24.7	——	——	
May, 1949	〃	509.0	11.5	2.2	113.0	22.2	16780	3725.1	
June, 1949	〃	4143.0	64.5	1.5	1161.0	28.0	17950	5026.0	
〃 , 〃	〃	1784.0	22.5	1.2	441.0	24.7	11000	2717.0	
〃 , 1950	Pollack	2119.0	48.7	2.2	781.0	36.8	1100	404.8	
July, 1949	〃	2859.0	60.0	2.0	680.0	23.7	9535	2259 7	
Aug., 1949	Codfish	1557.0	62.0	3.9	436.0	28.0	——	——	
Sept., 1949	〃	1515.0	62.0	4.0	437.0	28.8	——	——	
〃 , 1950	Pollack	1257.0	29.0	2.3	332.0	26.4	7480	1975.4	Whole internal organs
Oct., 1950	〃	4074.0	114.0	2.7	741.0	18.1	8080	1462.4	
〃 , 〃	〃	5761.0	176.4	3.0	922.0	16.0	7140	1142.4	
Nov., 1950	〃	8045.0	150.4	1.8	1528.5	18.9	6000	1134.0	
Dec., 1948	〃	828.5	15.5	1.8	270.0	32.5	——	——	

Table I B

Date	Species of fish	Liver quantity kg.	NaOH quantity of addition kg.	NaOH/ Liver %	pH value	Heating temperature °C	Oil quantity kg.	Ratio of oil extracted %	Vitamin A unit U.S.P.U.	Total vitamin A quantity per gr. of liver G.U.S.P.U.	Acid value	Remarks
Feb. 19, 1950	Codfish	789.0	9.7	1.22	8	80	230.0	29.15	11800	3439.7	2.5	By method A
Feb. 20, 1950	〃	986.0	12.0	1.21	8	80	307.6	31.19	11500	3586.8	3.2	〃
Feb. 21, 1950	〃	945.0	11.7	1.23	8	80	284.4	30.09	11500	3460.3	4.6	〃
Feb. 22, 1950	〃	858.0	11.8	1.37	9	80	303.0	35.31	11200	3954.7	2.9	〃
Sept. 22, 1950	Pollack "Whole internal organs"	1257.0	29.0	2.30	9	80	332.0	26.41	7480	1975.4	0.67	〃
Oct. 16, 1950	〃	2054.0	56.6	2.75	9	80	359.0	17.47	8160	1425.5	0.52	〃
Oct. 17, 1950	〃	2020.0	57.4	2.84	9	80	382.0	18.91	8000	1512.8	0.60	〃
Oct. 21, 1950	〃	1514.0	47.4	3.13	—	80	274.0	18.09	7480	1353.1	0.65	〃
Oct. 22, 1950	〃	4247.0	129.0	3.03	—	80	648.0	15.25	7000	1067.5	0.77	〃
Nov. 9, 1950	〃	862.0	24.6	2.85	9	85	151.0	17.51	4900	857.9	0.35	By method B
Nov. 10, 1950	〃	1140.0	20.1	1.76	9	85	237.8	20.85	5900	1230.1	0.30	〃
Nov. 11, 1950	〃	1515.0	27.7	1.82	9	85	304.2	20.07	8000	1605.6	0.25	〃
Nov. 13, 1950	〃	1623.0	28.7	1.76	9	85	266.4	16.41	6000	1312.8	0.31	〃
Nov. 14, 1950	〃	745.0	12.6	1.69	9	85	141.2	18.95	8000	1516.0	0.35	〃
Nov. 17, 1950	〃	900.0	16.3	1.81	9	85	182.6	20.28	7700	1561.5	0.27	〃
Nov. 18, 1950	〃	1260.0	20.4	1.61	9	85	245.3	19.46	7900	1537.3	0.40	〃

(A) Method is used. As to the adjustment of pH, it seems that the result is somewhat better when material is adjusted to pH 9.0 rather than 8.0 and then heated, though from the view point of centrifugal separation the latter pH value is preferable. For samples of the same period, when the pH values were adjusted to 8.0-9.0, the quantity of NaOH used was almost the same in each case, i.e., about 2%. Liver oil from pollack or from codfish is light yellow in color, of relatively less odor, and a good oil extracting ratio; its vitamin A unit is also 10,000 U.S.P.U. Liver oil from the whole internal organs has a light red color, of an unpleasant odor, and a rate of oil extraction inferior to that of the former case. Its vitamin A unit is less than 10,000 U.S.P.U. Raw materials obtained in the same period seen to have an equal total vitamin A quantity per gr. of liver regardless of which extraction method is used.

II. Shark Livers.

Liver oils of great blue shark and salmon shark have generally a vitamin A unit of 3,000 U.S.P.U.; they contain

carbohydrates and waxes for which reason their melting points are high and their degrees of transparency at lower temperatures are not good. They are difficult to be refined and, therefore, are unsuitable as a source of vitamin A oil. Hence, stress is placed technically on a high quantity of oil extracted and a simpler operation rather than on its vitamin A unit. However, in the liver oil of codfish, though its vitamin A unit differs according to the color of the liver, its vitamin A concentration is usually 20,000 to 40,000 U.S.P.U. In this case, care must be taken, as in the case with high-vitamin-A-unit fishes, to extract the oil by heating in order to obtain a higher vitamin-A-unit product in larger quantity.

METHOD OF EXTRACTION OF OIL:-

Free impurities from the raw material; after weighing, chop finely with a chopper and transfer it into a tank. Extraction of oil is then performed by either method (A), separating of the upper layer or by (B), separating of the whole liquor.

RESULTS:-

Table I A presents the monthly test results from fish taken in each month during a period from February 1947 to September 1950; B reports on a period from June to December 1949. Data indicated as "shark" only, are results obtained from a mixture of both great blue shark and salmon shark. Amount of solid NaOH used with these two kinds of shark livers was generally about 1%; the same percentage of NaOH was also used with dogfish. Quantities extracted were about 40% for the former two kinds and about 50% for dogfish. Vitamin-A-units were 3,000-6,000 U.S.P.U. and 8,000-15,000 U.S.P.U. respectively.

Some of the dogfish livers were black and some were white in color. They were sampled separately and their vitamin A units determined separately. It is clear that the black had much more vitamin A than the white livers, being about 40,000 U.S.P.U., twice that of the latter.

During the operation, care must be taken to note that, during transportation in summer from the seashore where fish were taken to the oil extraction plant, the oil would separate out of itself. This would be more evident when it was kept in the factory and the longer the period of keeping the more oil would be separated out which would then float on the surface of the container. This self-separated oil had to be transfered separately to another container before livers were chopped. This oil might be kept separately after weighing or added to the

Table II A

Date	Species of fish	Liver quantity kg.	NaOH quantity of addition kg.	NaOH/ Liver %	Oil quantity kg.	Ratio of oil extracted %	Vitamin A unit U.S.P.U.	Total Vitamin A quantity per gr. of liver G.U.S.P.U.
Jan, 1949	Shark	1996.0	50.5	2.5	825.0	41.3	—	—
Feb., 1947	〃	929.0	12.6	1.3	320.0	34.4	—	—
〃 , 1948	Great blue shark Mackerel shark	456.0	7.0	1.5	182.0	39.9	—	—
〃 , 1949	Shark	3577.0	73.0	2.0	1389.0	38.8	4300	1668.4
Apr., 1947	〃	243.0	0.8	0.3	75.0	30.8	—	—
May . 1948	〃	172.0	1.7	0.9	45.0	26.1	—	—
〃 , 1949	〃	460.0	2.5	0.5	205.0	44.5	6290	2799.5
〃 , 1950	Dogfish shark	65.0	1.0	1.5	45.0	69.2	8700	6020.4
June, 1949	〃	6004.0	56.0	0.9	3509.0	58.4	5000	2920.0
〃 , 〃	Shark	4521.0	68.7	1.5	1620.0	35.8	—	—
〃 , 1950	〃	22.0	0.5	2.2	6.0	27.2	—	—
July, 1947	〃	234.0	2.1	0.8	80.0	34.1	26400	9002.4
〃 , 1949	〃	5402.0	79.5	1.4	1984.0	36.7	—	—
〃 , 1950	Degfish shark	722.0	36.0	4.9	387.0	53.6	2250	1206.0
Aug., 1947	Shark	5103.0	16.5	0.3	1224.0	23.9	3300	788.7
〃 , 1948	Salmon shark	2229.0	50.7	2.2	631.0	28.3	—	—
〃 , 1949	Dogfish shark	753.0	13.0	1.7	300.0	39.8	—	—
〃 , 〃	Shark	17740.0	245 5	1.3	6776.7	38.2	—	—
Sept., 1947	〃	1200.0	7.1	0.5	530.0	44.1	6900	3042.9
〃 , 1948	Great blue shark	814.0	13.2	1.6	237.0	29.1	—	—
〃 , 1949	Dogfish shark	1424.0	12.3	0.8	739.0	51.8	—	—
〃 , 〃	Shark	5118.0	47.5	0.9	2047.2	40.0	—	—
〃 , 1950	〃	148.0	2.0	1.3	60.0	40.5	—	—
Oct., 1947	〃	613.0	4.9	0.7	261.0	42.5	—	—
〃 , 1949	〃	11304.0	108.1	0.9	5016.0	44.3	—	—
Nov., 1947	〃	979.0	10.0	1.0	386.0	39.4	3600	1418.4
〃 , 1948	Etmopterus shark	2710.0	11.5	0.4	1980 0	73.0	—	—
〃 , 〃	Shark	4828.0	76.2	1.5	1540.0	31.8	—	—
〃 , 〃	Hammer head shark	234.0	2.5	1.0	90.0	38.4	60000	23040.0
〃 , 1949	Dogfish shark	6533.0	81.4	1.2	3725.0	56.5	22000	12430.0
〃 , 〃	Shark	14066.0	158.7	1.1	7055.0	50.1	—	—
Dec., 1947	Dogfish shark	184.0	1.7	0.9	92 0	50.0	14400	7200.0
〃 , 1948	〃	483.0	8.8	1.8	212.0	43.8	1200	525.6
〃 , 1949	〃	2368.0	28.0	1.1	1170.0	49.4	—	—

Table I B

Date	Species of fish	Liver quantity kg.	NaOH quantity of addition kg.	NaOH/ Liver %	pH value	Heating temperature ℃	Oil quantity kg.	Ratio of oil extracted %	Vitamin A unit U.S.P U.	Total vitamin A quantity per gr. of liver G.U.S.P.U.	Acid value	Fish market
June 28, 1949	Shark	1330.0	18.8	1.41	8.6	80	498.0	37.44	—	—	—	Siogama
〃 29, 〃	〃	1530.0	25.0	1.63	9.2	80	582.0	38.04	—	—		〃
July 20, 〃	〃	1513.0	25.0	1.65	9.4	80	570.0	37.67	—	—	—	〃
〃 21, 〃	〃	1648.0	27.5	1.66	9.4	80	680.0	41.26	—	—	—	〃
Aug. 16, 〃	〃	2145.0	20.6	0.96	9.0	80	700.0	32.63	—	—		〃
〃 17, 〃	〃	2145.0	15.0	0.69	8.6	80	692 0	32.26	—	—	—	〃
〃 18, 〃	〃	2150.0	26.5	1.23	9.6	80	1075.0	50.00	—	—	—	〃
Sept. 22, 〃	〃	1379.0	10.9	0.79		80	514.0	37.27	—	—	-	Nemuro
〃 23, 〃	〃	1556.0	11.5	0.73	—	80	684.0	43.65	—	—	—	〃
〃 24, 〃	Dogfish shark	1424·0	12.3	0.86	—	80	739.0	51.89	—	—	—	〃
Oct. 25, 〃	Shark	1244.0	11.4	0.91	9.6	80	528.0	42.42	—	—	—	Hatinohe
〃 26, 〃	〃	1588.0	14.3	0.90	9.2	80	732.0	46.09	—	—	—	〃
〃 27, 〃	〃	1575.0	12.6	0.80	—	80	771.0	48.95	—	—	—	〃
〃 28, 〃	〃	1568.0	17.7	1.12	—	80	797.0	50.82	—	—	—	〃
〃 29, 〃	〃	857.0	10.6	1.23	—	80	436.0	50.87	—	—	—	〃
Nov. 1, 〃	〃	1595.0	17.9	1.12	—	80	697.0	43.69	—	—	—	〃
〃 2, 〃	〃	1947.0	19.2	0.98	—	80	957.0	49.15	—	—	-	〃
〃 3, 〃	〃	2010.0	18.6	0.92	—	80	1074.0	53.43	—	—	—	〃
〃 17, 〃	Dogfish shark "white liver"	1175.0	8.0	0.68	-	80	685.0	58.29	17700	10317.3	0.9	Nemuro
〃 18, 〃	〃	1853.0	10.6	0.57	—	80	1015.0	54.77	—	—	1.8	〃
〃 19, 〃	〃	1832.0	30.4	1.65	—	80	849.0	46.34	—	—	0.7	〃
〃 20, 〃	〃	1143.0	22.3	1.95	—	80	583.0	51.00	22690	11571.9	0.4	〃
〃 〃 〃	Dogfish shark "black liver"	575.0	9.1	1.58	—	80	243.0	42.26	44060	18619.7	—	〃
Dec. 23, 〃	Shark	1480.0	20.0	1.35	—	80	667.0	45.06	—	—	—	Hatin he
〃 24, 〃	〃	888.0	8.4	0.94	—	80	418.4	47.11	—	—	—	〃

Table III

Date	Liver quantity kg.	NaOH quantity of addition kg.	NaOH/Liver %	Pick up oil				pH value	Heating temperature °C	Oil quantity kg.	Vitamin A unit U.S.P.U.	Vitamin D unit I.U.
				Species of fish liver oil	Vitamin A unit U.S.P.U.	Quantity of addition kg.	Ratio of added %					
Aug. 3, 1949	150.0	4.2	2.80	Codfish	—	10.0	6.6	9.4	80	6.0	—	—
Oct. 5, 1949	418.0	15.7	3.75	Halibut yellow tail codfish	10000	29.2	6.9	9.4	80	29.4	30790	15700
June 8, 1950	176.0	9.2	5.22	Codfish	12000	12.0	6.8	9.2	80	13.0	22600	9780
July 11, 1950	—	—	—	Shark	—	—	—	9.6	80	—	22300	16400

heating tank when livers had been completely decomposed and stirred for some 30 minutes at about 80°C.

III. Bonito Liver.

The same oil extraction method was applied to bonito livers as that which had been used for codfish livers. Tests were made with the help of pick-up oil.

METHOD OF EXTRACTION OF OIL.

Water used was about twice that of the raw material. The pH value of the material was adjusted to approximately 9.6 by adding NaOH solution of 20°–30° Be′. At 50°–60°C., when the condition of dissolution and separation was good, 7% of pick-up oil was added. Then the pH was readjusted. About one hour later, temperature of material was raised and maintained at 80°–85°C., at which temperature it was stirred for nearly one hour. Water was led in to allow it to be skimmed easily. At 50°–60°C., stopped the stirring. Covered it until the next morning when the upper layer was skimmed and centrifuged to obtain crude oil.

RESULTS:–

Results were shown in Table III.

In this case the quantity of NaOH used was higher than that used for livers of the other fishes. Bonito liver has a very small oil content itself and its oil extraction without the help of pick-up oil is nearly impossible. The vitamin A unit and vitamin D unit values of bonito liver oil are 11,000-20,000 U.S.P.U. and 10,000-16,000 I.U. respectively.

Summary

(1) On extracting liver oil from codfish liver alone and codfish whole internal it is good to operate at pH 8.0. At this pH value rate of oil extraction is 20–30% and the vitamin A unit about 10,000 U.S.P.U.

(2) The optimum pH for the oil extraction of shark liver is 9.0–10.0. Oil rate is 40–50%. The vitamin A unit values of both great blue shark and salmon shark are ca. 3,000 U.S.P.U. while that of dogfish black liver is very large reaching to about 40,000 U.S.P.U. which is about twice of the white color liver form the same kind of shark.

(3) The oil extraction of bonito livers must be performed with the help of pick-up oil. Its vitamin A unit is 10,000–20,000 U.S.P.U. It contains a large quantity of vitamin D too.

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