Bureau of Commercial Fisheries Oil Research Program

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SINCE 1952 the Bureau of Commercial Fisheries has conducted an extensive program of research to broaden the potential marketing base for fish oils through the development of new industrial uses. This work is being carried out both in the laboratories of the Bureau and, through contract and collaborative agreements, in laboratories of universities and other qualified research agencies. The purposes of this report are to state the over-all objectives of the program, to enumerate the projects of which the program is composed, to give the objectives of each, and to list the publications that so far have been issued. No attempt is made to discuss in detail the findings of the various projects, many of which are in the early stages.

Uses for Fish Oil

In the past years a large proportion of our domestically produced fish oils were utilized in the manufacture of paint and soap. Owing to the substitution of synthetic materials for oils in these products (for example, development of rubber-base paints, alkyd resins, and synthetic detergents), the bulk of American-produced fish oil now is being exported to Europe, where most of it is hydrogenated for use in margarine. Since this use is predicated on the continuance of economic conditions that will enable European nations to remain in this market and upon continuing nonavailability, on a competitive basis, of vegetable oils in Europe, such use may be only temporary. Should a sudden change in one or more of these conditions develop that would greatly diminish or eliminate this market, new uses for fish oils would have to be found quickly to prevent a drastic reduction in their price. The present program is aimed at developing profitable uses that could replace this market should such a change become necessary.

Status of Research on Fish Oils

Fish oils differ chemically from other naturally occurring oils in having fatty acids that possess both greater length of carbon chain and greater number of double bonds. In most oils other than those from fish, only a minor portion of the fatty acids have chains with more than 18 carbon atoms and more than three double bonds. In fish oils however a substantial portion of the fatty acids have C_{20} and C_{22} chain lengths and as many as six double bonds. A small quantity of fatty acids with C_{24} and possibly longer chain lengths also are reported.

Most previous uses for fish oils have not exploited these chemically unique features. In many cases the unsaturation has been considered a disadvantage, in fact, and has been removed by hydrogenation.

Fish-oil odors, often a hindrance to wider exploitation, are in large measure caused by this same high degree of unsaturation. Nevertheless the presence of these fatty acids of unusual long-chain length and, particularly, the unique occurrence of the larger number of double bonds per fatty acid give fish oil chemical properties that, with adequate research, should make them of inestimable value for preparation of new compounds potentially important to industry.

Much less is known of the detailed structure of fish oils than of animal and vegetable oils. This situation arises because research on fish oils has lagged behind that on other oils. To some extent this lack of research activity is caused by the much greater complexity of fish-oil fatty acids and by the greater difficulty of working with them. The presence of long chains of carbon atoms and of high degrees of unsaturation both are inducive to high instability during analysis by fractional distillation, which makes establishment of structure greatly difficult. For these reasons there has been, for too long, no particular attention given to fundamental research on fish oils. The present program is attempting to correct this situation.

The Seattle Fishery Technological Laboratory of the Bureau of Commercial Fisheries undertook some limited studies, beginning in 1952, on both the separations of fatty acids and the chemical reactions of these acids. In 1955, with the availability of somewhat more adequate funds as a result of the Saltonstall-Kennedy Act, the Bureau was able to expand this research. Since that time 21 projects in 16 different laboratories have been undertaken. Nine of these projects have been completed, and 12 are continuing.

General Aspects of Program

The program was set up with major emphasis, in the early stages, upon basic research on composition, analytical methods, separations, and chemical reactions of fish-oil fatty acids and other components of fish oils as well as of the oils themselves.

At the same time limited attempts were undertaken to investigate certain possible applied uses for fish oils that could be made even before knowledge was available from the basic phases of the program.

The basic program was undertaken at three levels: a) investigation of constituents of fish oils, such as the fatty acids, b) investigation of the mechanism of oxidation of extracted fish oils, and c) investigation of fish oils while still in the tissue of the fish. Level a is under investigation primarily at the Seattle Fishery Technological Laboratory of the Bureau and at the Hormel Institute of the University of Minnesota. Level b is being investigated primarily in a collaborative program between the Seattle Laboratory and the Institute of Marine Resources, Food Technology Department, University of California, at Berkeley. Level c is under investigation in a collaborative program between the Seattle Laboratory and the Department of Food Technology, University of California, at Davis.

Condensed details concerning all the projects in this program are given in Table I. Additional details, not covered in this report, can be obtained by writing to the Bureau Laboratory at the city given in the fifth column of Table I opposite any particular project of interest. In the following discussion additional detail is included on some of the more important of these programs, particularly those that still are continuing.

Analysis and Composition Investigations

Determination of the chemical composition of fish-oil fatty acids is basic to all other phases of the program. Considerable information already was available in the literature as to the content of saturated and unsaturated fatty acids of various chain lengths in fish oils. The missing information involves the identification of the polyene fatty acids in the unsaturated portion. This phase of the program is being given especial emphasis in the investigation at the Hormel Institute. The most efficient method of analyzing the polyene fatty acids in an oil is by means of the alkali-isomerization-ultraviolet spectrophotometric technics. These can be applied, however, only to those methylene-interrupted fatty acids for which the spectral constants of the purified fatty acids are known. When this project was started, it was not known definitely whether fish-oil fatty acids were predominantly of the methylene- or ethylene-interrupted type, and the spectral constants of several of the fish-oil fatty acids never had been determined. The first objective of this project therefore has been devoted to investigations on these points, including development of analytical techniques for the concentration, isolation, and identification of several of the component fish-oil polyene fatty acids. When this phase is completed, it will be a matter of routine analysis to examine the commercially important fish oils to establish their content of these various acids.

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TABLE I

Projects on Fish-Oil Research Carried out, or Financed by, the Bureau of Commercial Fisheries

General phase of program	Project title	Laboratory	Project leader(s)	Bu. of Commercial Fisheries Coordinator [b]	Publications
Analytical methods and composition of fish-oil fatty acids	Structure and analysis of fish-oil fatty acids	Hormel Institute University of Minnesota Austin, Minn.	W. O. Lundberg O. S. Privett	M. E. Stansby Seattle, Wash.	22. 27
	Composition of fatty acids from salmon egg oil [a]	Fishery Products Laboratory Ketchikan, Alaska	Robert Kyte [c]	M. E. Stansby Seattle, Wash.	19, 20, 26
	Physical and chemical characteristics of fish body oils [a]	Department of Chemistry North Carolina State College Raleight, N. C.	R. O. Simmons	Hugo Nilson College Park, Md.	
Separations of fish-oil fatty acids	Separations of fish-oil fatty acids and fatty acid derivatives	Fishery Technological Laboratory Bureau of Commercial Fisheries Seattle, Wash.	Edward Gruger [c]	M. E. Stansby Seattle, Wash.	13, 15, 31
	Application of inclusion type compounds to separation and analysis of fish-oil fatty acids [a]	Hormel Institute University of Minnesota Austin, Minn.	W. O. Lundberg Hermann Schlenk	M. E. Stansby Seattle, Wash.	22, 27
Recreations of fish-oil fatty acids	New products from fish oils	Fishery Technological Laboratory Bureau of Commercial Fisheries Seattle, Wash.	Edward Gruger [c]	M. E. Stansby Seattle, Wash.	2, 15, 16, 17, 23, 28, 30
	Chemical reactions of fish-oil fatty acids	Hormel Institute University of Minnesota Austin, Minn.	W. O. Lundberg Hermann Schlenk	M. E. Stansby Seattle, Wash.	22
Composition of fish-oil components other than fatty acids	Analytical methods for fish-oil components [a]	Texas A & M Research Foundation College Station, Tex.	R. Reiser	Hugo Nilson College Park, Md.	25
	Composition of menhaden oil unsaponifiable fraction [a]	Chemistry Department University of Delaware Newark, Del.	William A. Mosher	Hugo Nilson College Park, Md.	
	Reactions of phospholipide complexes of fish oils	Department of Chemistry North Carolina State College Raleigh, N. C.	R. O. Simmons	Hugo Nilson College Park, Md.	
Oxidation of fish oils and fish-oil components	Mechanism of oxidation of extracted fish oils	Institute of Marine Resources University of California Berkeley, Calif.	Harold Olcott Edwin J. Kuta [c]	M. E. Stansby Seattle, Wash.	8, 14, 29
	Oxidation in fish tissue	Food Technology Department University of California Davis, Calif.	A. L. Tappel W. D. Brown [c]	M. E. Stansby Seattle, Wash.	6, 7, 8, 9, 29, 32
	Chemistry of odor problem in fish oils	Hormel Institute University of Minnesota Austin, Minn.	W. O. Lundberg J. R. Chipault	M. E. Stansby Seattle, Wash.	22
Nutritional aspects of fish oils	Nutritional aspects of fish oils	Hormel Institute University of Minnesota Austin, Minn.	W. O. Lundberg O. S. Privett Eldon Hill James J. Peifer R. T. Holman	M. E. Stansby Seattle, Wash.	
	Fish oils in poultry rations [a]	Storrs Agricultural Expt. Station University of Connecticut Storrs, Conn.	E. P. Singsen	Hugo Nilson College Park, Md.	
	Fish oils as supplements to swine rations [a]	Department of Animal Husbandry Oregon State College Corvallis, Ore.	J. E. Oldfield	M. E. Stansby Seattle, Wash.	1, 24
Industrial applications	Effects of processing variables on menhaden oil	Fishery Technological Laboratory Bureau of Commercial Fisheries College Park, Md.	Maurice Bender [c]	Hugo Nilson College Park, Md.	5. 18
	Fish oils and chemical derivatives as fungicides and insecticides in the citrus industry [a]	Florida Southern College Lakeland, Fla.	Boris Sokoloff	Hugo Nilson College Park, Md.	3, 21
	Fish oils in lubrication of leathers	Dept. of Basic Science in Tanning Research University of Cincinnati Cincinnati, O.	Frederick O'Flaherty	Hugo Nilson College Park, Md.	
	Preparation of new resins from fish oils [a]	Arthur D. Little Inc. Cambridge, Mass.	George C. Walker Jr.	S. R. Pottinger East Boston, Mass.	4, 12
	Fish-oil derivatives as ore-flotation agents	School of Mines & Metallurgy University of Minnesota Minneapolis, Minn.	S. R. B. Cooke Iwao Iwasaki	M. E. Stansby Seattle, Wash.	10, 11
	Fish-oil derivatives as fungicides	P.L.M. Laboratories Sarasota, Fla.	I. M. Chamelin	Hugo Nilson College Park, Md.	

[a] Program completed, others being continued.
[b] For further information, contact the person listed as coordinator.
[c] Bureau staff member

Workers on a project at the Fishery Products Laboratory, Ketchikan, Alaska (operated jointly by the Bureau and the Fisheries Experimental Commission of Alaska) identified the components of salmon-egg oil, an oil of unusually high iodine value, for which little use yet has been found. Another program, at the Department of Chemistry, North Carolina State College, has investigated the effect of the source (for example, area of catching, season, and method of processing) of oils from various species of fish upon physical and chemical properties. Preliminary studies on a) analytical methods for, and on b) composition of, some of the unsaponifiable components of fish oils have been carried out at Texas A and M Research Foundation and at the Chemistry Department, University of Delaware, respectively.

Investigations on Fatty Acid Separations

Fish oils, like vegetable oils, contain both saturated and unsaturated fatty acids. Whereas a substantial part of fish oil is made up of very highly unsaturated acids, this unique property is counteracted by the presence of considerable quantities of saturated acids so that the iodine values for certain fish oils are little higher than for certain vegetable oils that contain a much narrower range of saturated to unsaturated fatty acids with fewer of the extremes.

If fish oils are to be utilized commercially to take advantage of their content of very highly unsaturated fatty acids, better means of fractionation of the fatty acids must be developed. Research has been under way both at the Hormel Institute and at the Seattle Laboratory to investigate such separations by use of urea-complexes and other inclusion type of compounds and by various low-temperature crystallization procedures.

Reactions of Fish-Oil Fatty Acids

Investigations are under way both at the Hormel Institute and at the Seattle Laboratory on the preparation of new chemical derivatives from fish-oil fatty acids. In such work the reactions usually are studied first by employing purified individual unsaturated fatty acids that might occur in fish oils, then by adapting these successful reactions to mixed, partially fractionated, unsaturated fatty acids from an actual fish oil.

Reactions are being investigated both at the carboxyl group and at the double bonds. Special emphasis currently is being given to reactions at double bonds since greater difference in derivatives from fish-oil fatty acids, in comparison with derivatives of fatty acids from other oils, is anticipated, based on the extra double bonds rather than upon the increased length of chain. Increase in chain length from C_{18} to C_{22} would not be likely to alter properties as greatly as would an increase in double bonds from 3 to 6. Some of the types of compounds being investigated at the Hormel Institute and at the Seattle Laboratory include: polydichlorocyclopropane derivatives, hydroxylated polyunsaturated fatty acids, quaternary ammonium salts, polyunsaturated alkyl xanthates, polyepoxy esters, and polyaryl fatty acids.

Oxidation of Fish Oils and Fish-Oil Fatty Acids

Oxidation of fish oils is of great concern not only in connection with utilization of fish oils for industrial purposes but also in connection with preservation of certain species of fish that contain a high content of oil or contain oil of low stability, in which case rancidity may be a problem. In frozen fish, oxidized oil, for species such as salmon, may be the factor limiting storage life. Fish meals that contain oil oxidize and cause the meal to heat immediately after manufacture, which oxidation possibly impairs nutritive value when these meals are used in poultry rations. In the use of fish oils for industrial purposes, oxidation is the cause of undesirable odors and of "yellowing."

At the Hormel Institute a study on the oxidation of fish-oil fatty acids as related to odor development is under way. Compounds, such as carbonyls, responsible for odors in fish oils are being isolated and identified.

Collaborative programs between the Seattle Fishery Technological Laboratory and two laboratories of the University of California include investigation of several phases of this problem.

At the University of California laboratories in Berkeley, investigations are under way concerning the mechanism of oxidation of extracted fish oils. Currently being studied are a) the role of such factors as naturally occurring antioxidants and conditions influencing their action and b) the role of traces of heavy metals in the oil on oxidation.

At the University of California laboratories in Davis, the mechanism of oxidation of fish oils while still in contact with the original fish tissue (as occurs in storage of frozen fish) or in a product made from fish (for example, fish meal) is under investigation. Biochemical catalysts, such as the hematin compounds or certain enzyme systems, are involved in these oxidations. In connection with enzymatic oxidations so little is known about enzymes in fish that considerable exploratory work on the nature of oxidative enzymes in the living fish tissue is necessary before application to oxidative deterioration in *post-mortem* changes can be undertaken.

Nutritive Value of Fish Oils and Fish-Oil Fatty Acids

Two short-term studies have been completed on the use of fish oils in the diets of swine and of chickens at the Animal Husbandry Department of Oregon State College and at Storrs Agricultural Experiment Station, University of Connecticut, respectively.

A more fundamental study of the nutritional significance of fish-oil fatty acids and other components is now under way at the Hormel Institute. This program is to be carried out in three phases, the first two of which are now in progress, with the third to be started later.

Phase 1 involves determination of the extent of "essential fatty acids" in fish oils. Certain fatty acids, when added to a fat-free ration that has caused development in rats of certain symptoms (decreased growth, dermal disorders), will cure these symptoms. Some workers in this field however have contended that fish-oil fatty acids would not cure the symptoms and that therefore the content of "essential" fatty acids is low. This belief does not appear to be based upon well-documented experimental findings. Consequently, in phase 1 of this project, fish-oil fatty acids will be tested to determine whether any of them possess "essential" properties and, if so, to what extent.

Phase 2 is concerned with the effect of fish-oil fatty acids and of whole fish oils on atherosclerosis. Experiments are being conducted with miniature pigs and with rats as test animals. Both fractionated fish-oil fatty acids and whole fish oils are being tested.

Phase 3 will involve measurements of nutritive value of components of the unsaponifiable fraction of fish oils in contradistinction to the fatty acids of interest in phases 1 and 2.

Industrial Applications of Fish Oils

As shown in Table I, several projects are under way to investigate the potential application of fish oils for certain industrial uses. These projects include those concerned with utilizing fish oils or fish-oil derivatives for preparing fungicides, insecticides, resins, leather lubricants, and ore-flotation agents. A somewhat different project also is under way in connection with problems encountered in processing fish oil.

The knowledge obtained from the various basic research projects in the over-all program is used to facilitate carrying out the particular applied-research program. The manner in which these applied projects are developed can best be described by considering one of them in some detail.

Prior to 1920 fish oils were used as ore-flotation agents. Certain ores (for example, sulfide ores) can be separated and concentrated by treatment with chemical collectors that coat the particles to be floated with a nonpolar group, rendering them hydrophobic, thus permitting them to attach to a froth of air bubbles, which floats them away from the hydrophilic particles and leaves these particles behind. Unsaturated fatty acids, such as occur in fish oils and derivatives of them such as amines, are effective for this process

and are known as ore collectors. In the future ore collectors may be required in much greater quantities because the continuing depletion of higher grade iron ore ultimately will result in the need to concentrate low-grade ore. Although magnetic separation now is being used widely, flotation methods also are applicable, especially where they can compete on an economic basis. Because the processing of iron ores makes up the largest portion of the domestic mineral industry, the adoption of flotation methods for the concentration of iron ore, if successful, could mean a tremendous increase in markets for ore-flotation collectors.

For these reasons a project was set up at the School of Mines and Metallurgy, University of Minnesota (which has played a leading role in iron-ore concentration research) to investigate the use of fish-oil derivatives in iron ore and other ore-flotation processes.

To determine the effect of degree of unsaturation of fish-oil fatty acids upon their efficiency as ore collectors, investigators at the Hormel Institute separated the fatty acids of tuna and menhaden oils into a large number of fractions. These fractions then were tested for efficiency as ore collectors at the School of Mines and Metallurgy. In other phases of the program fish-oil derivatives are prepared both at the Hormel Institute and at the Seattle Laboratory and are submitted for test as ore-flotation agents, or as "frothers"—a second possible application for these new chemical compounds.

In a similar way the various results of the basic research programs are being used on certain aspects of the other applied research programs. The applied projects thus, in many cases, provide a means for testing the practical application of new materials or of findings obtained from the basic research programs.

Summary

The Bureau of Commercial Fisheries has had under way since 1955 an extensive research program to develop wider uses for fish oils. The program is carried out in the Bureau's own laboratories, in university laboratories, and in other qualified laboratories.

The initial effort has been concentrated largely on basic research in an effort to learn more about the chemistry of fish oils, a field heretofore incompletely explored. Some applied research projects also were begun concurrently.

Basic studies are being carried out on the chemistry of the components of fish oils (for example, polyene fatty acids), on the extracted fish oils themselves, and on *in situ* fish oils of the fish tissue.

Investigations of fish-oil fatty acids are being made on chemical structure, methods of separation, chemical reactions, oxidative deterioration, and nutritive value, with especial emphasis on possible therapeutic aspects for human beings.

The applied research projects include investigation of fish oils and the chemically modified compounds thereof as fungicides, as leather lubricants, and as ore-flotation agents.

The applied and basic programs are coordinated so that findings of the basic work can be put to use in the applied work as soon as available.

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On the Educational Front

Grants in aid of education totaling $486,000 for the calendar year 1958 have been announced by the General Foods Fund Inc., an increase of $127,000 over 1957. The fund, an independent foundation sponsored by General Foods Corporation, has made educational grants of more than $1,786,000 since its formation in 1953.

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The master of arts degree in chemistry will be offered at Western Michigan University, Kalamazoo, Mich., beginning in September 1958. The new program will offer advanced work in analytical, physical, organic, inorganic, and biochemistry.