Progress in Technological Studies on Menhaden Products Under The Saltonstall-Kennedy Program

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THIS PAPER discusses the development and progress of the fish meal and oil program largely made possible by Saltonstall-Kennedy funds. These programs, as organized and undertaken early in 1955, have important implications to food fish and to all classes of industrial fishery products, but in this paper they are discussed in terms of importance to the menhaden industry.

The research objectives deal with three categories (1) the raw material, (2) the rendering process and (3) products derived from menhaden. Investigations concerned with the raw menhaden are intended to find out about structure and composition of the fish. It is important to know how these vary with species, size, season, postmortem changes, stowage conditions, treatment with preservatives, and method of unloading from boats. In dealing with the reduction process we want to know the effects of variations in raw material and processing conditions. Also, there is interest in the nature of plant losses, possibility of modifying processing methods, introducing new equipment, and use of quality control. Fish meal, solubles and oil, the three important products of the menhaden industry, require extensive work to further our knowledge of chemical, physical and nutritional properties. We want constant improvement of quality and methods of utilization, and are anxious to develop new uses and markets.

The Saltonstall-Kennedy program on fish meal was established because of urgent requests from the fishing industry and from the Nutrition Council of the American Feed Manufacturers Association. It bears the title, "Quality Index for Fish Meal," a succinct way of stating a complex problem. Its objective is to develop a rapid method of predicting performance of fish meal in animal and poultry rations. There are two reasons why this is difficult. First, there are countless variables in fish meal manufacture resulting from differences in raw material and in processing conditions. Second, fish meal offers multiple feeding values dependent upon protein quality, vitamins, growth factors, lipids and minerals. To work out the problem it is necessary to establish the importance of variables in fish meal in correct relation to these multiple feeding values. Then, when the correct perspective has been reached it must be demonstrated in terms of simple laboratory techniques, which in turn relate to practical feeding results. This formidable problem, when attacked through well organized investigation, will extend our knowledge of our raw materials and processing methods. A quality index test for fish meal will be tremendously helpful to the fishing and feed industries.

The planning and organization of the "Quality Index" program involved numerous discussions between Government and industry people. While agreed that fish meals vary in quality, there was practically unanimous disagreement on the extent to which this occurs. Almost everyone expressed strong views regarding specific factors which lower quality of fish meal. In most instances these conjectures could not be fully supported with well founded laboratory

data. Miss Neva Karrick of the Seattle Fishery Technological Laboratory, in an effort to illuminate the problem, prepared a group of abstracts entitled, "A Literature Review on Factors that May Affect the Quality of Processed Feeds." Although useful in spotlighting some critical factors, the conclusions drawn in many of these articles could no longer be accepted as valid because the evaluation methods had become obsolete. Obviously this program would require standard samples representing excellent, medium and poor fish meals. There was little agreement as to how such fish meals could be obtained.

Because of these difficulties, the program was organized to embody collection of extensive data and use of screening tests to be carried out on samples representing commercial averages, and also those in which important variables had been introduced. Since carefully documented fish meals were needed, this job was assigned to a group of field men who supervised their preparation under full scale and pilot plant conditions. These were subjected to proximate analysis at the College Park, Boston and Seattle Technological Laboratories, and at the Alaska Fisheries Experimental Commission and the State of California Department of Agriculture. Nitrogen partition studies were undertaken at Maryland State College, and lipid investigations started at University of California. It was hoped that these data, together with a knowledge of the processing variables introduced in making the samples, could be correlated with the results of feeding tests on poultry. Here, there was a three-fold approach. Dr. Grau of the University of California, using a rapid chick assay method, determined protein quality. Dr. Bird at the University of Wisconsin undertook to investigate unknown growth factors, while Dr. Runnels, of University of Delaware, set up feeding tests intended to determine how the meals would perform in modern high efficiency feeds. Recently a project dealing with amino acid availability and vitamin content was established at Wisconsin Alumni Foundation. The work of collating data is still in progress. While manifestly impossible for the individual project leaders to interpret their data fully without knowledge of the whole picture, some of their interim findings may be of interest:

Dr. Vaughn, at Maryland State College, carried out an examination of over 70 samples which had been processed under various conditions and determined true protein, water soluble protein, bone protein and ammonia nitrogen. He recently examined these data in comparison with broiler tests on some 38 samples and found little correlation. He hastens to point out that these conclusions are not based on statistical analysis.

Dr. Brown, who is working under a collaborative agreement at the University of California Food Technology Dept., has furnished some recent information on the progress of this program. This concerns oxidative deterioration in fish and fishery products, a subject with interesting implications applying to fish meal manufacture. Their work has included studies of protein-oil reactions, protein catalysis of unsaturated fat oxidation, and use of antioxidants and synergistic mixtures in retarding oxidation of fish flesh, meals and oils. Rates of oxidation of fish meals and oils have been measured. Dr. Brown cites, as one important result, their finding that the antioxidant Santoquin is effective in reducing heating rate of oxidation and rancidity of fish meal.

Dr. Grau, of University of California, has been studying protein quality of fish meals as judged by chick feeding tests. His work has included 95 samples of menhaden fish meal and in describing his results he states that, "As is

often true in exploratory research, we did not find what we thought we might: In the first tests the wide range of fish quality and processing variables did not result in meals that were detectably variable as amino acid sources. Later studies indicated greater variability, but it has not been possible to correlate this variability with known variables in raw material or processing." He makes the further observation that the standard menhaden meal, upon storage at room temperature for eight months, deteriorated significantly, and an effort is now being made to determine if this deterioration is an isolated instance, or a general phenomenon. In addition, they now plan to investigate some possible effects of antioxidants upon fish meal quality, particularly as they may "relate to fat-protein combination and digestibility of protein content with oxidized fat."

Dr. Bird, of University of Wisconsin, has furnished some interesting comments regarding interim results of his project on growth factors. He states that this is probably "the first attempt to assay a wide range of samples of any material for the currently unknown growth factors" since such assays have usually dealt with improving the method rather than in applying it. Regarding the importance of such work, he maintains that, "Unknown growth factors are the primary selling point for fish meal used in poultry feeds." Dr. Bird reports that the best fish meals were about equal to, and the poorest about one-fourth as potent as 50 per cent condensed fish solubles. He has not been able to draw conclusions as to why this variation exists.

Dr. Runnels, of University of Delaware, is conducting the project entitled "Assay of Fish Meal for Feeding Quality in Chicks." To quote Dr. Runnels, "This project consists of feeding chicks a simplified diet calculated to be iso-caloric and iso-nitrogenous, with and without fish meals. The experiments are designed to locate factors such as season of catch, holding time, location of catch, type of processing and numerous other variables that may result in biological differences. When these factors are located a more detailed study designed to demonstrate methods of improvement is carried out." He further states that in, "Research of this type it is unwise to draw positive conclusions from preliminary data, however it does appear that we may have located some interesting variations between samples of fish meal that may prove very beneficial to the industry." In discussing results measured by particular diets used to date, Dr. Runnels comments that, "From a broad aspect it appears reasonable to conclude at this time that biological variations between samples of fish meal is smaller than had originally been thought."

Dr. Derse, of Wisconsin Alumni Foundation, is approaching the problem of measuring the possible variability of fish meals in quite another way. This work concerns determination of availability of amino acids through enzymic release. So far they have found that enzymic amino acid release follows a definite pattern. It is still to be determined if such patterns vary with the age and type of sample.

These comments, together with reports from other sources, indicate the validity of the approach made to the "Quality Index" program. There is less of a tendency to simplify the problem. Instead, it appears now that more basic work will have to be done. The massive data collected so far will probably be insufficient to arrive at a satisfactory solution to the problem. On the other hand, much of this information will fall into place when the picture becomes clear. Meanwhile, important bonuses are appearing along the way. Field work has increased interest in quality control at the producing plants. The nitrogen

partition studies of Dr. Vaughn have filled important gaps in our knowledge of composition variations of fish meals. The work on oxidation at the University of California and their finding of an effective antioxidant, relates directly to applied work being done in the menhaden plants. Meanwhile, some exciting concepts regarding methods of using fish meal in high energy rations have resulted from consideration of the feeding tests. If these conjectures can be supported by factual data then additional evidence regarding economic gains resulting from the use of fish meal in feed formulas can be expected.

We turn now to the extensive Saltonstall-Kennedy Fish Oil Research Program. This deals with a class of fats and oils which have received little technological attention in spite of long historical background. A fat which cannot be examined analytically and which is poorly understood chemically tends to occupy an inferior position in a competitive market. Interchangeability of fats and oils applies more frequently to the cruder uses. Fats selected for such purposes can often be described as being "good for everything, but good for nothing." The more valuable products resulting from fats and oils technology depend upon reliable raw materials of known structure and composition. Fish oils, with their long chain fatty acids, and high degree of unsaturation, will undoubtedly become valuable when fundamental information concerning them is available. Applied research, which develops more immediate markets, also has a place in this program. This again is not an easy path, since one must dig deeper than was required when Edisonian methods were in vogue.

The Fish Oil Research Program, as established in 1955, consisted of many parts. It included field work for collection of authentic samples, a literature search, and an analytical project concerned with showing variations occurring due to species, geographic locality, size and other causes. The greatest effort was to be devoted to basic research concerned with structure and analysis, composition, reactions, inclusion compounds, non-glyceride components and odor. Applied studies dealing with feeding, leather uses, fungicidal applications, resins and mineral flotation were also established. Although these projects cannot be completely discussed in a short paper let us outline highspots recently reported by the project leaders themselves.

Dr. Simmons, of North Carolina State College, is conducting a project intended to ascertain the variations occurring in fish oils as indicated by the usual oil constants (iodine value, color, refractive index, etc.). This work is being done on fish oils collected weekly from a large number of production areas and it is expected that the data, after statistical analysis, will be helpful to purchasers and users of fish oils.

Dr. Lundberg, Director of Hormel Institute, has furnished some information on the progress of projects under way in that institution. These were established early in 1955 to deal with structure and analysis of fish oil fatty acids, chemistry of the odor problem and separation of fatty acids by means of inclusion compounds. At the end of the first year the latter problem was replaced by another dealing with chemical reactions of fish oil fatty acids.

Dr. Privott and associates are concerned with the project on structure and analysis of fish oil fatty acids. In order to achieve a complete determination of structure of the more unsaturated fish oil fatty acids and to establish analytical constants for the examination of common fish oils they must isolate the individual fatty acids in purified form. Good progress is being made in doing this using methods which include solvent segregation, urea-complex fractionation,

distillation, and finally chromatography. By means of isomerization with alkali followed by spectral studies on various fish oils, and even more conclusively, through studies using soybean lipoxidase, they have established that at least 97 per cent (and possibly more) of the polyunsaturated acids of menhaden oil have double bonds which are separated by methylene rather than by ethylene groups. This implies increased reactivity which is distinctly important in many applied uses, particularly in the coatings field.

Another Hormel project involves the chemistry of odor and is being worked upon by Dr. Chipault and co-workers. Although commercial de-odorization processes are capable of complete removal of odor from fish oils, reversion soon occurs. Rather than attempt improvement of methods which may be basically wrong they consider it more promising to find out the chemical reactions involved, and then to seek additives capable of inactivating the causative factors. There is evidence that odor development in deodorized fish oils is due to liberation of low molecular weight substances which are nitrogenous, or which are formed by reaction of atmospheric oxygen with unsaturated fatty acids. There are indications that these are largely unsaturated carbonyl and dicarbonyl compounds. Selection of additives to destroy these odorous substances must await positive identification. However, one such additive may have turned up in the work on inclusion compounds. It was noted that thiourea is effective in removing peroxides. This finding could turn out to be significant since peroxides may be the precursers of the odor components. Thus the research work on one project can often be applied to advantage in the conduct of work in a related field.

Starting in 1953, the Seattle Fishery Technological Laboratory undertook a limited amount of work on fish oils, some of which was devoted to inclusion compounds of urea. There was interest in continuing this work at Hormel, and Dr. Schlenk and co-workers were selected because of their background in this field. Fatty acids have a peculiar property of forming solid complexes, or "inclusion" compounds with such substances as urea. This tendency varies with each fatty acid, offering an effective means of separating them. The potential is indicated by a recent Standard Oil (Indiana) process for separating petroleum hydrocarbons, based on similar principles.

In this project Dr. Schelenk placed most emphasis upon thiourea and deoxycholic acid. Neither of these compounds are considered practical because of cost, but they gave better separations than urea. An important result is that deoxycholic acid makes possible easy separation of fatty acids by chromatography. The purity of individual fatty acids, by this means, can be readily established. It was also used to demonstrate that the content of fatty acids of different chain lengths in menhaden oils is quite different from some of the published values.

Following completion of the inclusion compound project Dr. Schlenk was assigned another one concerned with new chemical reactions of fish oil fatty acids. Emphasis will be placed upon reactions occurring at the double bonds in an effort to exploit the long chain, highly unsaturated fatty acids present in fish oils, but not often available in such diversity and abundance in other fats and oils.

In view of the importance of analytical techniques a project dealing with development of a procedure for measuring some of the constituents of fish oils was established at Texas A & M under the direction of Dr. Raymond

Reiser. To quote Dr. Reiser, "It is hoped that studies on the chromatographic analysis of marine oils will be of value in evaluating the quality of various marine oil products by much simpler means than are now available. In a matter of a few hours it is possible to determine qualitatively and roughly quantitatively, (by the procedure developed) the various fat soluble vitamins, triglycerides, waxes, hydrocarbons and phosphlipids." Dr. Reiser's report states that menhaden oil was found to contain squalene, Vitamin A and D cephalin, but no lecithin, syphingeyelin, vitamin esters or waxes. The presence or absence of such substances is a matter of interest in many commercial applications. Another attack on these non-glyceride components of menhaden oil is reported by Dr. Mosher of University of Delaware. They have found so far that the non-saponifiable material in the oil, representing less than 5 per cent, contains squalene, chloresteral, and at least three other unidentified sterole-like substances. The non-saponifiable fraction is very subject to autoxidation and develops bad odor on standing. In line with the findings of Dr. Reiser, they report that several components of this fraction can be removed from the whole oil by chromatographic adsorption, including color body fractions. A good portion of the color associated with whole oil appears to be in the non-saponifiable portion. The presence or absence of substances of the type covered by the latter two projects is a matter of interest in many commercial applications.

Turning now to some of the applied research projects we find some interesting reports from some of these investigators, dealing with insecticidal and fungicidal uses, leather uses, ore flotation and with the feeding of fish oils to swine:

Dr. Sokoloff, of Florida Southern College, has found that menhaden oil exerts anti-fungal activity and that this activity can be increased by fortifying with hydrides. This "hydrogenized" menhaden oil has proven non-toxic for citrus seedlings and active against citrus fungi and certain citrus insects. For convenience in use, an attempt is being made to produce the product in powdered, water-soluble form.

Messrs. Roddy and Mattei, of the Tanner's Council Laboratory, University of Cincinnati, are conducting experiments on the use of fish oils in the fat liquoring of leathers. Tanners have objected to menhaden oil because of its high degree of unsaturation and oxidative properties. Preliminary tests involving fat liquoring of leather with menhaden oil have produced better results than expected. This work is to continue, using various modified menhaden oils. Also, the trade has reported objectionable features to this oil in connection with sulfation processes. By introducing an additive to concentrated sulfuric acid they have developed a better procedure for sulfating menhaden oil and are preparing to test this procedure on a pilot plant scale.

In quite another field, it is interesting to consider Dr. Cooke's investigation at University of Minnesota, on utilization of derivatives of fish oils in ore flotation. The objective is to extend the usefulness of these products and their applicability to ore concentration by flotation. Dr. Cooke points out many variables involved in this work and the difficulty of drawing firm conclusions based upon incomplete results. It appears so far that "the bulk unsaturated fatty acids seem to give as satisfactory results as a relatively pure (93 per cent) technical grade oleic acid. Comparative tests have been made using commercial grades of oleic acid, but analysis of the results are not yet available." These results seem promising. Less encouraging is his comment that work done with

purified acids prepared by Hormel Institute indicates that best results are obtained at iodine values of 80 to 120. Adequate selectivity is not obtained at higher or lower levels.

The last of the applied research projects discussed in this paper is concerned with feeding of fish oils. This subject is important to the menhaden industry because it serves to expand our knowledge of the nutritional possibilities of menhaden oil, for humans, animals and poultry. The part that unsaturated fats may play in the prevention or treatment of coronary heart disease recently received national attention through an article appearing in the November 12 issue of "TIME" magazine. Our interest also stems from the fact that fish oils, and their counterparts in fish meal and solubles, have proven useful in animal and poultry rations when used at proper levels. Fat content of fish meal and solubles is a useful energy source contributing to the caloric value of the ration. One of two projects involving feeding of fish oils was concerned with its use in swine rations. This was conducted by Dr. J. E. Oldfield of Oregon State College. He found that swine grow satisfactorily when 5 to 10 per cent of the grain is replaced by crude fish oil, but that 15 per cent causes them to go off feed. He found that even 5 per cent levels of crude and alkali refined fish oil will impair carcass quality from the standpoint of flavor. Five per cent kettle bodied oil, on the other hand, produces vastly improved carcasses. Dr. Oldfield feels that adequate protection of the oil prior to feeding, perhaps through polymerization, might eliminate the undesirable effects upon carcass quality. It is difficult to say where these findings may lead. Present practice would involve use of only small amounts of fish oils in swine rations and presumably, insofar as he has studied the problem, the quantities introduced as a part of condensed fish solubles, or fish meal, are too small to be significant.

In conclusion it is well to restate a portion of what has been said about the impact these fish meal and oil studies are having upon the menhaden industry. It is evident that many of our research objectives are being met. Our knowledge of the raw material menhaden is increasing as a result of field work which seeks well documented samples for extensive chemical, physical and nutritional evaluation. The selection of samples having known processing variables has stimulated interest in taking a long, hard look at some phases of the reduction process. This re-examination of old concepts regarding processing has already brought about some improvements. There is a daily increase in our knowledge of menhaden products resulting from the fish meal and oil program. Such knowledge is coming to us in the form of extensive data relating to composition, physical properties and biological activity, and also in suggesting improved methods of utilization. These findings offer the promise of increasing the effectiveness of fish meal in animal and poultry rations, a result which would further prove the economic value of this important product.

The basic studies seem to be leading directly to some of the more valuable applications of fats and oils. The applied projects, in delving deeper into specific fields, appear to be bringing us within striking distance of new and important outlets for fish oils. This progress, in so short a time, is a source of satisfaction, and certainly a tribute to the people concerned with this program.