

COD-LIVER OIL AND OTHER FISH OILS.

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My attention was called to the question of the adulteration of cod-liver oil by some samples which were submitted to me officially early last year. On looking up the matter, I found that analyses of cod-liver oil adulterants were scarce and incomplete. I therefore obtained a number of samples and analysed them. At a subsequent date the late Mr. J. Barclay kindly sent me samples of brusmer, hoi, and ling oils, which he informed me had been prepared in Norway from the fish indicated. As I could find no record of the two former names, I asked Professor Bridge, of the Birmingham University, for help. He kindly informed me that "brusmer" was probably the "brismak" of the Shetlands, or *Brosmius brosma*, one of the Gadidæ or cod family. He could not speak positively with regard to "hoi," but suggested it might be the common piked dog-fish, one of the shark tribe, which is known in the Orkneys as "hoe." For comparative purposes three samples of vegetable oil were also examined.

Table A gives the analytical figures of the samples of cod-liver oil. Samples A and B were two qualities from the same wholesale house. The Newfoundland oil E differed in several respects from the other samples. I communicated with the wholesale house as to its genuineness, and was assured that it was obtained from a reliable Newfoundland firm, and had not been adulterated after importation. Samples F to J had been bought officially.

TABLE A.—SAMPLES OF COD-LIVER OIL.

	Norwegian.			Newfoundland.		Origin unknown.			
	A	B	C	D	E	F	G	H	J
OIL.									
Specific gravity, 15·5° C. -	0·928	0·928	0·928	0·928	0·926	0·927	0·928	0·927	0·928
Zeiss butyro-refractometer at 25° C. - - - -	80·0	79·7	79·7	79·0	76·3	79·0	80·0	77·3	80·0
Zeiss butyro-refractometer at 40° C. - - - -	71·0	70·7	70·3	70·3	67·7	70·0	71·0	68·7	71·0
Rotation (200 - millimetre tube) - - - -	-0·5°	-0·5°	-0·5°	-0·5°	-0·5°	-0·6°	-0·7°	-0·4°	-0·6
Hübl, iodine per cent. - -	168	162	167	164	154	160	165	154	164
KHO required per cent. for free acid - - -	0·1	0·1	0·2	0·2	0·1	0·2	0·1	0·2	0·1
KHO total per cent. - -	18·7	18·5	18·7	18·7	18·8	18·7	18·6	18·9	18·6
Valenta test (° C.) - -	95	95	96	95	94	95	96	93	94
Unsaponifiable matter per cent. - - - -	—	—	1·2	—	1·1	—	—	—	—
FATTY ACIDS.									
Zeiss butyro-refractometer at 40° C. - - - -	57·0	56·7	56·7	55·7	53·7	56·3	57·0	54·7	56·7

Table B gives the analysis of the other oils. In several cases the oils were turbid when received, and were filtered clear before analysis. Both shark and menhaden oils were dark brown in colour.

TABLE B.—SAMPLES OF FISH AND OTHER OILS.

OIL.	Seal.	Shark.*	Dugong.*	Haddock.*	Menhaden	Whale.	Brusmer.	Hoi.	Ling.	Arachis.	Sesame.	Cotton-seed.
Specific gravity, 15.5° C. -	0.925	0.962	0.919	0.934	0.931	0.917	0.923	0.919	0.923	0.916	0.922	0.923
Zeiss butyro-refractometer at 25° C. -	72.7	87.3	60.3	84.0	80.7	65.0	75.0	73.7	74.0	63.7	68.0	68.7
Zeiss butyro-refractometer at 40° C. -	64.0	77.7	52.0	74.3	71.3	56.0	66.3	64.7	65.0	55.3	59.7	60.0
Rotation (200-millimetre tube) -	0°	-0.5	-0.1	-0.5	-0.4	-1.0	-0.5	-4.0	-0.6	0°	+0.9	0°
Hübl iodine per cent. -	132	142	69	179	174	94	138	124	133	84	106	112
KHO required per cent. for free acid -	0.5	2.2	0.5	0.6	0.5	0.4	0.1	0.1	0.1	0.3	0.2	0.1
KHO total per cent. -	19.4	6.0	20.2	19.3	19.3	18.8	18.3	16.9	18.8	19.1	19.2	19.6
Valenta test (° C.) -	88	35	86	73	78	100	108	113	105	102	85	90
Unsaponifiable matter per cent. -	1.0	84.0	0.9	1.0	0.6	1.0	—	—	—	—	—	—
FATTY ACIDS.												
Zeiss butyro-refractometer at 40° C. -	49.7	—	37.7	60.7	57.3	43.3	53.3	52.7	52.3	42	46	46

Specific Gravity.—The British Pharmacopœia gives the range of specific gravity as 0.920 to 0.930. My samples of cod-liver oil only varied from 0.926 to 0.928. Five of the foreign oils came within the official limits, menhaden and haddock were slightly heavier, shark was notably so (0.962), while arachis, whale, hoi, and dugong were below 0.920.

Refractions.—The samples were examined in a Zeiss butyro-refractometer at 25° C., and also at 40°. The sodium flame was used in each case to give a sharp reading. Seven of the cod-liver oils gave readings from 79 to 80; the other two were 76.3 and 77.3. The refractometer sharply distinguished most of the other oils, but menhaden (80.7) and brusmer (75) were very near to cod-liver oil. Readings were also taken at 40°, with the hope that the differences might vary with different oils. An alteration of 1° C. in temperature produced a difference of 0.69 scale division with shark oil; all the other oils were included in the limits 0.55 to 0.62 scale division.

May I here express the hope that workers with the refractometer will adopt one or two standard temperatures for their readings? Figures have been published at each 5° between 20° and 45°. These variations make the comparison of published values unnecessarily difficult. I would suggest that butter and liquid oils should be

* Filtered clear before analysis.

observed at 25°. The heating spiral cannot be used for a lower temperature than this all the year round, and when more heat is used the temperature of the instrument is not so constant. If the fat is not melted at 25°, it may be examined at 40°. These two temperatures would, I think, cover all practical purposes.

Rotation.—Hoi was the only oil that had any marked effect on polarized light. It gave a rotation of -4° in a 20-centimetre tube. Arachis was the only oil that gave a positive rotation ($+0.9^\circ$). All the other oils are included in the limits 0° to -1° .

Iodine Absorption.—In each case 25 c.c. of Hübl's iodine solution was added to about 0.25 gramme of oil and allowed to stand all night before titration. Some analyses of cod-liver oil have been published giving absorption values of about 140 per cent. of iodine. In these cases a shorter time has been probably taken, or a smaller excess of iodine used. Two samples of cod-liver oil absorbed 154 per cent. of iodine; the remaining seven from 160 to 168 per cent. Menhaden (174) and haddock (179) absorbed more iodine than cod-liver oil; the other oils required less, brusmer (138) being the nearest to cod-liver oil.

Acidity and Saponification Values.—These figures were obtained by adding 10 c.c. of ether and 5 c.c. of alcohol to about 5 grammes of oil, and titrating with seminormal alcoholic potash and phenolphthalein. When neutralized, 50 c.c. of alcoholic potash were added, and after saponification titrated back with seminormal hydrochloric acid. Shark oil contained most free acid, and required 2.2 per cent. of KHO to produce neutrality. The samples of cod-liver oil required 0.1 to 0.2 per cent., and the other oils 0.1 to 0.6 per cent., to neutralize the free acid present. The total saponification values of the cod-liver oils only varied from 18.5 to 18.9 per cent. of KHO. Shark oil only required 6.0 per cent., of which more than one-third was due to free acid. Dugong oil required most KHO (20.2), while hoi was below the average with 16.9 per cent. of KHO.

Valenta Test.—The acetic acid used gave a figure of about 65° C. with butter. The nine samples of cod-liver oil gave results which only varied from 93° to 96°. Another sample that had been in the laboratory eight years had a turbidity temperature of 94°. Cotton-seed oil (90°) and whale oil (100°) were the nearest values to cod-liver oil. Shark oil was the lowest (35°), and hoi the highest (113°). This is a useful test and one easily applied.

Unsaponifiable Matter.—Shark oil gave about 84 per cent., and five other oils about 1 per cent. As the quantities obtained in these five were very similar, and as emulsification gave considerable trouble, the amount of unsaponifiable matter was not determined in the other samples.

Fatty Acids.—The refractometer readings do not appear to be of any greater value than those obtained directly on the oils, and probably the same remark would apply to their iodine absorptions. I attempted to obtain values for the titre of several of them, but failed to get constant readings.

TABLE C.—ACETYL VALUES.

	Cod-liver Oil.		Seal.	Haddock.	Ling.
	A	C			
Soluble acid, per cent. KHO :					
Acetylated oil - - -	1·4	1·5	1·7	2·4	1·3
Oil - - - - -	0·2	0·3	0·4	0·8	0·3
Difference - - - -	1·2	1·2	1·3	1·6	1·0
Saponification, per cent. KHO :					
Acetylated oil - - -	19·5	19·7	20·5	20·6	19·6
Oil - - - - -	18·7	18·7	19·4	19·3	18·8
Difference - - - -	0·8	1·0	1·1	1·3	0·8
Zeiss butyro-refractometer at 25° :					
Acetylated oil - - -	80·7	80·3	72·7	84·7	74·3

Acetyl Values.—The determination of these is very tedious, and the results are useless for the detection of seal or ling oils, though it might be of some use for haddock oil. The refractions of the acetylated oils are also given, but the results are very similar to those obtained with the oils themselves.

The British Pharmacopœia gives the following test: "A drop of sulphuric acid added to a few drops of the oil on a porcelain slab develops a violet coloration." All the cod-liver oils except J gave a violet colour, as did also brusmer, hoi, and ling oils. The other oils gave more or less dark browns. By careful observation differences may be noted in the sequence of colours after adding H_2SO_4 . They are best observed by watching a genuine oil side by side with one or two others. The colours change too rapidly to observe many samples at once. The three Norwegian oils, with F and G, gave a quick change of the violet colour into crimson, which finally became red-brown. The violet colour given by the Newfoundland oils turned to a darker colour than that given by the Norwegian ones—purple rather than crimson. Hoi, ling, and brusmer oils gave a more intense violet than the Norwegian oils, but no crimson colour followed. Brusmer rapidly turned black.

The British Pharmacopœia also requires that, "When nitric acid is carefully poured into some of the oil contained in a test-tube, a precipitate of coagulated albumin should be formed at the surface of contact of the two liquids." All the samples of cod-liver oil except H and J gave a distinct white ring, though in some cases it was a long time in appearing. None of the other oils gave a white ring.

Another of the British Pharmacopœia reactions is probably intended as a test of quality rather than genuineness: "No solid fat should separate on exposure of the oil for two hours to a temperature of 0°C ." Most of the oils complied with this test, the exceptions being as follows: Slight deposits were obtained with Newfoundland oil E, menhaden, hoi, and ling oils; while Newfoundland D, dugong, whale, and arachis oils gave large deposits.

One other colour-test was tried: Three drops of HNO_3 were added to about 12 drops of oil, and stirred at once. All the samples of cod-liver oil gave a fiery-red colour at once; seal and dugong oils gave a pale-pink colour; arachis gave no change; sesame gave a pale green; and the other oils gave browns or yellows.

The analytical work in the above communication was finished last October, and I intended making further experiments, but have not had an opportunity of doing so. These results are therefore published as a contribution to the solution of a problem which the present high price of cod-liver oil makes somewhat important.

DISCUSSION.

The PRESIDENT (Mr. Fairley) remarked that the author had made no reference to the question of age, which was of importance in regard to some of the points referred to, and particularly in regard to acidity. The fresh cod-liver oil, with regard to which some experiments were quoted, was, he presumed, last season's oil.

Mr. BODMER said that recently there had been three successful prosecutions in Bermondsey for adulterated cod-liver oil. Twenty-six samples were examined at one time, and it had been found that the adulterated samples were sharply differentiated by the Zeiss butyro-refractometer from those which afterwards proved to be genuine—as far, of course, as it was possible to say, because he did not think it practicable to distinguish analytically between cod-liver oil and any other fish-liver oil, though a distinction could be made with certainty between an oil derived from the bodies of the fish and a fish-liver oil. In the case of the three adulterated samples in question, the refractometer readings at 25°C . (the temperature mentioned by the author) were respectively 73, 74.3, and 72. A specimen of undoubtedly genuine cod-liver oil gave a reading of 79, and Mr. Chattaway, who had kindly assisted him in the matter, considered 79 to 80 scale divisions to be about the limit for genuine oil. The colour tests used had been the British Pharmacopœia test with sulphuric acid and Meyer's test with a mixture of two volumes of nitric acid and one volume of sulphuric acid. The latter test was an excellent one for the purpose, a magnificent salmon-pink colour being given when about 1 drop of the mixture was added to about 15 drops of genuine oil. The three samples in question gave no such colour, but only a dirty yellow, and the sulphuric acid test showed, not violet, but a brown colour. The other constants had been determined, but did not help much. The iodine values were respectively 135, 138, and 123; but the published iodine values varied greatly, and it was difficult to get an average. Mr. Chattaway and Mr. Moor, however, who had worked a great deal at the subject, were of opinion that 140 was probably a good average. The saponification values (18.9, 18.47, and 18.62 per cent. KHO) were also of but little assistance. From the colour tests and from the low iodine values the presence of vegetable oils seemed possible, but none of the samples gave any cotton-seed or sesame oil reaction, and none of them gave any reaction with gold chloride. The last-named was supposed to be a test for arachis oil, and it was true that some samples of arachis oil were susceptible to reduction by gold chloride, but he did not think it could be regarded as a definite test. The three samples easily passed the British Pharmacopœia freezing test, which simply meant that they would stand at freezing-point without any solid fat separating; but that

was the case with a great many oils. Evidently, however, there was, practically speaking, no cod-liver oil in any of the samples. From experiments made by Mr. Chattaway and himself, it seemed that only a comparatively small proportion of real cod-liver oil was necessary in order to produce the violet colour in the British Pharmacopœia test. The specific gravity limits were much too wide, and the other tests were of little value. The results of the albumin test, in particular, seemed to depend upon the conditions under which the oil had been expressed from the livers; some genuine oils gave no albumin ring.

Mr. BEVAN inquired whether Mr. Bodmer had applied the Maumené test.

Mr. BODMER said that, on account of the small quantity of oil (only about 2 ounces) at his disposal in each case, it had not been possible to include the Maumené test.

Mr. J. B. P. HARRISON said that he had recently examined an oil which contained nearly 3 per cent. of unsaponifiable matter, and which appeared to be a mixture of cod-liver oil and shark oil.

(AUTHOR'S NOTE.—Most of the samples of oil were obtained in May and June last year, and with few exceptions the analytical figures determined in the same month.)
