

OIL & FAT INDUSTRIES

VOLUME IV

DECEMBER, 1927

NUMBER 12

The Chemical and Physical Characteristics of Cod Liver Oil

Results Obtained from Examination of Over
One Hundred Samples of Known Origin

BY ARTHUR D. HOLMES* and WALTER Z. CLOUGH*

NUMEROUS investigators have shown that cod liver oil is the richest known natural source of fat-soluble vitamins. Since this fact became generally recognized, there has been a constantly increasing tendency to evaluate cod liver oil very largely on the basis of its vitamin content. Of late this tendency to grade cod liver oil solely by its vitamin content has led many to judge the value of cod liver oil largely, if not wholly, by the amount of vitamin D that it contains. In this connection, it is perhaps well to call attention to the fact that there is no official method for the determination of vitamin D and that the method for determining vitamin A appearing in the present edition of the United States Pharmacopœia is optional. As a matter of fact, at the present moment the only official standard for cod liver oil is embodied in the specifications set forth in the United States Pharmacopœia for the chemical and physical characteristics of cod liver

oil. Furthermore, it may not be amiss at this point to call attention to the fact that the Federal Government insists in no uncertain terms that cod liver oil labeled as such cannot be lawfully sold for consumption by men, animals, or poultry unless it is in accord with the specifications for the chemical and physical characteristics of cod liver oil required by U.S.P.X.¹

From the foregoing, it is evident that information concerning the chemical and physical characteristics of present day cod liver oil is of considerable interest. In some localities manufacturing conditions have changed very materially during the past years. Present day manufacturers of medicinal cod liver oil insist on strictly fresh cod livers. The livers are cooked promptly and the oil that is obtained is stored out of contact with the air. Inasmuch as this procedure is materially different from the manufacturing and storage conditions previous to the last few

*Research Laboratories, the E. L. Patch Company, Boston, Mass.

¹The Pharmacopœia of the United States of America. Tenth Decennial Revision. J. B. Lippincott Company, Philadelphia, Pa. P. 263-264.

years, the question very materially arises as to whether the present day medicinal cod liver oil is more uniform than that of former times.

In a study of the nutritive value and market quality of cod liver oil, Drummond² and co-workers found that the "growth dosage" or vitamin content of the oils under consideration varied over wide limits. A later paper by one of us³ reported the results of a vitamin study of a number of medicinal cod liver oils procured in the open market. In that study it was found that the oil having the highest vitamin content had a potency of ten times that of the oil with minimum vitamin content. It is evident from data of this character that the vitamin potency of medicinal cod liver oil is not at all uniform. In fact, it is becoming quite generally recognized that the vitamin potency of any brand or grade of cod liver oil varies from lot to lot. In view of the wide variation in the vitamin potency of cod liver oil, the question naturally arises as to whether present day cod liver oils have uniform chemical and physical characteristics. Accordingly, this study was undertaken to secure definite data concerning the chemical and physical characteristics of cod liver oil produced under commercial conditions.

Origin of Oils Studied

In order that the results of this investigation should be of general application, samples of cod liver oils were obtained from plants located all along the coast from New York

to Labrador. A total of 111 samples of cod liver oil manufactured along the eastern North American coast were studied. These samples were collected during the period July 1926—July 1927, and, therefore, represent oils manufactured at all seasons of the year. Obviously, there are included in this group of samples, oils that were manufactured at all stages of the reproductive cycle of the cod fish. Accordingly, it was hoped that this study would yield general information concerning what might be termed average American cod liver oil.

Inasmuch as the samples of oil under consideration were obtained from different manufacturers, complete information is not available concerning all the details of the manufacturing process. However, it is probably safe to assume that practically all the oils under consideration were made by the direct steam process. All oils coming from Newfoundland were obviously made by the direct steam process since the Newfoundland Government has ruled that only this process may be used in that country. Furthermore, the direct steam process is now largely used in New England, New Brunswick, Nova Scotia, and along the Gaspé Peninsula. In some isolated localities, a certain amount of "pot oil" is produced by the direct fire process. It is, therefore, possible that a small amount of "pot oil" may have been included in some of the oils represented by the samples studied. In general, one may assume that the oils studied were separated from fresh cod livers by cooking at approximately boiling temperature in contact with whatever water was derived from condensing steam.

Ordinarily it is rather too diffi-

²The Use of Cod Liver Oils in the Feeding of Farm Animals, J. C. Drummond, S. S. Zilva, and J. Golding, Jour. Agri. Science, Vol. XIII, April, 1923, p. 153.

³Studies of the Vitamin Potency of Cod Liver Oils—X—Vitamin Potency of Medicinal Cod Liver Oils—Arthur D. Holmes, *Ind. & Eng. Chemistry*, Vol. XVI, No. 11, Nov., 1924.

cult to convey a definite conception concerning color by the use of terms which are of a general rather than a specific nature. The color of the oils in this study ranged from a very light or pale yellow to one or two samples which were of a slightly reddish yellow color. In general, however, the oils had what might be termed "a light yellow color."

In the tests which are reported below, all the oils were chilled to 0°C. Since no cloudiness was observed in the samples at this temperature, it is evident that all the oils under consideration were "cold pressed" or "non-freezing oils." Such oils are ordinarily produced by chilling crude cod liver oil to 0°C. At this temperature the crude oil becomes a semi-solid mass which is then pressed to remove the "stearin" that has solidified at freezing temperature. As a matter of fact, the so-called "stearin" of commerce is not pure cod liver

stearin for when the stearin solidifies it occludes within it a certain amount of non-freezing cod liver oil. Thus commercial "cod liver stearin" is a mixture of stearin and cod liver oil.

Experimental

In the routine analysis of the cod liver oils, the methods described in detail in the U. S. Pharmacopœia¹ were followed in the determination of the specific gravity, saponification value, iodine number, free fatty acid content, and the percent of unsaponifiable matter. In addition, the refractive index of all the oils was determined by means of a Zeiss refractometer and the results obtained are included in the following table so that the data concerning the chemical and physical characteristics of the oils under consideration may be as complete as possible.

¹ The Pharmacopœia of the United States of America. Tenth Decennial Revision. J. B. Lippincott Co., Philadelphia, Pa. P. 263-264.

THE CHEMICAL AND PHYSICAL CHARACTERISTICS OF COD LIVER OIL

Sp. Gr.	Ref. Ind.	Sapon. Value	Iodine Number	F. F. A. Per cent	Unsapon. Per cent
0.922	1.4781	185.6	159.0	1.65	1.28
0.920	1.4780	189.1	165.7	1.54	1.32
0.921	1.4782	188.4	165.8	1.53	1.40
0.922	1.4780	190.8	167.4	0.75	1.21
0.923	1.4780	186.3	167.9	0.74	1.14
0.922	1.4780	187.9	156.4	0.78	1.26
0.923	1.4778	188.5	162.7	0.91	1.08
0.922	1.4778	187.6	163.2	0.74	1.11
0.923	1.4780	189.4	164.3	0.78	1.21
0.923	1.4778	188.4	163.9	0.77	1.10
0.923	1.4778	189.7	165.4	0.79	0.97
0.922	1.4780	186.7	164.4	0.87	1.00
0.921	1.4780	181.9	165.2	0.91	1.19
0.923	1.4780	188.7	157.0	0.64	1.10
0.921	1.4775	183.2	154.4	1.27	1.15
0.920	1.4775	186.2	155.7	1.02	1.02
0.920	1.4778	184.9	156.3	0.80	1.01
0.921	1.4780	184.0	151.6	0.77	1.04
0.921	1.4780	186.9	157.7	0.74	1.08
0.921	1.4780	185.3	151.4	0.86	1.08

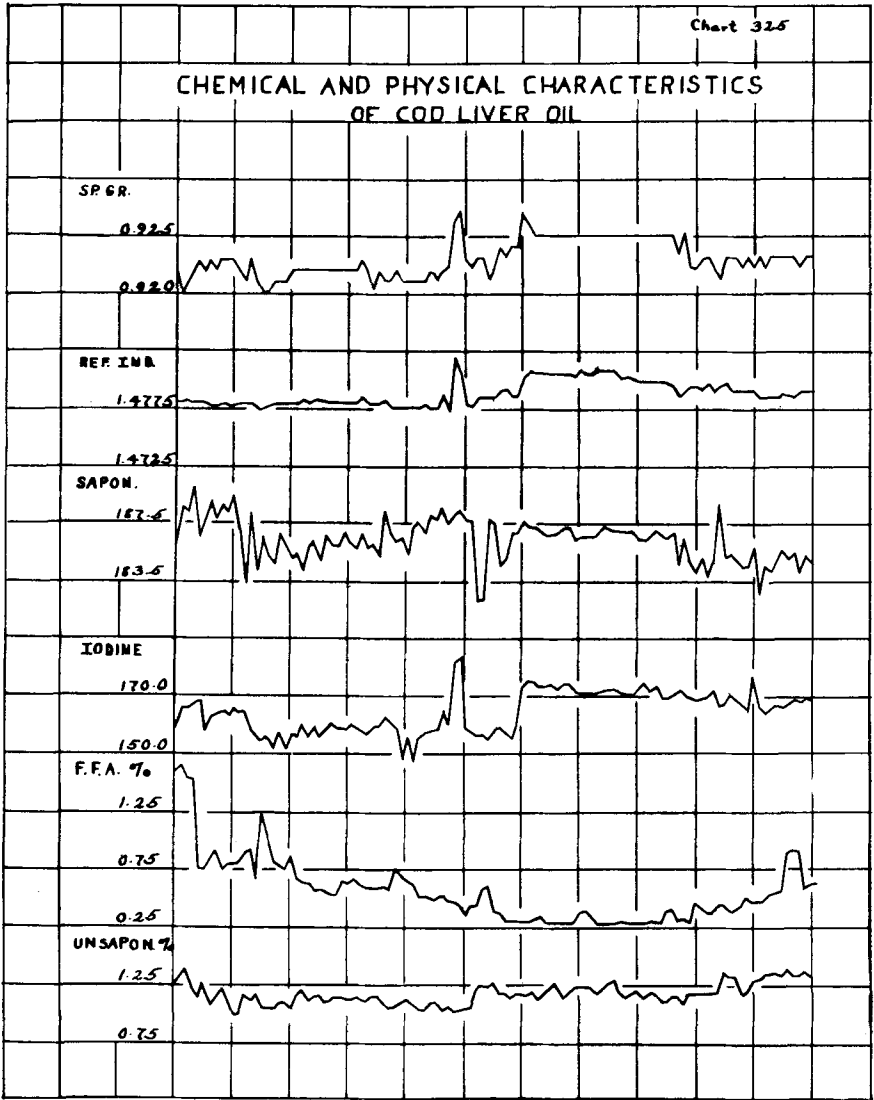
Sp. Gr.	Ref. Ind.	Sapon. Value	Iodine Number	F. F. A. Per cent	Unsapon. Per cent
0.922	1.4780	184.4	156.3	0.65	1.03
0.922	1.4780	184.9	154.8	0.62	1.15
0.922	1.4783	183.4	160.1	0.61	1.19
0.922	1.4780	185.5	155.1	0.65	1.10
0.922	1.4782	185.8	158.0	0.58	1.14
0.922	1.4781	184.1	155.3	0.55	1.14
0.922	1.4780	186.5	157.0	0.53	1.05
0.922	1.4780	185.6	160.1	0.51	1.13
0.922	1.4780	185.4	159.4	0.67	1.13
0.922	1.4780	186.8	158.6	0.63	1.13
0.922	1.4780	185.1	159.6	0.60	1.10
0.922	1.4780	185.1	159.6	0.60	1.10
0.923	1.4786	186.7	158.5	0.58	1.12
0.922	1.4780	185.2	156.7	0.57	1.10
0.920	1.4780	185.8	158.9	0.59	1.13
0.922	1.4780	184.6	158.9	0.60	1.12
0.921	1.4782	188.7	162.3	0.54	1.09
0.921	1.4778	186.8	161.1	0.79	1.02
0.922	1.4778	186.6	158.9	0.68	1.06
0.921	1.4778	186.2	149.5	0.66	1.08
0.921	1.4778	184.9	156.3	0.63	1.12
0.921	1.4776	187.3	147.6	0.50	1.06
0.921	1.4775	187.5	155.2	0.51	1.03
0.921	1.4777	186.5	156.6	0.48	1.04
0.922	1.4775	188.3	157.2	0.49	1.08
0.921	1.4775	187.9	157.6	0.53	1.08
0.922	1.4779	188.9	164.5	0.48	1.04
0.922	1.4772	187.2	159.2	0.49	1.05
0.926	1.4820	187.8	181.3	0.41	1.00
0.927	1.4805	188.6	183.1	0.31	1.01
0.923	1.4778	187.8	159.3	0.44	1.01
0.922	1.4778	187.9	158.2	0.41	1.04
0.923	1.4785	180.8	156.1	0.58	1.21
0.923	1.4785	180.9	156.9	0.60	1.25
0.921	1.4785	188.0	154.9	0.36	1.22
0.922	1.4785	187.9	158.5	0.36	1.27
0.924	1.4790	183.9	159.7	0.30	1.16
0.923	1.4790	184.2	156.3	0.30	1.17
0.924	1.4785	186.7	154.9	0.30	1.11
0.924	1.4785	186.5	160.7	0.30	1.20
0.927	1.4800	187.8	173.6	0.29	1.19
0.926	1.4806	187.1	175.3	0.30	1.15
0.925	1.4805	187.0	174.0	0.35	1.20
0.925	1.4805	186.8	173.6	0.29	1.12
0.925	1.4805	186.4	173.2	0.28	1.15
0.925	1.4805	186.5	174.7	0.29	1.23
0.925	1.4805	186.6	172.8	0.29	1.25
0.925	1.4805	187.0	174.3	0.29	1.12
0.925	1.4805	187.0	174.1	0.27	1.16
0.925	1.4803	186.0	171.2	0.36	1.24
0.925	1.4809	186.3	171.1	0.36	1.23
0.925	1.4805	186.1	171.1	0.34	1.23
0.925	1.4805	186.2	171.3	0.29	1.23

Sp. Gr.	Ref. Ind.	Sapon. Value	Iodine Number	F. F. A. Per cent	Unsapon. Per cent
0.925	1.4807	186.4	171.2	0.29	1.17
0.925	1.4807	187.3	172.0	0.28	1.20
0.925	1.4807	186.8	172.4	0.29	1.27
0.925	1.4805	186.7	172.6	0.30	1.29
0.925	1.4800	186.6	171.5	0.29	1.19
0.925	1.4802	186.6	171.3	0.28	1.11
0.925	1.4800	186.8	170.0	0.29	1.18
0.925	1.4798	186.0	173.9	0.29	1.19
0.925	1.4798	185.7	174.2	0.30	1.12
0.925	1.4798	186.5	172.5	0.30	1.19
0.925	1.4798	186.6	173.2	0.29	1.18
0.925	1.4798	186.5	169.4	0.37	1.10
0.925	1.4793	186.0	169.7	0.36	1.08
0.925	1.4791	186.7	170.7	0.30	1.14
0.923	1.4783	183.7	172.2	0.34	1.14
0.925	1.4790	186.3	171.1	0.30	1.07
0.922	1.4794	184.1	169.0	0.47	1.17
0.922	1.4794	183.4	168.2	0.43	1.18
0.923	1.4790	184.5	169.0	0.36	1.19
0.923	1.4796	182.7	170.6	0.36	1.19
0.922	1.4789	184.3	172.3	0.45	1.19
0.921	1.4794	189.6	166.0	0.44	1.19
0.923	1.4795	184.4	168.6	0.39	1.36
0.923	1.4790	184.8	171.3	0.41	1.33
0.923	1.4790	184.2	168.1	0.41	1.31
0.922	1.4790	183.8	167.0	0.50	1.16
0.923	1.4790	183.8	165.6	0.48	1.19
0.922	1.4790	185.3	177.1	0.47	1.26
0.923	1.4781	181.1	167.6	0.46	1.27
0.922	1.4782	184.0	164.0	0.55	1.35
0.923	1.4782	183.3	165.9	0.58	1.32
0.923	1.4782	184.0	167.0	0.58	1.35
0.923	1.4787	185.1	166.2	0.91	1.32
0.923	1.4785	184.1	167.1	0.93	1.37
0.923	1.4785	184.6	169.5	0.92	1.34
0.922	1.4788	183.1	168.6	0.59	1.32
0.923	1.4788	184.6	169.0	0.64	1.35
0.923	1.4788	184.1	168.7	0.63	1.31

Ordinarily it is rather difficult to quickly summarize results of this character when reported in a lengthy table. Accordingly, for the convenience of those who may wish to quickly summarize the results of the analyses, the results given above have been plotted as curves. These curves are reported in chart No. 325 which follows:

In order to make it possible for one to compare the chemical and physical characteristics of the above oils with the official specifications¹ for the chemical and physical characteristics of medicinal oil, the latter data are reported on next page:

¹ The Pharmacopœia of the United States—Tenth Revision. J. B. Lippincott Company, Philadelphia, Pa. Page 263.



Graphic representation of variations in the chemical characteristics of 111 samples of cod liver oil

CHEMICAL AND PHYSICAL CHARACTERISTICS OF MEDICINAL COD LIVER OIL

Sp. Gr.	Ref. Ind.	Sapon. Value	Iodine Number	F. F. A. Per cent	Unsapon. Per cent
0.918-0.927	Not reported	180-190	140-180	1.41	1.5

Comparing these values with those obtained in the analysis of the samples discussed here, it will be noted that with the exception of one or two minor deviations, all the samples in question met the specifications of the U. S. Pharmacopœia. Nevertheless, it is interesting to note the extent to which the chemical and physical characteristics of the different samples vary. The minimum and maximum specific gravities obtained for the oils in question were 0.920 and 0.927 respectively. The refractive index of the samples varied from 1.4772 to 1.482. The saponification number of the different oils varied from 180.8 to 190.8 and within these limits the different samples varied to such an extent that few samples had the same saponification number. The iodine values varied from 147.5 to 183.1, but within these limits the iodine values were somewhat more constant than was the case with the saponification numbers. The free fatty acid content of the oils in question varied considerably for the first few samples analyzed. Only four samples exceeded a fatty acid content of 1.25%. The majority of the samples had a free fatty acid content under 0.75% and approximately one third of the total of samples had free fatty acid content of less than 0.3%.

In general, the unsaponifiable content of the oils under consideration was between 1.0% and 1.25%. A comparison of the analyses of the oils shows that the percent of unsaponifiable matter in the oils was more nearly uniform than the values obtained for specific gravity, refractive index, saponification value, iodine number, or free fatty acid content.

As one considers these results the question naturally arises as to

the cause for the variation in the different oils. Without doubt, many factors contribute to this condition, but in the absence of evidence to the contrary one may assume that the nature of the diet of the fish probably very materially influenced the characteristics of the liver oils. Numerous investigators, such as Shutt⁴, Richardson⁵, Rosenfield⁶, and Mendel and Anderson⁷, have shown that the nature of the diet of land animals has a profound influence on the characteristics of the body fat. Furth⁸ claims that the characteristics of human fat are influenced by the nature of the diet. As evidence, he states that the skin fat of babies fed breast milk is richer in unsaturated fatty acids than that of babies fed artificial milk.

The conclusion to be drawn from these results is that the chemical and physical characteristics as well as the vitamin potency vary with different cod liver oils. Accordingly, investigators using cod liver oil as a subject of investigation and others who interpret the results of cod liver oil investigations should remember that cod liver oil can not be considered as a chemically pure substance with uniform characteristics and vitamin content. Instead it should be remembered that any cod liver oil obtained in the open market will in all probability have somewhat different chemical and physical characteristics and vitamin content than those of another cod liver oil obtained in the open market.

⁴ Canada Expt. Farms Repts. (1889) pp. 151-155; Idem. Bull. 38 (1901).

⁵ Jour. Amer. Chem. Soc., Vol. 26 (1904) No. 4, pp. 372-374.

⁶ *Ergebn. d. Physiol.*, Vol. 1 (1902) p. 676.

⁷ *Oil & Fat Industries*, Vol. III, No. 11, Nov., 1926, p. 396.

⁸ *Problems of Physiol. & Pathological Chem. of Metabolism* (1916) p. 383, Lippincott Co., Phila. and London.