STUDIES ON DETERIORATION OF VITAMIN A IN FISH LIVERS AND LIVER OILS 1/

PART II - LOSS OF VITAMIN A POTENCY AND STABILITY IN FROZEN GROUND GRAYFISH LIVERS

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ABSTRACT

There was no appreciable loss of vitamin A in grayfish livers stored for as long as 41 weeks at about -22.5° C. The free fatty acid content increased slightly, and the relative stability of vitamin A decreased about 50 percent at 27 weeks in storage.

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In a previous experiment 2/ ground grayfish liver samples 3/ stored from 4 to 7 weeks under three different conditions--room temperature (23° C.), in ice (0° C.), and in frozen storage (-22.5° C.)--were tested at varying intervals. These tests showed no significant change in the vitamin A potency, but with increase in temperature of storage the free fatty acid content tended to rise and the vitamin A stability decreased rapidly. Further tests were made on the liver samples held up to 41 weeks in frozen storage. In this paper, the results of these additional tests are combined with the data accumulated from the tests conducted on the livers held in frozen storage in the previous experiment mentioned above.

SAMPLING LIVERS

After storage in the frozen state had continued for periods of 3, 7, 27, and 41 weeks, two or three samples of ground grayfish livers were removed from the freezer, thawed, and analyzed for their vitamin A and oil contents (Table 1). Each sample was analyzed in replicate, and the average vitamin A potency for each sample was calculated from these replicate analyses. The differences in the vitamin A potencies of the replicates for any one sample indicate the variation occurring in the method of analysis, while the differences between the average potencies for each of the several samples show the variation involved in the analytical and the sampling processes. A statistical analysis of these data showed that the difference in vitamin A potency of the oil from the fresh livers and of that from the livers stored 41 weeks is without significance.

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1/ This is one part of a series of articles on this subject. Part I appeared in the February 1947 issue and Part III in the March 1947 issue of Commercial Fisheries Review. Also available as Separate Nos. 167 and 170, respectively.

2/ F. B. Sanford, D. Miyauchi, and G. I. Jones. Part I - Loss of Vitamin A and Stability in Grayfish Livers in Storage. Commercial Fisheries Review, February 1947, pp. 11-15.

3/ The samples of ground grayfish were obtained as follows: Approximately 30 pounds of grayfish livers were passed through a meat grinder, stirred until homogeneous, filled into pint Mason jars to within one-half to one inch of the top, and then covered.

Ratios of the E values at various wave lengths between 300 and 350 mmu. to the E value at 328 mmu. are given in Table 2. The results indicate that during

Table 1 - Analyses of Ground Grayfish Livers Stored in Refrigerator at an Average Temperature of -22.5° C. (-8.5° F.)[1]

Storage Period	Replicate	Oil Content of Liver Sample[2]	Free Fatty Acid in Liver Oil[3]	Vitamin A Potency of Liver Oil[4]				Relative Vit. A Stability of Liver Oil[5]
				Sample 1	Sample 2	Sample 3	Average	
Weeks	Number	Percent by Weight	Percent as Oleic Acid	USP Units Per Gram	USP Units Per Gram	USP Units Per Gram	USP Units Per Gram	Hours for 50% Decomposition
0	1	-	-	14,792	14,209	-	-	17.1
	2	-	-	14,332	13,973	-	-	18.0
	3	-	-	13,968	14,019	-	-	-
	Average	73.52	0.15	14,364	14,067	-	14,215	17.55
3	1	-	-	14,449	14,393	14,319	-	15.73
	2	-	-	14,417	14,313	14,246	-	15.80
	Average	72.41	0.17	14,433	14,353	14,282	14,356	15.76
7	1	-	-	14,605	14,385	-	-	16.4
	2	-	-	14,380	14,225	-	-	16.9
	Average	72.59	0.14	14,492	14,305	-	14,398	16.65
27	1	-	-	14,012	14,128	-	-	8.15
	2	-	-	13,978	14,141	-	-	8.45
	3	-	-	-	-	-	-	8.85
	Average	72.79	0.18	13,995	14,135	-	14,065	8.48
41	1	-	-	13,781	14,089	14,216	-	7.47
	2	-	-	13,880	14,206	14,258	-	7.49
	3	-	-	13,971	14,252	14,392	-	-
	Average	72.96	0.28	13,877	14,182	14,289	14,116	7.48

1/ Temperature ranged from -28° C. to -20° C. with -22.5° C. as the average.
2/ Oil was obtained by simple solvent extraction using petroleum ether.
3/ The tests were made on water-extracted oil using the method of analysis of the AOAC.
4/ Vitamin A potency was determined by the ultraviolet absorption method using the Beckman spectrophotometer. The values listed under Samples 1, 2 and 3 are values obtained in replicate for 12 different samples. Sample 1 merely designates the first sample chosen at random and analyzed at the end of a test period, and Sample 2, the second sample analyzed, etc.
5/ Oil was obtained by the water-extraction method.

the test period no appreciable amount of any substance was formed that could increase the extraneous absorption and thus change the E value ratios. Oser, et al,[4] have shown that the validity of the spectrophotometric estimate based upon E_{328} may

Table 2 - E Value Ratios for Oils Extracted from Ground Grayfish Livers at the End of the Storage Period[1]

Storage Period	Extinction Ratio D_λ / D_{328} (λ) for Wave Lengths in mmu.						
	300	310	320	325	330	340	350
Weeks							
0	0.667	0.842	0.972	0.991	0.980	0.806	0.570
3	0.653	0.847	0.955	0.998	0.978	0.813	0.560
41	0.678	0.844	0.961	1.003	0.983	0.813	0.570

1/ Oil obtained by simple solvent extraction using petroleum ether.

be in question when the ratio E_{300}/E_{328} exceeds 0.72. Since the E value ratios E_{300}/E_{328} in Table 2 are lower than 0.72 and have changed but little during the storage time of the livers, it is unlikely that a drop in vitamin A potency was masked by increased extraneous absorption at 328 mm.

4/ Determination of Vitamin A. B. L. Oser, D. Melnick, M. Pader, R. Roth, and M. Oser. Ind. & Eng. Chem., 17 pp. 559-62 (September 1945).

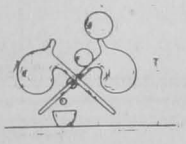
The average free fatty acid varied only slightly in the oils extracted from livers stored as long as 27 weeks in the freezer. In the oil extracted from livers stored 41 weeks in the freezer, the average free fatty acid increased from 0.15 percent to 0.28 percent. This amount of free fatty acid is small in comparison with the average free fatty acid of 0.68 percent for the oil from livers stored 4 weeks at room temperature.

The vitamin A stability tests were made as follows:5/ Air, at the rate of 350 ml. per minute, was passed through 15 ml. of the liver oil held at a temperature of 100° C. in a bubbling tube. At the beginning of the test period and periodically thereafter, samples of approximately 0.15 grams of oil were taken for vitamin A analysis. The time taken for 50 percent decomposition of the original amount of vitamin A in the liver oil under these conditions was used as the measure of relative stability. The decrease in the relative stability of the vitamin A oil from livers examined after 7 weeks of storage was small. However, after 27 weeks of storage the decrease in stability was about 52 percent, and after 41 weeks the decrease was about 57 percent. Several changes could be responsible for this pronounced loss of stability. It is possible that the anti-oxidants present in the liver are destroyed, that pro-oxidants are formed, or that some other combination of factors is involved under this condition of storage.

The stability of vitamin A oils extracted commercially, such as by the alkali digestion method, may be affected differently from that of water-extracted oil used in this experiment. Because the commercial extraction method may diminish the stability of vitamin A oils rendered even from fresh livers, the conclusion on vitamin A stability given in this paper may be non-indicative for commercially-produced liver oils.

In summary, the results of the experiment indicate that there is no appreciable loss, if any, of the vitamin A in grayfish livers stored as long as 41 weeks at an average temperature of -22.5° C., but that the free fatty acid content increased slightly and the relative vitamin A stability decreased over 50 percent at 27 weeks of storage.

5/F. B. Sanford, R. W. Harrison, and M. E. Stansby. A Rapid Test for Vitamin A Stability. Commercial Fisheries Review, March 1946, pp. 16-18. Also F.L. 212.



DEHYDRATION OF FISHERY PRODUCTS

Tests conducted by the Technological Laboratories of the U. S. Fish and Wildlife Service indicate that dehydration of fish is a relatively simple process yielding a product of good palatability. Successful storage, however, is difficult to attain. Furthermore, cost of the dehydrated product is high, perhaps too high for commercial production for domestic markets.

--Fishery Leaflet 120