THE INFLUENCE OF STORAGE ON THE FATTY ACID CONTENT OF COD LIVER OIL

by

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THE free fatty acid content of cod liver oil varies over wide limits. Nevertheless the quality of a cod liver oil is frequently judged by the amount of free fatty acid that it contains. An oil of low acid content is considered superior to one with a high free fatty acid content. This manner of judging the quality of cod liver oil by its acid content is easily understood when it is recalled that oil recently manufactured, by modern processes, from strictly fresh, fat livers, is light colored and has a low fatty acid content while oil obtained from livers which have commenced to deteriorate is darker in color and of a higher fatty acid content. The variation in the free fatty acid content of different types of cod liver oil is without doubt due to several factors such as the freshness of the livers from which the oil is made, the type of manufacturing process, the duration and conditions of storage and the nature of the fatty acids present in the oil.

• Not Yet Complete

Many investigations of the nature of the fatty acids of cod liver oil have been conducted since the early studies of Wurzer,[1] Spaarmann,[1] Marder,[1] Hopfer de l'Orme,[1] Wachenroder,[1] Herberger,[1] Stein,[1] De Jongh[1] and others at the beginning of the nineteenth century. However in spite of the numerous investigations which have been undertaken during a hundred years or more information concerning the exact composition of cod liver oil is not yet complete. Lewkowitsch[2] reports that cod liver oil may contain acetic, asellic, butyric, capric, clupanodonic, erucic, gadoleic, jecolic, myristic, palmitic, stearic, therapic and valeric acids and that in the fresh state cod liver oil is free from hydroxylated acids. Möller[3] states that therapin has been found only in cod liver oil, sometimes as much as 20% is present, and it "is without doubt one of the active principles of that valuable remedy." The studies of Lewkowitsch,[2] Heyerdahl[4] and others show that the fatty acids present in cod liver oil are quite different from those present in the common animal and vegetable oils. As a consequence the results of oxidation are different for cod liver oil than for animal and vegetable oils. Lewkowitsch[2] reports that cod liver oil, like fish oils, absorbs oxygen but does not form a flexible skin. However in this laboratroy it has been frequently observed that cod liver oil, when stored under conditions which permit atmospheric oxidation, forms a gummy substance around the sides of the container at the zone of contact of air and oil and often a tough, viscous film forms on the surface of the oil.

The U. S. Pharmacopoeia[5] specifies that medicinal cod liver oil shall not contain more than 1.41% free fatty acid calculated as oleic acid. This means that all cod liver oil marketed as "cod liver oil" regardless of whether it is crude or refined and whether it is intended for human or animal consumption must meet this specification. The better grades of medicinal cod liver oil have an acid content of about 0.5% or less and high-grade cod liver oils manufactured for animal and poultry feeding have a free fatty acid content of approximately 1%. On the other hand oils produced from livers which have undergone some decomposition may contain five or ten times as much acid. The latter type of oils are largely used for industrial purposes such as tanning leather but occasionally some such oils, which are not too dark colored and which do not contain more than 2% to 5% acid, have been sold for poultry feeding. However, feeding studies[6] conducted with growing chicks have shown that oils of such high fatty acid content are inferior to oils which contain 1% or less of free fatty acid.

Practically no cod liver oil is used as soon as it is prepared. Hence any changes which may occur in the fatty acid content of cod liver oil during storage are of interest. Since cod liver oil contains highly unsaturated fatty acids it undergoes spontaneous oxidation the first stage of which, according to Jamieson,[7] is the formation of peroxides at the ethnoid linkages of the unsaturated acids. Davies[8] has pointed out that the higher the free fatty acid content of a fat the shorter the induction period and that exceedingly small changes caused by oxidation are sufficient to spoil the taste and smell of a fat. King, Roschen and Irwin[9] have called attention to the accelerating effect of metals on the development of peroxides in oils and fats and Emery[10] has suggested possible deleterious effects that may result from storage of edible fats and oils in metal containers. From a consideration of the various observations noted above it seemed highly desirable to determine the rate of increase of free fatty acid in representative samples of cod liver oils during an extended period of storage.

• Experimental

For the purpose of this study thirty samples of cod liver oil were obtained on the open market. The samples were so selected that their fatty acid content varied from 0.38% to 20.88%. The oils represented three types of cod liver oil. Nine samples were medicinal oils, six samples were animal feeding oils, and fifteen were industrial cod oils. The medicinal oils were fairly light colored, the animal feeding oils were somewhat

darker and all the industrial oils were decidedly dark colored—in fact some were nearly black. It was assumed that the medicinal and animal oils were made by the steam process and that some of the industrial oils were cooked from livers which had deteriorated more or less and that the very dark oils were obtained by the rotting process.

• Somewhat Similar

The samples were placed in four-ounce amber bottles which were approximately three-quarters full at the beginning of the study. The bottles were closed with cork stoppers and were stored during the period of the investigation in a cupboard at room temperature. Thus the samples of oil were in contact with a small amount of air and subject to some atmospheric oxidation but they were not in contact with moisture or light. These conditions were chosen since they are somewhat similar to those for an opened bottle of cod liver oil in the average home.

• Slight Irregularities

The free fatty acid content of the oils was determined by the U. S. Pharmacopoeia[5] method. The acid content of each oil was determined twelve times during a period of three and one-half years. At the initial determination the fatty acid content of the medicinal oils varied from 0.38% to 0.87%, the animal feeding oils varied from 0.63% to 1.20%, and the industrial oils from 6.15% to 20.88%. The results which were obtained have been plotted as curves which appear in Charts 1 and 2. It will be noted that in general the fatty acid content of all the oils increased fairly consistently throughout the test period. Slight irregularities in rate of increase of fatty acid will be noticed for the first twelve curves of Chart 1 and for the curves of Chart 2. The cause of the more pronounced irregularity in curves 11 and 12 of Chart 2 and the decided irregularity in the last three curves of Chart 1 is not known. However, the rate of increase of fatty acid content as indicated by the first portion of the last three curves of Chart 1 is in agreement with that of the other curves for oils of low fatty acid content. The decrease in fatty acid—curves 2, 8, 11 and 15 Chart 2, at the end of the period and curves 12 and 14 just before the end of the study—is also unexplained but Kerr and Sorber[11] have previously reported that the free acid content of a fat, after being stationary or slightly increasing for a time, may suddenly drop.

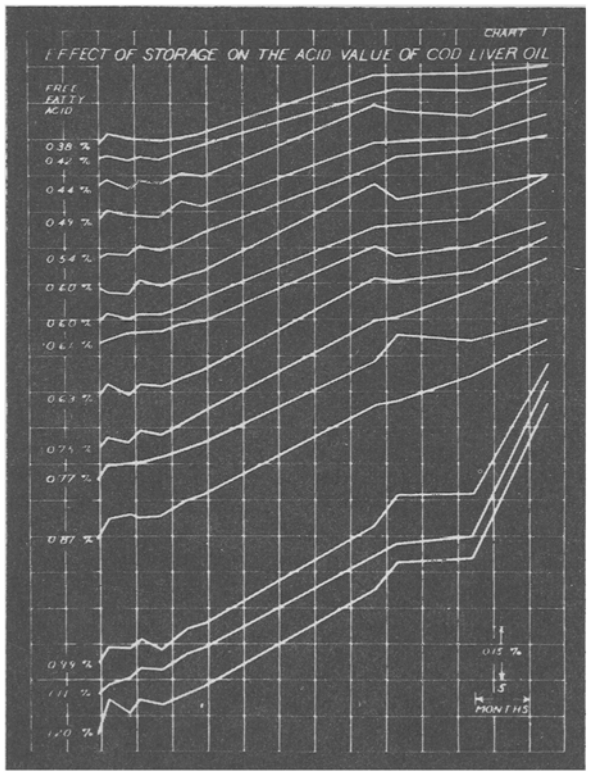

Chart 1—Curves showing rate of increase of free fatty acid in medicinal and animal feeding cod liver oils during 42 months' storage in partially filled amber bottles.

While at first sight the curves for the different oils would seem to indicate that the rate of increase of free fatty acid was fairly consistent for all of the oils studied a careful inspection of the data reveals that the percentage increase was different for the different types of oils. The computed percentage increase in free fatty acid content for the various oils is reported in Table 1 which also reports the initial and final free fatty acid content. The range of percentage increase of free fatty acid of the medicinal oils was from 50.00% to 68.33% with an average of 59.09%, of the animal oils was from 57.14% to 84.80% with an average of 73.33%, and of the industrial oils was from 7.42% to 25.85% with an average of 14.80%. The initial free fatty acid content of both the medicinal and animal feeding oils was well within the U.S.P. specification but the average percentage increase in free fatty acid was 73.33% for the animal oils as compared with 59.09% for the medicinal oils. To be sure the average initial free fatty acid content differed somewhat, being 0.55% for the medicinal oils and 0.91% for the animal oils. However, this difference in free fatty acid content of the medicinal and animal oils is not large and probably is not as significant as the difference in the character of the oils. The medicinal cod liver oils were cold pressed oils, that is, sufficient stearin had been removed so that the oils would remain clear at any temperature above 32° F. The animal oils on the other hand contained the original amount of stearin and may have also contained small amounts of moisture. However, Emery and Henley[12] found the effect of moisture on the development of oxidative rancidity to be negligible as compared with that of air, light and metals. On the other hand Robertson and Campbell[13] report that the free fatty acid content of cottonseed, with 14% or more of moisture, increases rapidly during storage. The lowest percentage increase in fatty acid content, 14.80%, was for the industrial oils. This was doubtless due (1) to initial high acid content and (2) to nature of the oils and the process by which they were probably manufactured. Furthermore, it is reasonable to assume that the industrial oils were older than either the medicinal or animal feding oils.
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The average fatty acid content of the fifteen industrial oils at the initial determination was 13.88%. This value happens to coincide rather closely with an average value of 13.38% for twenty industrial cod oils

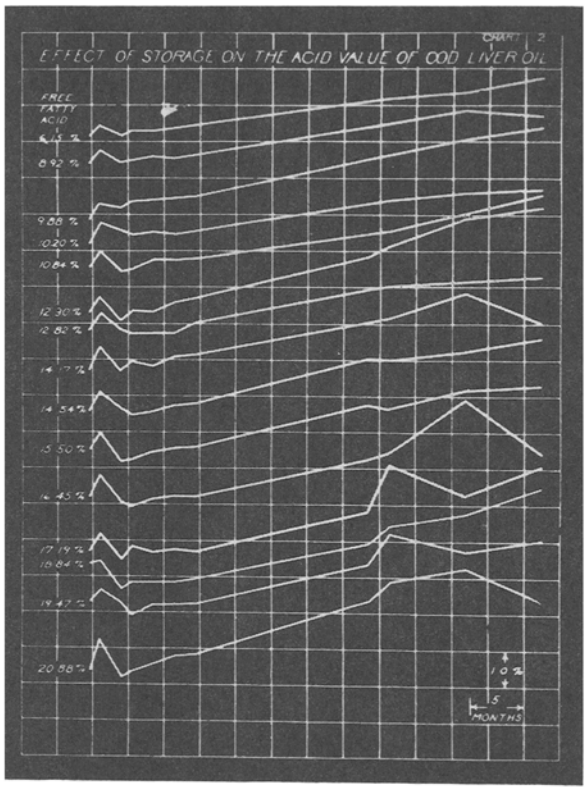

Chart 2—Curves indicating the change in free fatty acid content of industrial cod liver oil during 42 months' storage.

previously studied.[14] In connection with the industrial oils it is interesting to note that oils No. 16 to No. 21 inclusive had an average initial free fatty acid content of 9.71% and showed an average percentage acid increase of 20.50% whereas oils No. 22 to No. 30 inclusive had an average initial acid content of 16.67% and showed an average percentage acid increase of 11.00%. Judged by these data the percentage increase in the free fatty acid content of similar oils during storage is influenced by the initial fatty acid content.

• Summary

A study has been made of the change of fatty acid content of cod liver oils during storage. Thirty oils varying in acid content from 0.38% to 20.88% were procured in the open market. They represented three types of oils—medicinal, animal feeding and industrial oils. The samples of oil were stored at room temperature, in the dark, in three-fourths filled, four-ounce, amber, cork-stoppered bottles. The acid content was determined twelve times during a period of forty-two months. The acid content of each oil increased. The amount of increase varied from 7.42% for a sample of industrial oil with an initial acid content of 16.45% to 84.80% for a sample of animal feeding oil with an initial acid content of 0.99%. In general, the cod liver oils with initial high acid content showed a lower percentage increase in free fatty acids than oils with a low initial free fatty acid content.

• Bibliography

1. Heyerdahl, P. M., Chronological synopsis of chemical researches on cod-liver oil, Cod Liver Oil and Chemistry, F. P. Möller, London, lxxi, (1895).
2. Lewkowitsch, J. and G. H. Warburton, Chemical Technology and Analysis of Oils, Fats and Waxes, Sixth Edition, Vol. II, MacMillan & Co., London, 435 (1922).
3. Möller, F. P. Cod-Liver Oil and Chemistry, London (1895).
4. Heyerdahl, P. M., New Chemical Researches on Cod-Liver Oil, Cod Liver Oil and Chemistry, F. P. Möller, London, lxxxviii (1895).
5. *Pharmacopoeia of the United States*, Tenth Decennial Revision, J. B. Lippincott Co., Philadelphia, 263 (1926).
6. Holmes, A. D., W. B. Moore, J. S. Bennett and M. G. Pigott, Poultry Sci., 9, 164 (1930).
7. Jamieson, G. S., Vegetable Fats and Oils, The Chemical Catalog Co., Inc., New York (1932).
8. Davies, W. L. Oil and Fat Ind., 7, 427 (1930).
9. King, A. E., H. L. Roschen and W. H. Irwin. Oil and Soap, 10, 204 (1933).
10. Emery, J. A. U. S. Dept. Agriculture Bull. Animal Ind., 26th Annual Rpt. *(1908)*.
11. Kerr, R. H., and D. G. Sorber, J. Ind. & Eng. Chem., 15, 383 (1923).
12. Emery, J. A., and R. R. Henley, J. Ind. & Eng. Chem., 14, 937 (1922).
13. Robertson, F. R., and J. G. Campbell, Oil and Soap, 10, 146 (1933).
14. Holmes, A. D., W. Z. Clough and R. J. Owen, Oil and Fat Ind., 6, 15 (1929).

TABLE I—EFFECT OF STORAGE ON THE ACID VALUE OF COD LIVER OIL

Sample No.	Nature of Oil	Initial F. F. A. %	Final F. F. A. %	Difference %	Percent Increase	Average Percent Increase
1	Medicinal	0.38	0.59	0.21	55.26	
2	Medicinal	0.42	0.63	0.21	50.00	
3	Medicinal	0.44	0.72	0.28	63.63	
4	Medicinal	0.49	0.78	0.29	59.18	
5	Medicinal	0.54	0.89	0.35	64.81	
6	Medicinal	0.60	0.91	0.31	51.67	
7	Medicinal	0.60	1.01	0.41	68.33	
8	Medicinal	0.61	0.95	0.34	55.74	59.09*
9	Animal	0.63	1.08	0.45	71.43	
10	Animal	0.75	1.28	0.53	70.67	
11	Animal	0.77	1.21	0.44	57.14	
12	Medicinal	0.87	1.42	0.55	63.22	
13	Animal	0.99	1.83	0.84	84.80	
14	Animal	1.11	1.99	0.88	79.28	
15	Animal	1.20	2.12	0.92	76.66	73.33**
16	Industrial	6.15	7.74	1.59	25.85	
17	Industrial	8.92	10.21	1.29	14.46	
18	Industrial	9.88	12.40	2.52	25.51	
19	Industrial	10.20	11.69	1.49	14.61	
20	Industrial	10.84	12.87	2.03	18.72	
21	Industrial	12.30	15.23	2.93	23.82	
22	Industrial	12.82	14.30	1.48	11.55	
23	Industrial	14.17	15.51	1.34	9.46	
24	Industrial	14.54	16.62	2.08	14.32	
25	Industrial	15.50	17.33	1.83	11.81	
26	Industrial	16.45	17.67	1.22	7.42	
27	Industrial	17.19	19.61	2.42	14.08	
28	Industrial	18.84	21.02	2.18	11.57	
29	Industrial	19.47	21.26	1.79	9.19	
30	Industrial	20.88	22.89	2.01	9.63	14.80

*This average includes sample No. 12.
**This average does not include sample No. 12.