THE RESIDUAL LIPIDS OF FISH PROTEIN CONCENTRATES

Previous papers (Medwadowski, Van der Veen, and Olcott, 1967, 1968; Medwadowski et al., 1971), presented data on the residual lipids in fish protein concentrates (FPCs) from red hake, *Urophycis chuss*; Gulf menhaden, *Brevoortia patronus*; pout, *Macrozoarces americanus*; and alewife, *Alosa pseudoharengus*; and some preliminary data on the effects of storage on the lipids. After 6 mo at 37° or 50°C, there were decreases in the contents of highly unsaturated fatty acids (C20:5 for alewife and C20:5 and C22:6 for pout and Gulf menhaden), and an appreciable decrease in the amount of lipid extractable from a menhaden FPC that originally contained 0.56% lipid, but no change in the amount extractable from FPCs that originally contained 0.11% (pout) or 0.06% (alewife) lipids.

In this paper we present data on the composition of lipids extracted from additional samples of FPCs (from Pacific hake, *Merluccius productus*; northern anchovy, *Engraulis mordax*; Atlantic menhaden, *Brevoortia tyrannus*; and Atlantic herring, *Clupea harengus harengus*) and also on the effects of storage, at several temperatures and humidities, on the composition of the residual lipids in a hake FPC preparation.

Materials and Methods

The FPCs had been prepared at National Marine Fisheries Service laboratories by countercurrent extraction of ground fish with hot isopropyl alcohol, followed by solvent removal and milling (Knobl et al., 1971).

Samples of a hake FPC were stored at the College Park Fishery Products Technology Laboratory at 21.1°, 32.3°, and 43.3°C and at 50% and 90% relative humidities for each temperature for periods of 1, 3, 6, and 12 mo (Green, 1972). The control was held at −29°C and ambient freezer humidity. The samples were shipped in plastic bags, cooled with dry ice (except for the zero time control sample which was shipped at ambient temperature), and stored at −18°C pending analyses.

Two procedures for determining moisture content (volatile matter) of the hake FPC samples were compared: 30-45 h at 110°-115°C, and 1 h at 130°C (Association of Official Analytical Chemists method, Horwitz, 1970:211). In the latter case, the drying was interrupted after 30 min; the caked meal was broken with a stirring rod; and the meal adhering to the rod was brushed back into the glass-stoppered weighing bottle in which the sample was being dried and weighed. Results from the two methods were in close agreement. The shorter method with the modification of the intermittent stirring was used thereafter.

The lipids were extracted (Soxhlet) in duplicate or triplicate with chloroform-methanol (2:1) from 200-g portions of the FPCs in large prewashed thimbles and analyzed as described by Medwadowski et al. (1971) with the following modifications in some cases. Purification was accomplished with a 2 × 22 cm Sephadex[1] column chromatography (Siakotas and Rouser, 1965; Rouser, Kritchevsky, and Yamamoto, 1967) and flow was by gravity. The saponification-methylation procedure used for determination of fatty acids was that described by Metcalfe, Schmitz, and Pelka (1966). The amounts of lipid were determined by drying aliquots of their solutions on a warm hot plate in preweighed disposable aluminum pans (Rouser et al., 1967).

Results and Discussion

Yields and fatty acid composition of the lipids extracted from seven separate runs—three from Pacific hake, two from northern anchovy, and one each from Atlantic herring and Atlantic menhaden—are shown in Table 1.

The two anchovy FPCs had somewhat similar fatty acid compositions; the main differences were in the amounts of C16:0 and C20:5. Herring FPC contained relatively larger percentages of C20:1 and C22:1. The Pacific hake FPCs, samples 8, 9, and 10, were similar in fatty acid composition but contained relatively more C18:1 than the FPCs from the other fish. The lipids of samples 8, 9, and 10, in general, resembled those of a red hake FPC, P-5 (reported previously by Medwadowski et al., 1967), and those of fresh red hake (Medwadowski et al., 1967, 1968). The Pacific hake FPCs, samples 8, 9, 10, and 78-103 (Table 3), contained higher percentages of C20:5 and C22:6 than red hake FPC P-5 and fresh red hake. Possibly less oxidation had occurred during processing, or the fish from which the FPCs were made had been subsisting on different foodstuffs.

[1]Reference to trade names does not imply endorsement by the National Marine Fisheries Service, NOAA.

TABLE 1.—A comparison of lipids extracted from several fish protein concentrates.

FPC	Volatile matter (%)	Lipid[2] (%)	Fatty acid composition[1] (%) 14:0	15:0	16:0	16:1	17:0	iso 18:0	18:0	18:1	18:2	18:4	20:0	20:1	20:5	22:1	22:5	22:6
Anchovy	—	0.08	8.0	1.0	26.2	7.4	1.3	0.2	7.0	13.9	2.3	1.2	0.7	1.9	9.5	2.4	0.5	13.0
Anchovy (B0308)	2.17	0.28	8.2	1.2	16.7	10.6	1.4	0.6	5.8	18.1	1.8	tr	2.0	0.9	15.4	tr	0.8	14.7
Hake - 8	4.12	0.12	4.1	0.4	17.0	10.2	—	—	4.4	29.2	1.1	—	—	3.3	15.4	—	0.4	11.3
Hake - 9	3.95	0.28	4.4	0.4	18.2	9.6	—	—	5.7	28.2	1.2	—	—	3.9	14.4	—	0.8	10.0
Hake - 10	3.77	0.21	3.3	0.3	21.1	8.5	—	—	4.2	31.5	1.0	—	—	2.7	14.2	—	0.5	10.5
Menhaden (B0204)	2.89	0.30	9.6	1.1	17.9	14.3	2.3	2.4	7.7	16.8	1.8	—	1.8	1.6	12.5	—	1.7	5.5
Herring	—	0.17	5.8	0.6	15.9	4.6	—	0.1	3.4	12.2	1.9	0.2	—	13.2	5.7	24.3	—	8.8

[1]Number of carbon atoms: number of double bonds. Additional fatty acids, tentatively identified but present in amounts of 1% or less, were: 12:0, anteiso 15:0, iso 16:0, 16:2, 18:3, 19:0, iso 20:0, 20:2, 20:3, 21:0, 22:2, 22:3, 22:4, 24:1.
[2]Dry basis

The percentages of volatile matter in the Pacific hake (78-103) samples stored at different temperatures and humidities are shown in Table 2. The moisture content of the different samples was relatively constant during several month's storage in plastic bags at −18°C. The increase in volatile matter after equilibrium had presumably been reached, in the samples stored at 90% relative humidity might indicate gradual changes in the affinity of the FPC samples for water or, possibly, the formation of volatile components other than water.

Gas chromatographic analyses of the methyl esters of the fatty acids from the Pacific hake FPC show that it was relatively stable under most of the storage conditions described (Table 3). Shono and Toyomizu (1972) suggested that the rate of decrease of C22:6 acid could be used as an indication of oxidative deterioration in fish products. There were no apparent decreases in C22:6 acid content at 50% relative humidity. However, at 90% relative humidity, there were very significant decreases of C22:6 acid content of from 8.9 to 26.1% in the temperature range of 21° to 43°C. Thus water activity had more effect than temperature on the stability of this FPC preparation.

Each hake FPC extract described in this paper was separated by silicic acid chromatography into three separate fractions, as previously described (Medwadowski et al., 1971). There were little or no significant changes in the amounts recoverable from each fraction (not shown), and they were not analyzed further.

In general, these observations confirm the relative stability of FPC during storage, even under adverse conditions of temperature and humidity.

Acknowledgments

This investigation was supported in part by contract no. USDC 1-36062 NOAA, U.S. Department of Commerce, and in part by a grant from the Tuna Research Foundation, Inc., Terminal Island, Calif.

TABLE 2.—Changes in the volatile matter of Pacific hake FPC (78-103) with storage at different temperatures and humidities.

Storage time (month)	Average volatile matter (%) Storage conditions[1]: Control	21-50	21-90	32-50	32-90	43-50	43-90
0	5.2						
1	5.4	7.6	10.5	7.8	12.8	7.9	12.5
3	5.2	7.8	10.7	8.1	13.1	8.0	12.4
6	5.3	8.1	11.5	8.7	14.2	7.9	13.4
12	5.8	7.9	12.2	8.3	14.8	7.7	15.4

[1]Hyphens separate degrees Celsius and percent relative humidity.

TABLE 3.—Effect of storage on the lipid composition of Pacific hake FPC (78-103).[1]

Storage conditions[2] T (°C)	Storage conditions[2] RH (%)	Storage time (month)	Total lipid[3] (%)	Percentages of the major fatty acids[4]										Reduction of C22:6 (%)
				14:0	16:0	16:1	18:0	18:1	20:1	20:4	20:5	22:5	22:6	
		0	0.09	1.3	15.8	3.1	7.5	25.3	3.3	2.9	9.9	1.9	29.1	
		1	0.09	1.4	15.6	3.1	7.4	25.3	3.3	2.8	10.1	1.9	29.2	
-20	AF	3	0.10	1.5	15.9	3.2	7.0	24.9	3.1	2.8	10.2	2.0	29.4	
		6	0.10	2.3	15.1	5.0	6.0	22.8	2.2	2.5	15.1	1.4	27.5	5.5
		12	0.12	2.2	15.4	4.8	6.4	23.7	2.2	2.8	13.7	1.4	27.5	5.5
		1	0.10	1.4	15.6	3.1	7.3	25.4	3.0	2.9	10.3	2.1	28.9	
		3	0.11	1.4	15.6	3.4	8.4	22.8	2.8	3.0	11.1	1.8	29.8	
21	50	6	0.10	1.8	13.7	4.3	7.8	23.2	2.7	3.1	12.9	1.8	28.6	1.7
		12	0.12	2.1	16.2	4.9	6.8	24.2	2.2	2.8	12.9	1.1	26.9	7.6
		1	0.11	1.4	15.4	3.0	7.5	25.1	3.1	2.9	10.2	2.0	29.2	
		3	0.12	1.3	15.2	3.2	9.0	23.7	3.6	2.9	10.2	1.8	29.3	
21	90	6	0.10	1.9	16.8	4.7	7.2	24.1	2.3	2.8	12.3	1.5	26.5	8.9
		12	0.12	2.3	16.1	5.2	6.4	24.1	2.0	3.0	12.9	1.5	26.5	8.9
		1	0.10	1.4	15.9	2.9	7.5	25.3	3.3	2.8	10.6	2.0	28.4	
		3	0.10	1.5	15.4	3.3	8.0	23.5	3.2	2.8	10.6	2.0	29.8	
32	50	6	0.11	1.9	15.2	4.9	8.5	25.1	2.4	2.8	11.5	1.6	26.0	10.7
		12	0.10	2.2	16.7	5.4	5.6	24.4	1.4	2.7	13.9	1.0	26.6	8.6
		1	0.11	1.4	15.5	3.2	7.5	24.3	2.9	2.9	10.1	2.1	30.0	
		3	0.12	1.5	16.3	3.6	8.0	23.5	3.0	3.0	10.5	1.9	28.8	
32	90	6	0.12	1.6	16.4	4.2	8.1	25.3	2.6	2.6	11.2	1.2	26.8	7.9
		12	0.12	2.1	17.6	5.0	7.0	25.8	2.2	2.5	11.4	1.1	25.3	13.1
		1	0.10	1.5	15.2	3.0	8.4	24.7	3.2	3.0	9.6	2.0	29.4	
		3	0.12	1.4	16.5	3.1	8.4	25.2	3.4	2.8	9.3	1.8	28.1	3.4
43	50	6	0.10	1.8	16.6	4.5	7.9	25.6	2.3	2.6	11.5	1.1	26.0	10.7
		12	0.12	2.2	15.6	4.9	6.9	24.4	2.1	2.7	12.9	1.2	27.0	7.2
		1	0.10	1.3	15.5	3.1	8.5	25.9	3.6	3.0	9.0	1.8	28.2	3.1
		3	0.12	1.5	17.0	3.4	8.6	24.9	3.2	2.9	9.1	1.8	27.6	5.2
43	90	6	0.12	2.4	16.7	4.9	7.7	25.3	2.3	2.7	11.3	1.3	25.5	12.4
		12	0.13	3.1	18.8	5.8	7.9	27.9	2.3	2.4	9.7	0.7	21.5	26.1

[1]Values are averages from duplicate or triplicate samples.
[2]T—Temperature, RH—Relative humidity, AF—Ambient freezer humidity.
[3]Based on dry weight of FPC.
[4]Number of carbon atom:number of double bonds. The weight percentages were calculated on the basis of the 10 major acids (shown) constituting 100%.

Literature Cited

GREEN, J. H.
1972. Storage stability of fish protein concentrate under varying conditions of temperature and time. Presented at 32d Annual Meeting, Institute of Food Technologists, Minneapolis, May 1972 (Abstr. 211).

HORWITZ, W. (editor).
1970. Official methods of analysis of the Association of Official Analytical Chemists, 11th ed.

KNOBL, G. M., JR., B. R. STILLINGS, W. E. FOX, AND M. B. HALE.
1971. Fish protein concentrates. Commer. Fish. Rev. 33(7-8):54-63.

MEDWADOWSKI, B. F., J. VAN DER VEEN, AND H. S. OLCOTT.
1967. Nature of the residual lipids in fish protein concentrate (FPC). J. Food Sci. 32:361-365.
1968. Nature of residual lipids in menhaden fish protein concentrate. J. Am. Oil Chem. Soc. 45:709-710.

MEDWADOWSKI, B., A. HALEY, J. VAN DER VEEN, AND H. S. OLCOTT.
1971. Effect of storage on lipids of fish protein concentrate. J. Am. Oil Chem. Soc. 48:782-783.

METCALFE, L. D., A. A. SCHMITZ, AND J. R. PELKA.
1966. Rapid preparation of fatty acid esters from lipids for gas chromatographic analysis. Anal. Chem. 38:514-515.

ROUSER, G., G. KRITCHEVSKY, AND A. YAMAMOTO.
1967. Column chromatographic and associated procedures for separation and determination of phosphatides and glycolipids. *In* G. Marinetti (editor), Lipid chromatographic analysis, Vol. 1, p. 99-162. Marcel Dekker, Inc., N.Y.

SHONO, T., AND M. TOYOMIZU.
1972. Decrease rate of $C_{22:6}$ acid as an index to oxidative deterioration of lipids in fish products. Sci. Bull. Fac. Agric. Kyushu Univ. 26:233-239.

SIAKOTOS, A. N., AND G. ROUSER.
1965. Analytical separation of nonlipid water soluble substances and gangliosides from other lipids by dextran gel column chromatography. J. Am. Oil Chem. Soc. 42:913-919.

VEGA J. SMITH
JAMES S. LINN
HAROLD S. OLCOTT

Institute of Marine Resources
Department of Food Science and Technology
University of California at Davis
Davis, CA 95616