FISH-OIL RESEARCH AT THE SEATTLE FISHERY TECHNOLOGICAL LABORATORY

ABSTRACT

FISH-OIL RESEARCH AT THE SEATTLE TECHNOLOGICAL LABORATORY HAS BEEN DIRECTED PRIMARILY TOWARD UTILIZATION OF THE UNIQUE FEATURES OF UNSATURATION FOUND IN FISH OILS.

INTRODUCTION

A study of the chemistry of fish oils can be approached from two distinct points of view. The first approach investigates chemical reactions that employ the terminal reactive groups of the triglycerides, fatty acids, alcohols, and esters found in or made from fish oils. The second approach investigates the unsaturated portion of the oil, which portion forms a substantial part of fish oils. This laboratory has employed both approaches, but current work is primarily concerned with the latter one.

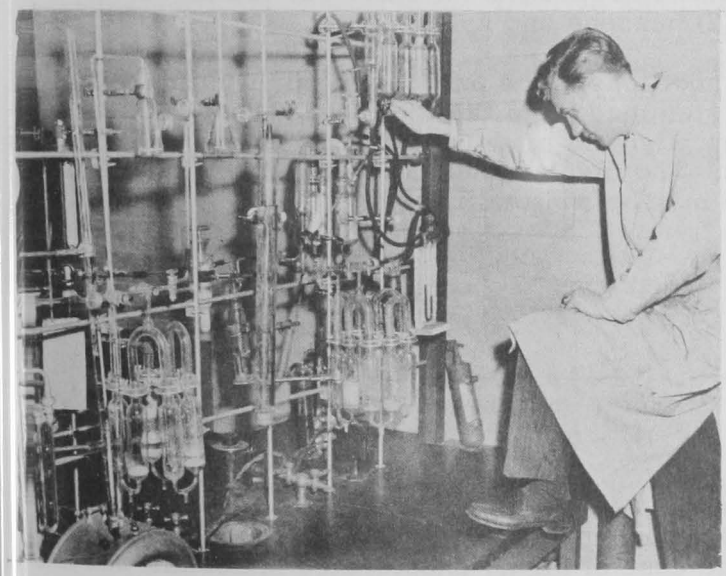


FIG. 1 - ORGANIC CHEMIST PREPARING LONG-CHAIN ALKYL XANTHATE SALTS FROM FISH OIL FATTY ACIDS.

REACTIONS AT THE SITES OF UNSATURATION

In an attempt to utilize the unsaturated portion of fish-oil molecules, we have studied commercially-attractive reactions at the carbon-to-carbon double bonds. These reactions have employed epoxidation and certain additions.

EPOXIDATION REACTIONS:

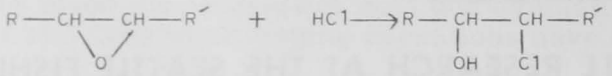
An epoxidation is simply an oxidation of a carbon-to-carbon double bond with an organic peracid to give an oxirane (—C—C—) or epoxy derivate. The reaction may be expressed thusly:

$$R-CH=CH-R' \xrightarrow{R''CO_3H} R-CH-CH-R'$$

(WHERE "R" REPRESENTS THE NONRE-ACTING PORTION OF THE MOLECULE.)

Our specific concern with the epoxidation reaction is the preparation of the epoxy derivatives of highly unsaturated butyl or hexyl esters derived from fish oil. The resultant epoxides would be potential plasticizers and stabilizers of polyvinyl chloride.

The stabilization of polyvinyl chloride by epoxides exhibits an interesting property of the oxirane ring. When polyvinyl chloride ages, it evolves hydrogen chloride, and the oxirane group captures the evolved hydrogen chloride in the following manner:

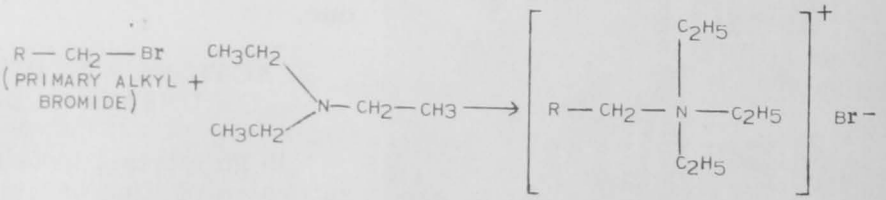


The oxirane ring also is broken easily by a variety of other compounds, including other halogen acids, primary, and secondary amines, alcohols, water, and any other compounds with a labile hydrogen atom. The epoxides therefore would act as intermediates in the preparation of further products, in addition to acting in their primary function as plasticizers.

Epoxidations have been carried out in this laboratory using two organic peracids: peracetic acid formed in situ and preformed perbenzoic acid. To date, perbenzoic acid has been the more effective reagent in the epoxidation of highly unsaturated materials.

ADDITION REACTIONS: The addition reactions have been of two kinds: (1) bromine and hydrogen bromide and (2) benzene and xylene.

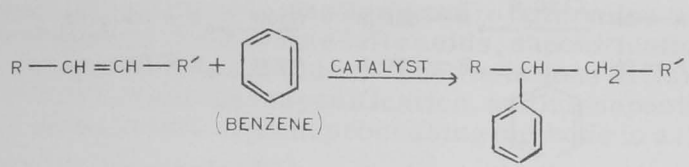
Bromine and hydrogen bromide additions: The purpose of our addition work with bromine and hydrogen bromide stemmed from the idea that perhaps displacement of the secondary bromine atoms might be made with triethylamine to form polyquaternary ammonium bromides. The displacement reaction works well in the case of a primary alkyl bromide and may be written thusly:



The addition reactions therefore were investigated. It was found--as would be expected--that bromine was easily added but, surprisingly, that hydrogen bromide was difficult to add. Especially in the case of highly unsaturated materials was the hydrogen bromide addition difficult. Different solvent systems, catalysts, and reaction temperatures were tried, yet the highly unsaturated materials were not completely hydrobrominated.

The brominated products therefore were used in the attempted displacement reactions. The attempts met with failure, for dehydrobromination occurred far more easily than did displacement, and the resultant products were triethylamine hydrobromide and an unsaturated material.

Benzene and xylene addition: Preliminary studies have been carried out on the Friedel-Crafts addition of benzene to the carbon-to-carbon double bonds in triglycerides and fatty acids. The reaction equation may be written in the following manner:



The reaction conditions so far used have led to polymerization and incomplete reaction.

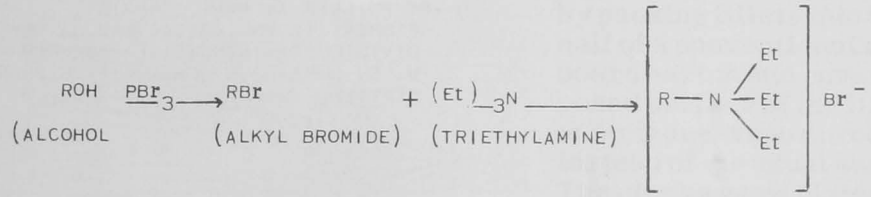
An investigation of the addition of meta-xylene to unsaturated fatty acids was carried out. It was demonstrated that a product could be isolated that had approximately 50 percent of the unsaturation consumed in the reaction with a minimum of polymerization.

REACTIONS AT THE TERMINAL FUNCTIONAL GROUPS

In addition to the foregoing reactions, which utilize the unsaturated portion of the long-chain compounds derived from fish oils, substances have been prepared that are derived from reactions at the terminal functional groups. These substances represent three separate types of compounds: (1) the unsaturated quaternary ammonium salts, (2) the unsaturated potassium alkyl xanthates, and (3) the unsaturated sodium alkyl sulfates.

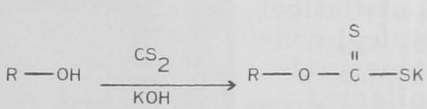
THE UNSATURATED QUATERNARY AMMONIUM SALTS: Quaternary ammonium salts are known to be effective sanitizers, surface-active agents, insecticides, and fungicides. We have prepared a mixture of unsaturated quaternary ammonium salts to be tested for the latter use and for use as a possible ore-flotation agent.

The preparation proceeds through the following series of reactions:



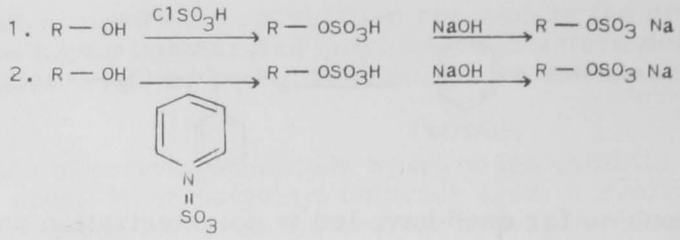
The fatty alcohols are prepared from triglycerides or methyl esters by reduction with sodium or lithium aluminum hydride.

UNSATURATED POTASSIUM ALKYL XANTHATES: The xanthates were prepared by the following reaction:



The reaction was carried out easily, and the product--even from unsaturated alcohols--was a soapy solid that was easily separated from the reaction mixture. The unsaturated xanthates have been sent to the University of Minnesota, School of Mines and Metallurgy, to be tested as possible ore-flotation agents.

UNSATURATED SODIUM ALKYL SULFATES: The sodium alkyl sulfates can be prepared from alcohols by means of a sulfation reaction using chlorosulfonic acid or pyridine-sulfur trioxide as well as by means of many similar sulfating reagents. The reaction is as follows:



When chlorosulfonic acid is used, a byproduct of the reaction is hydrogen chloride. Chlorosulfonic acid therefore is unsuitable for use with unsaturated fatty alcohols. In the case of the unsaturated alcohols, use of the pyridine-sulfur trioxide reagent, however, is satisfactory.

As in the preparation of the alkyl xanthates, the sodium alkyl sulfates were prepared with ease. When a method of assay is developed, the sulfates also will be tested as potential ore-flotation agents.

SUMMARY

To summarize briefly then, the Seattle laboratory has approached and carried out the study of the chemistry of fish oils from the points of view of reactions at the sites of unsaturation and reactions at the terminal functional groups. The former approach has led to a study of oxidation and certain addition reactions, and the latter approach has led to the synthesis of unsaturated quaternary ammonium salts, potassium alkyl xanthates, and sodium alkyl sulfates.

Since one of the unique features of fish oils is their high degree of unsaturation, it is logical that we employ that unique property to the fullest extent. Future research therefore will be concerned more and more with chemical reactions involving the sites of unsaturation.

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EFFECT OF SEASON, FISHING AREA, AND PROCESSING TECHNIQUES ON PHYSICAL CONSTANTS OF FISH BODY OILS

Results obtained from a statistical study of variations in the physical constants of 161 samples of commercially produced fish-body oils collected from each of the menhaden reduction plants on the Atlantic and Gulf coasts during 1955 and 1956 has pointed out the changes due to area of fish capture, seasons of the year, and the different processing techniques. The research week was conducted by North Carolina State College under the terms of its contract with the U. S. Fish and Wildlife Service financed by funds made available by the Saltonstall-Kennedy Act

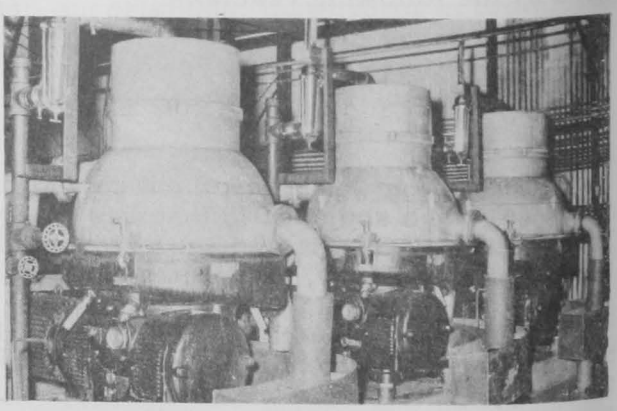

FIG. 1 - FISH OIL NOZZLE-SEPARATORS IN MODERN MENHADEN REDUCTION PLANT.

of 1954. Each fish-body oil sample was analyzed to determine its refractive index, iodine number, percentage content of free fatty acids, saponification number, nonsaponification number, and Gardner color index. The variations in Gardner color index, percentage content of free fatty acids, saponification, and nonsaponification numbers were found to correlate with individual plant processing methods to a highly significant degree.

This type of basic research will be valuable to the byproducts manufacturer as a means of knowing the significance of those constants as related to processing variables and as a aid in manufacturing his product at the highest possible quality level. Each of the constants studies has a bearing on the utilization of the oil. The fish-oil buyer can be assured within those known ranges in the several physical constants that he can specify and expect to get oils most nearly suited to his particular needs.

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NEW METHODS OF PACKAGING FISH FILLET BLOCKS

The application of modern packaging materials and techniques to fish fillet blocks will result in decreased package costs and increased product shelf life during frozen storage tests conducted by the Boston Fishery Technological Laboratory of the Bureau of Commercial Fisheries reveal.

Fish fillet blocks are customarily packaged in a waxed chipboard carton, plate-frozen, and then 3 or 4 blocks are placed in a corrugated master carton and put in frozen storage. This type of package does not provide an effective moisture-vapor barrier. Therefore, excessive dehydration occurs during extended periods of frozen storage.

FIG. 1 - FISH BLOCKS IN MASTER CARTONS BEING REMOVED FROM HOLD OF REFRIGERATED VESSEL.

At the Laboratory 13.5-pound haddock fillet blocks were prepared by packing fillets into the bottom half of a conventional waxed chipboard carton and covering the exposed surface of the fish with a sheet of moisure-vapor proof cellophane instead of the usual carton cover. The blocks were plate-frozen and packaged in lots of 4 in 1.5-millimeter (.0015-in.) thick polyethylene bags. The bags were heat sealed, put in master cartons, and stored at -5° to -10° F.

Preliminary results of this test, after 12 months' storage of the samples, indicate that the use of this package results in (1) a decrease of 22 percent in package costs, (2) a decrease of 90 percent in weight loss, and (3) maintenance of a higher level of quality during frozen storage, as compared with the waxed chipboard carton-package usually employed.

Other tests under way at this laboratory indicate that reduction in weight loss and increased product shelf life of 13.5-pound haddock fillet blocks can also be obtained by overwrapping the usual waxed chipboard carton with cellophane or waxed sulfite paper laminated to kraft paper. However, the use of an overwrapping material results in increased package costs.

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