CHEMISTRY OF MENHADEN:

Report on Literature Study

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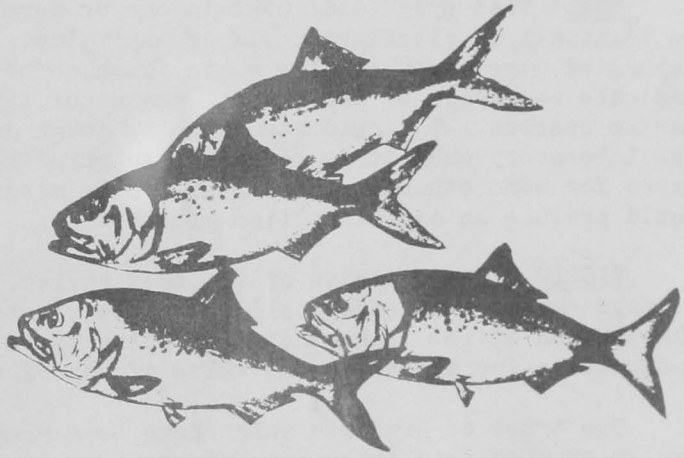
INTRODUCTION

A survey of the literature pertaining to menhaden, and to the non-food and byproduct use of fish in general, was undertaken with two objectives in mind: to provide a background for the selection of the particular phase of the chemistry of menhaden which would be the initial research project of this laboratory; and to stimulate interest of other laboratories or individuals in the study of some of the possible, and even not so probable, new uses for the menhaden.

The first objective was established by the fact that the very limited staff at the laboratory made a general assault on the problem impossible. The desirability of the second, in view of these limitations, is obvious. The more investigators in laboratories of all types - commercial, educational, or governmental - that become interested in the problems of the menhaden industry, the sooner some concrete results should be forthcoming.

The literature is replete with references on uses of fish byproducts which are specific to certain species in ways that virtually eliminate the menhaden from similar consideration. Examples are the use of fish skin for leather or the use of livers for vitamin oil. In many other cases, our present lack of knowledge of the menhaden does not permit the line of practicability to be drawn with any degree of certainty. In the discussion to follow, uses for menhaden are mentioned by analogy, based on little more evidence than that it, too, is a fish. Generally, an effort has been made to include mention of such factors as are now known for and against the use of menhaden for the purpose under discussion. It should be emphasized, however, that because of the paucity of information on the subject, these qualifications are not intended to be conclusive in either direction as to the ultimate practicality of any use considered for the menhaden.



MENHADEN

Among the sources inspected in the course of this survey were Chemical Abstracts, Industrial Arts Index, Agricultural Index, and microfilm 85171S of the chemical literature survey made in connection with the study of the "Industrial Utilization of Salmon Waste." In this report, an effort has been made to systematically summarize and discuss the literature but without mention of particular sources. The material has been divided into four sections. Possible uses of the component parts of the menhaden will be considered first, then possible new uses for the whole fish. Third, the literature concerning the present use for menhaden

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products - oil, meal, and solubles - has been considered, with a brief preview of future research on these products. Finally, a brief mention has been made of certain problems of the industry itself which would benefit by a research program.

POSSIBLE USES FOR COMPONENT PARTS OF MENHADEN

As far as the literature is concerned there is none on this subject specifically related to the menhaden and we do not have the information necessary to properly evaluate the applications by analogy that we are thus forced to resort to.

In this connection, it might be recalled that the menhaden (Brevoortia sp.), which includes 6 subspecies, is found only along portions of the Gulf Coast, the East Coast from northern Florida to Long Island, and off the Brazilian coast; while sea herring are to be found in almost all the colder waters of the Northern Hemisphere. This lack of any European or Asiatic representatives of Brevoortia is responsible, in the main, for the absence of experimentation with the unusual, less obvious uses for the menhaden. Shortages in these foreign areas have been an incentive to make the most of every resource and to search the bountiful sea for the products their lands could not provide.

The suggestion has been made that the possibilities of the menhaden should be considered from head to tail and backbone out to skin. Pursuit of this scheme leads to the head as our first object of interest.

HEAD: Fish eyes (cod) contain one or more flavins, of which one is said to be identical to riboflavin. If of any value, the eyes could be fairly easily separated, the capsule being quite tough. The menhaden has no teeth, nor is the head the reservoir of any unusual amount or type of oil, as is true of some marine species. The head structure is tough and horny, a characteristic noted in the laboratory when it is necessary to grind the raw fish. If the head was separated for some other purpose, it is quite possible that this horny head skeleton would produce an excellent fish glue.

VISCERA: The contents of the body cavity, or viscera, are a raw material for a large number of theoretically possible new and valuable products. It is also the portion of the fish concerning which there exists the absolute minimum of information for assessing the value of any of these possible uses.

The types of products which have been prepared from the viscera of any fish may be grouped into three categories:

1. VITAMIN OIL PRODUCTS. THESE ARE USUALLY PREPARED FROM THE LIVER, OCCASIONALLY THE WHOLE VISCERA IS USED. EITHER VITAMIN A OR D, OR BOTH, ARE FOUND IN SIGNIFICANT AMOUNTS IN THE LIVER OF CERTAIN SPECIES.

2. PRODUCTS FROM MILT OR ROE. IN SOME CASES, THE ROE IS USED FRESH (SHAD OR HERRING); IT MAY ALSO BE CANNED (ALEWIFE) AND, OCCASIONALLY, SMOKED. MILT, OF HERRING AND SALMON FOR EXAMPLE, IS KNOWN TO CONTAIN A FAIRLY SIMPLE PROTEIN MADE UP OF PROTAMINES AND HISTONES, AND ON HYDROLYSIS THESE YIELD RELATIVELY SIMPLE AMINO ACID MIXTURES. SALMON ROE, AND POSSIBLY OTHER ROES, HAS BEEN USED FOR FEEDING HATCHERY FISH AND HAS BEEN CANNED FOR BAIT. SALMON ROE ALSO CONTAINS AN OIL WITH A VERY HIGH NATURAL IODINE NUMBER, GREATER THAN 220.

3. PRODUCTS FROM OTHER MINOR ORGANS. ENZYMES HAVE BEEN PREPARED FROM THE WHOLE VISCERA OR, MORE COMMONLY, FROM THE PYLORIC CAECA OR STOMACH. THESE ENZYMES ARE MOSTLY PROTEOLYTIC; ALSO LIPASES ARE REPORTED PRESENT IN LOW CONCENTRATION, ESPECIALLY IN FAT FISH. CRUDE ENZYME PREPARATIONS HAVE BEEN USED CHIEFLY AS LEATHER BATES,

ALTHOUGH THERE IS ONE REPORT OF PREPARATION OF A PEPTONE FROM FISH FLESH, SUITABLE FOR BACTERIOLOGICAL MEDIA, BY ACTION OF VISCERAL ENZYMES FROM THE SAME SPECIES.

Insulin may be the only hormone actually prepared from fish, but the field is largely unexplored due to the small size of the organs in most fish and also to the difficulty in obtaining suitable material. Fish are caught under circumstances that make the immediate recovery of desired organs highly impractical, and by the time the fish are landed either they have been gutted or considerable decomposition has occurred in the body cavity. ACTH is the newest of the hormone drugs; and every possible source, including fish, will doubtless be explored. A news item, dated June 7, 1951, states that the Norwegians have developed a process for producing ACTH from whales, but these animals can hardly be compared with the fish under consideration. It indicates the trend, however.

Besides enzymes and hormones, other chemicals are known to be present, for example in the bile where taurine, and cholic and taurocholic acids have been found.

To go from the general to the specific and consider menhaden as a source of any of these products, we are, as already said, handicapped by a total lack of concrete information. In consideration of the first type of compounds we are led to conclude that the menhaden has a small liver of low oil and vitamin content by analogy with the herring, mackerel, and sardine. These are characteristics of small, oily-bodied fish none of which have ever yielded a valuable liver oil. Possibility for production of the fat-soluble vitamins from menhaden is about nil.

The menhaden is somewhat of a biological mystery as far as spawning habits are concerned. Although herring, alewives, and shad are commonly taken in a spawning condition in season, sizable catches of ripe menhaden are quite uncommon. The fish presumably spawn in winter, in deeper waters than they are normally caught. The scarcity of fish in spawning condition makes the available catch of little value for the production of materials from milt or roe.

As for products from the other minor organs, any definite conclusions regarding the possibilities of the menhaden should await results of future work under consideration. Without any desire to be unduly pessimistic, it should still be noted that the menhaden, in common with the herring, sardine, and other largely planktonic feeders, has a proportionately smaller body cavity than the predatory fish.

BONES: The menhaden bony structure is similar to that of shad or herring, the flesh being liberally laced with fine bones. One investigator has determined the availability to the rat of the calcium content of fish bones. He found the calcium in a highly available form equivalent to the calcium of milk. In addition to the available calcium and phosphorus, dried uncalcined bone contains a substantial amount of protein, approximately 30 percent, so that dried ground bone would be a valuable supplementary source of both protein and mineral elements.

MEAT: In considering the meat of the menhaden, the discussion in this section shall be limited to new or special products from the meat, saving the consideration of food and feed usages for the following section on whole fish. Most of the unusual uses to which the meat of fish has been put are dependent upon the meat protein. Uses for the oil fraction of the meat, which have been more extensively developed already, will be grouped under the heading of present products in the final section.

Fish proteins as a rule are readily hydrolyzed, perhaps with greater ease

than most of the vegetable proteins. Acids, alkalies, enzymes, or conditions of heat and pressure have been used for effecting protein hydrolysis. By variation in the type and concentration of reagent and in the temperature and time of reaction, a great variety of products of every degree of hydrolysis may be obtained.

In theory, at least, proteins can be completely hydrolyzed and the component amino acids isolated, but because fish body proteins are "complete" proteins (hence their high feeding value), the resulting amino acid mixture is too complex to make this procedure valuable as an amino acid source. Preparations of mixtures of amino acids, particularly from casein, have been used recently in medicine in cases where protein digestion is faulty because of operations on the alimentary tract or for numerous other causes. Fish proteins would be a "natural" for this type of product if certain difficulties arising from undesirable flavors and colors could be eliminated.

Isolation of certain of the amino acids may be possible by partial or selective hydrolysis in several steps. A great deal of work might be expended on one such single isolated phase of the chemistry of menhaden.

Most of the reports in the literature dealing with fish protein, other than straight analysis for constituent amino acids, have been concerned with various partially hydrolyzed mixtures. Such "protein" solutions can usually be precipitated by chemicals neutralizing the solubilizing agent. This principle is the basis of numerous fibers and fabrics that have been prepared from fish, especially in Germany. A somewhat similar procedure, with removal of inorganic salts and some of the simpler hydrolytic products, yields a so-called "synthetic egg white" which can be substituted, at least in part, for the natural product in some food products. This also was a European development. Even more mild treatment with alkali at relatively low temperatures removes easily hydrolyzed material and fats without dissolving the major part of the protein. The remaining protein is rather gelatinous and when washed and dried gives a food product similar to Scandinavian "lütefisk."

Still another type of protein product results from the action on the meat of fish of an aldehyde, such as formaldehyde, or other chemical agent to produce various types of plastics.

For all of the above protein products, the oil in menhaden flesh would be an undesirable impurity. While the presence of the oil would not prevent the use of menhaden in this manner, it would probably mean one or more additional processing steps and extra equipment not required when non-oily fish, such as cod, pollock, or shark, are used.

SKIN: The skin of menhaden does not appear to present a possibility of producing any products of value sufficient to warrant its separation. If removed in connection with some other product, the skins would probably yield a good fish glue. They are too small for use for the specialty leather products that have been prepared from some fish skins. The literature contains one report of "flavins" (not further identified) in the skin of some teleost fish, and another report, of Japanese origin, claims the existence of substances with "estrogenic" activity in the skin of "small fish." Evaluation of this and similar reports of Japanese origin is very difficult. A great deal depends on the interpretation of the translator, and species definition is frequently lacking.

SCALES: The scales of the menhaden are similar to herring scales, but do not separate from the skin with the same readiness. If a method of separation could be found, there would be numerous possibilities for the use of the "pearl essence"

substance with which they are coated. This material is already prepared from herring, sardines, and alewives. It is used in paints, lacquers, and various plastics to give an attractive sheen difficult to duplicate with any synthetic product. It is also used in the manufacture of artificial pearls.

The chief constituent of this pearly material has been identified as guanine, 2-amino 6-oxypurine, and one reference stated that a guanine isomer is also present. These substances are related to caffein, theobromine, and other of the purine-base alkaloids and could no doubt be used as a starting point for various syntheses for this type of compound. A newspaper account, dated June 6, 1951, mentioned the trial of a new drug for the treatment of certain cancers that delayed development of the tumors. The drug was identified as 8-azo-guanine, another member of the purine-base series. Nothing is known about the synthesis of this compound but guanine would appear to be the obvious raw material.

The cleaned scales consist of a horny substance that would be a good glue base and also are stated to be convertible to a plastic compound. Hydrolysis of the scale substance gives a stabilizer that is said to be used in the alkaline bicarbonate solution of foam-type fire extinguishers. Further study might point out other ways in which such stabilizer could be used. Cleaned scales may be a good source of cystine since on hydrolysis an amino acid mixture rich in this substance is obtained.

One entirely novel possibility was suggested by a staff member of the Beaufort, N. C., biological laboratory. While the scales are normally considered the external covering of the fish, there is actually another protective coating for the fish present in various degrees when fish are first removed from the water. This substance, commonly called fish slime, protects the fish from fungus and bacterial infection. So far as is known, the mechanism of this protection has not been studied, and the possibility that some fungostatic, fungucidal, or antibiotic substance may be present in the fish slime was suggested.

POSSIBLE NEW USES FOR THE WHOLE FISH

The foregoing section covers almost all present possibilities, some highly improbable, for products which might be prepared from various parts of the menhaden. There are in addition several ways besides oil and meal in which the whole or cleaned fish might be used. These uses, new only as far as the menhaden is concerned, are already absorbing large quantities of non-edible, or marginally-edible, fish and fish waste from fillet lines or canneries but are capable of absorbing even larger quantities in many cases.

One such use is the rapidly growing cat and dog food industry for which menhaden has already been used in small quantities. Another industry, similar except that it uses the fish fresh rather than canned, is fur farming, mostly fox and mink. Menhaden should be tested for the presence of the thiamin-destructive enzyme, thiaminase, before it is used raw in large quantities. Possibilities as a hatchery-food might also be considered. The very voluminous literature on this subject -- almost half the byproducts abstracts were concerned with it -- indicates that the dietary requirements for trout and other salmonoid fishes maintained in ponds are quite complex. Menhaden would seem to be about the only fish byproduct that has not been tried, in one combination or another, for hatchery food. The supply of menhaden is, however, rather far removed from most fur and fish farms. The former are located largely around the upper Great Lakes States, New England, and the Pacific Northwest; and the latter are most numerous in the Rocky Mountain and West Coast States.

There are uses of the menhaden described in a report prepared in 1875, when the industry was in its infancy, that suggest possible application to present-day practices. In those days, the commercial fishery for cod, halibut, pollock, and flat fish was entirely a bait fishery, and menhaden was considered the best bait fish available, several hundred thousand pounds yearly being used for this purpose. Whole menhaden were also ground and used as a chum bait in seining mackerel. The line trawler has just about disappeared from the scene, but chumming mackerel might be revived with a resulting increase in catch and a market for bait in the field of sport fishing might be developed. The worm industry that has developed recently in Maine and Massachusetts is an example of the possibilities that exist in this direction.

Another use for menhaden in the 1870's, now discarded almost entirely and perhaps unwarrantedly, was for human food. It seems strange, but menhaden were once considered very good eating when strictly fresh-caught, better than early-run shad or small striped bass. This was at a time when bluefish and trout were extremely plentiful in the same area. The large fat fish were preferred and were utilized pan-fried, salted, canned in oil like sardines, or put up in vinegar and spice like herring. Of course, revival of interest in menhaden as a food fish would be counter to a prejudice built up over many years, and label laws as to identity would not permit much leeway as to nonprejudicial naming of any product. Many people away from the East Coast may not have this depressing association, however. Some effort in the direction of developing food usage might be justified.

USES FOR PRESENT PRODUCTS

The discussion in the preceding sections is based for the most part on literature references to uses of products or byproducts of fish other than the menhaden, and the probable explanation of this situation was considered briefly. There is a considerable amount of literature on the menhaden; specifically relating to meal,

MENHADEN BEING CONVEYED ON BELT SYSTEM FROM THE HOLD OF THE VESSEL TO THE COOKERS.

oil, and solubles, in that order of abundance. Since our present concern is with new developments and new products, the literature, much of it ancient history due to the rapid developments in the field of nutrition, will be considered only briefly.

MEAL: When menhaden meal was first proposed as a feed ingredient, its contents of vitamin D, and to a much less extent vitamin A, were important talking points. Between 1930 and 1945 the meal was shown to contain relatively large amounts of riboflavin, choline, niacin, and pantothenic acid. Of course, it was considered a good protein source also, but the real spur towards full appreciation of its value as a protein supplement was the development of microbiological tests for many of the amino acids. With these tools, a comparative study of the amino acid ratios in the many vegetable protein sources and fish meals was feasible.

The latest, and perhaps the most important discovery to date, was the outcome of evidence that something more than just optimum balance of amino acids was contributed by fish meal, along with the natural "animal" protein, to the diet of chicks and rats. This so-called "animal protein factor," or APF, was soon concentrated and, in a surprisingly short time, a red substance known as vitamin B_{12} was isolated. The most recent development is the conviction of some investigators that in addition to vitamin B_{12} at least one (perhaps more) growth factor is contained in fish meal and in a few other natural protein or vitamin sources.

Menhaden meal has been used in much of the research on these various growth factors. However, the generic term "fish meal" is frequently used. For all practical purposes this nonspecific grouping as fish meals is not undesirable. Differences between kinds of meals -- menhaden, herring, or pilchard -- no doubt exist, but the accuracy of the various assay methods is insufficient, and the study of the influence of seasonal and regional factors and production methods has not reached the point where these differences can be clearly defined.

Further research on menhaden meal will probably be directed toward the clarification of the effect of some of these variables on meals, particularly in regard to protein quality, content of vitamin B_{12} and B_{13}, and other factors as yet unidentified.

Much remains to be done in the improvement of assay methods for the new growth factors. With suitable assay methods of not too great complexity, an interesting research problem would be the concentration of these new factors from menhaden meal or solubles; and some study of their properties might be possible also.

OILS: Reports of research on menhaden oil are somewhat less numerous than for the meals. There are three or four reports concerned with separation and identification of the fatty acids or glycerides present in menhaden oil, all indicating extreme complexity of the original glyceride structure. Fatty acids composed of from 16 to 24 carbon atoms are present, and the amount of unsaturation ranges from zero to six or more double bonds for each carbon group. The glycerides are composed, in the great majority of cases, of mixed fatty acids rather than being single acid tri-glycerides, so there is an extremely large number of isomeric glycerides possible.

The more saturated glycerides are removed in cold pressing, and the resulting oil is more reactive chemically. Double bonds can be shifted to conjugated positions in the molecule by treatment with alkali under certain conditions; and any desired degree of hydrogenation, catalytic splitting of the carbon chain, sulfation, polymerization or heat-bodying and blowing, are only a few of the presently-used or possible reactions of the cold-pressed oil. The resulting products are already

used in a very wide variety of ways. Paints, linoleums, inks, rubber, lubricants, detergents, and many others could be listed with new uses constantly being discovered for the more recently developed compounds prepared from the oil.

Future research on the oils might be carried out on the saturated fraction. This portion of the oil, as removed in the cold-pressing process, amounts to approximately 30 percent of the crude oil. In the past it has been used largely as a cheap soap stock. Some has been hydrogenated and deodorized for use as an edible fat, and a small amount is purified and used in pharmaceuticals, such as creams, lotions, and similar products. It is quite possible that further study of the constituent fatty acids and unsaponifiable matter present might lead to the development of more valuable products from this portion of the oils. Guanine, for example, is in all probability present in small quantities, derived from the scales during the cooking and pressing of the fish. As indicated in the earlier section concerning scales, this material might be the starting point for many valuable derivatives if methods for separation from the oil could be developed.

Another phase of oil chemistry requiring further research is the development of methods for the separation on a commercial or industrial scale of oil fractions having relatively narrow ranges of unsaturation. The cold-pressing process gives a very crude separation, the press cake containing about 50 percent of liquid oil. Various solvent fractionation procedures have been developed which give much sharper separations; but these involve low temperature operations, in the range of minus 10° C. to minus 60° C., and the use of inflammable and volatile solvents, such as acetone. The development of a method of separation using cheaper or less hazardous chemicals in a higher temperature range would be a very valuable contribution towards the further development of menhaden oil products.

SOLUBLES: Research on condensed fish solubles has been relatively limited. It has been shown, in general, that valuable growth factors that are present in the meal are present in greater concentration in the solubles. It has usually been assumed also that the protein portion of the solubles was equally as effective as fish meal for supplementing vegetable protein, although recent research tends to disprove this theory.

The recent rapid increase in the number of stickwater recovery units has resulted in a virtual glut in the solubles market, so that future research will probably be directed toward methods for retaining or returning the "solubles" fraction to the finished meal. Operations of this type are used in Norway, and have been reported in use in this country to a limited extent. In the meantime, fish solubles might offer a source superior to fish meal for the concentration and study of vitamin B_{13} and other still unidentified growth factors.

FURTHER RESEARCH DEVELOPMENTS IN THE MENHADEN INDUSTRY

There are several phases of the industry requiring additional study of a directly practical as well as a research nature. One of these pertains to the preservation of the raw fish on the boats before reaching port. This has become a problem of great importance, following the extraordinarily rapid development of the Gulf Coast menhaden fishery. This is a warm-weather fishery, extending from approximately May to September, and when longer trips to the grounds are necessary some operators find the fish arriving at the plants in a virtually liquid state. This results in many difficulties in handling during unloading, cooking, and pressing. Of even greater importance is the fact that soft fish lead to high solids in the stickwater and low oil recovery. The losses resulting from these factors may well approach one-half million dollars annually. The Norwegians have

reported work on the preservation of herring when immediate processing to meal is not practicable, but the problem in that country is hardly comparable. The periods of time involved are much longer, but normal air and water temperature are much lower than on the Gulf Coast. Sodium nitrite and formic acid have been found the most effective of the numerous chemicals and combinations of chemicals tried in Norwegian operations. However, there is no assurance that either chemical would be satisfactory under the conditions found on the Gulf Coast. A study of preservatives to be of practical value would almost certainly require field operations in the area involved because of the impossibility of reproducing boat-hold conditions in the laboratory.

Another practical research problem, also essentially a field operation, would be a more generalized extension of the preceding problem. This would be an over-all study of plant operations to determine losses, cause of losses, and methods of minimizing or preventing losses. This is a general problem for the whole industry, and is becoming more important as falling prices for oil and meal are rapidly reducing the margin of profit in menhaden plant operation. This project is in a sense an extension and modernization of the work carried out by the Bureau of Fisheries in 1928-30. This original work was so far ahead of the stage of technological development of the industry of that time that it was not generally accepted. There is every reason to believe that the industry would be far more receptive to a modern revised report of this nature, however, and quite valuable results might accrue from such a program.

SUMMARY

This report has not attempted to point out any certain phase of research on the chemistry of menhaden as the one and only future program. In the discussion of many of the projects, opinions have been expressed as to their desirability or otherwise. Some are repetitions of opinions voiced by the numerous plant owners and supervisors whom it has been the author's pleasure to interview in the past six months; others are entirely the opinion of the author. In neither case should undue weight be given to this discussion of the project. Approval has been given a program of research more than sufficient to occupy a force of several chemists for many years. The problem at hand is the selection of the most urgent or most promising of the projects.