OXIDATIVE DETERIORATION IN FISH AND FISHERY PRODUCTS -- NO. 1

SCOPE OF PROGRAM

Among the most adverse alterations which occur spontaneously in fish and fishery products are those involving oxidation of oils, pigments, and other chemical components of the fish. These changes give rise to deterioration in the flavor and odor, development of off-colors, and diminishment of nutritive value. The chemical composition of the oils may become so altered that the value of the extracted oil is lessened for certain industrial applications.

While considerable research has been carried out on oxidation of oils and pigments in animal and vegetable products, work along these lines with marine products has been extremely limited. Much needed basic information as to what the mechanism of such oxidations is and how it can be controlled is lacking.

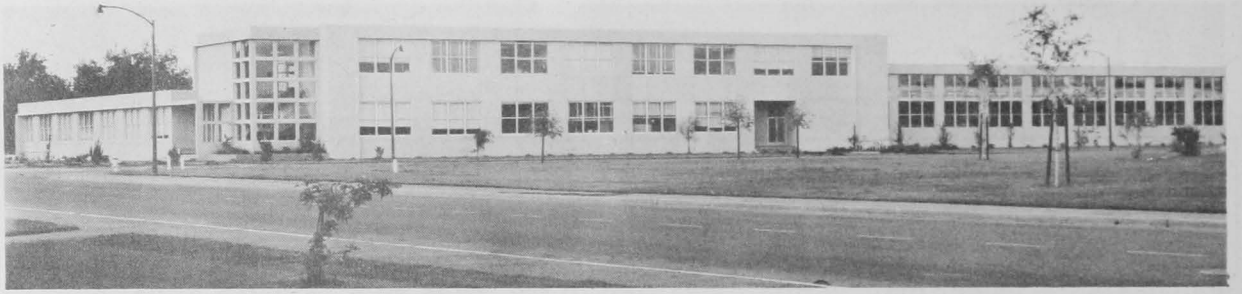

Fig. 1 - Food Technology Building, University of California, Davis, Calif.

A new program with Saltonstall-Kennedy funds was inaugurated in August 1955 by the U. S. Fish and Wildlife Service to make a thorough study of these problems. In a collaborative program, Service employees are stationed in the laboratories of the Food Technology Department of the University of California to undertake this research.

PERSONNEL AND FACILITIES AT UNIVERSITY OF CALIFORNIA: The Food Technology Department of the University of California operates with Dr. Emil Mrak as head of the department on two of the campuses of the university. The main laboratories are located at Davis, Calif., where the program is now under way. Dr. A. L. Tappel of this department at Davis has had considerable experience in the field of oxidation in food products other than fish. He received his doctor's degree under Dr. Lundberg of Hormel Institute and hence is well trained in the field of oil chemistry. He has published a series of papers on the mechanism of oil oxidation in food products such as meat. Under the Service's new program, this research is now being extended to oxidation in fishery products.

The Food Technology Department occupies a new building at Davis, with the best of equipment for research in the field of food technology. The building is located adjacent to the Poultry Husbandry Department, where the Fish and Wildlife Service has another collaborative program under way on nutritive value of fish meal. This makes possible close collaboration on those phases of the oxidation program dealing with changes in the nutritive value of fish meal caused by oxidation of the oil or of other components in the meal.

Dr. Harold Olcott has been employed by the Institute of Marine Resources of the University of California to inaugurate work by the University in the field of fishery technology. This program operates through the Food Technology Department, and Dr. Olcott will work on the Berkeley campus of the University of California. A part of the Fish and Wildlife Service's collaborative program will be supervised by Dr. Olcott. Much of the basic research in the field of mechanism of vegetable-

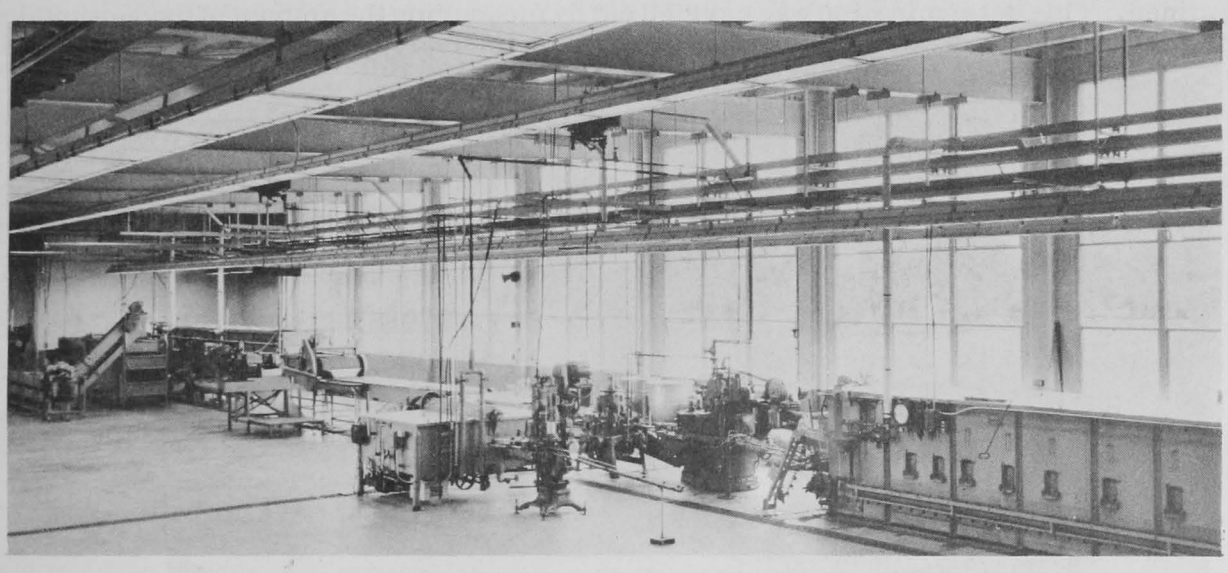

Fig. 2 - Canning equipment and general view of the processing laboratory, Food Technology Department, University of California, Davis, Calif.

and animal-oil oxidation and action of antioxidants was carried out by Dr. Olcott when he was working with Dr. Mattil at the University of Iowa. That portion of the Service program dealing with oxidation of extracted fish oils will be carried out under Dr. Olcott's supervision.

The Fish and Wildlife Service now has two full-time and one part-time chemists, as well as one part-time food technologist and one part-time laboratory aid working on this program at the University of California. A good start has already been made on some phases of this work.

PROGRESS MADE ON PROGRAM

GENERAL APPROACH TO THE PROBLEM: Two phases of the program are now under way. One of these on which most of the work up to now has been concentrated is a study of the mechanism of oxidation of fish oils while present in the meat of fish. This phase is basic to applications, whether involving changes in oil in the stored meat of fish, or in fish meals, or in the oil itself because in all these cases the oil starts out in the meat and some changes always take place initially in the meat before any manufacturing steps have been started. Accordingly, chief emphasis in the initial stages of the work will be toward elucidating the mechanism of oxidation of oil in the meat of fish. Some work is proceeding concurrently in collaboration with the Poultry Husbandry Department of the University of California on ox-

idation of oil in fish meal. Work on oxidation of pigment and on oxidation of extracted oil will get under way later. The latter program will eventually be carried out at Berkeley as soon as the Institute of Marine Resources' new laboratory for fishery technological work at Berkeley is completed.

HEMATIN COMPOUNDS IN FISH: Work began on the first phase of the program by the analysis of a number of species of fish for their content of hematin compounds, substances which have been shown to be powerful biocatalysts for oil oxidation in other foods. Nine species of fish were examined, and hematin compounds were present in all samples, the content varying from 5.4×10^{-5} M in pilchard down to 0.1×10^{-5} M in cod.

EFFECT OF HEMATIN COMPOUNDS ON FISH-OIL OXIDATION: The effect of hematin compounds in the meat of fish on catalysis of oil oxidation was next determined. This determination was carried out by measuring the amount of oxygen uptake of a salt of an unsaturated fatty acid, ammonium linoleate, when subjected to aeriation

Fig. 3 - Weighing freeze-dried meats (the freeze drier is in the background) at Food Technology Department, University of of California, Davis, Calif.

in a Warburg respirometer. The reaction was carried out at 20° C. at a pH of 9.0, and extracts of fish were added to the ammonium linoleate substrate to determine their effect on the oxidation rate. The fact that the catalysis was due primarily to hematin compounds and not to some other biocatalysts in the fish was confirmed by repeating the experiment in the presence of cyanide, in which case no catalytic effect resulted. Cyanide inhibits hematin catalysis of unsaturated fatty acids.

In another series of experiments (1) cubes of fish meat and (2) extracted fish oil from different species were measured for rate of oxygen uptake in a Warburg apparatus.

The results of all these experiments showed a correlation between the hematin compound content of the various species of fish and the catalytic effect of fish extracts on the linoleate oxidation. The rate of oxidation of the meat of fish also was correlated with the content of hematin compounds.

CATALYTIC EFFECT OF PROTEINS ON FISH-OIL OXIDATION: Some experiments were carried out to determine the effect of various proteins on the catalytic oxidation of fish oils. It was shown that all proteins studied had a measurable effect but that none of the proteins investigated approached hemoglobin in activity, in this respect.

ANTIOXIDANTS: Work is now under way to appraise the effect of antioxidants on the rate of oxidation of fish oils in fish meat. Antioxidants being investigated include d-tocopherol and certain compinations of synergistic compounds previously developed by the Food Technology Department of the University of California for use with other food products.

OXIDATIONS IN FISH MEAL AND EFFECT ON NUTRITIVE VALUE: Some work has been started on investigation of the mechanism of alteration in nutritive value of fish meals which accompanies heating and oxidation of the oil in such meals. This program is being carried out jointly with Dr. Grau of the Poultry Husbandry Department. Three possible mechanisms are being considered:

1. Copolymerization of lipids with protein.

2. Formation of carbonyl-amine browning reaction products by combination of lipid oxidation products with protein of the fish meal.

3. Oxidation of oxygen-labile amino acids to form products of lowered nutritive value.

Some evidence has been obtained to indicate that mechanisms 1 and 3 are possible, and further work is continuing.

Considerable work is under way in the Food Technology Department on another project on the browning reaction occurring with dehydrated meat. Experience gained in this other project is being applied to investigation of the role of browning in fish meal and its effect on nutritive value.

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COMPOSITION OF FRESH-WATER FISH--NO. 1

INTRODUCTION

Information on the composition of fish is of basic importance and is essential if fish are to be utilized to the best advantage. From a technological standpoint, knowledge of the makeup of fish is necessary in the application of methods of preservation or in attempts to utilize it as a food staple or in the preparation of industrial products from the whole fish or the waste portions.

Examples of the importance of composition can be found in every phase of fishery technology. In processing fish for human consumption, a knowledge of the chemical composition of the fish will help to determine the most suitable processing methods. The difficulties encountered in the storage of frozen fish can be more readily overcome if the amount and nature of the oils present in the meat are known. A

knowledge of the oil content of the fish will also help to determine the most suitable method for processing fish waste into meal and oil.

Over many years much data on the composition of fish have appeared in the literature. Unfortunately, many of these data are worthless to workers in the field because the samples used for the analyses were too limited and did not take into consideration the variation occurring within species or with season. In most instances there has not been enough information given concerning the samples that the results could be included in the determination of either average values or a range of values for the species.

In the present project, samples of various species of fresh-water fish are being analyzed for their moisture, oil, protein, and ash contents.

SAMPLES

The samples of fresh-water fish used for these analyses were obtained in the Great Lakes, Mississippi River, and small lakes in Minnesota and Wisconsin. The fish were shipped to Seattle either in ice or frozen. The analyses were done on the edible meat portions and on the waste trimmings. The samples of the edible meat

Table 1 - The Oil Content of Sheepshead (Aplodinotus grunniens) from Several Sources

Location Where Caught		Date Caught		Fish in Lot	Oil Content of Fish		
Body of Water	State	Month	Year		Maximum	Average	Minimum
				Number	.....(Percent).....		
Lake Erie	Ohio	Oct.	1951	16	8.60	5.97	2.70
		June	1952	16	10.30	6.90	2.20
		Aug.	1954	16	9.65	6.04	1.17
Mississippi River	Iowa (Clinton)	May	1952	16	13.09	7.15	1.87
		May	1953	15	14.20	8.39	1.45
		Aug.	1953	16	11.30	7.34	1.52
		June	1954	16	14.20	8.78	3.57
		June	1955	16	13.30	5.50	3.23
	Wisconsin (La Crosse)	Aug.	1953	11	16.00	9.68	2.61
	Minnesota (Lake Pepin)	Aug.	1955	16	20.36	11.53	5.54
Lake Winnebago	Wisconsin	July	1953	16	15.30	2.72	0.56
		Jan.	1954	16	3.83	1.53	0.50
		Sept.	1954	16	14.60	2.70	0.91
		Feb.	1955	16	15.34	4.04	0.74
Red Lake	Minnesota	Aug.	1954	16	9.10	4.33	1.63
Clearwater Lake	Minnesota	May	1953	16	1.67	1.04	0.72
Lake Kegonsa	Wisconsin	Oct.	1954	16	8.84	4.89	2.00

were prepared as follows: The fish were filleted. Then the fillets were skinned, retaining as much as possible of the oil deposited directly beneath the skin. The two fillets from a single fish were ground through a Hobart food cutter for 6 minutes, the machine being stopped after each 2-minute period in order that the contents of the cutting bowl could be mixed. After the meat of the fish was thoroughly ground and mixed, the sample was vacuum-sealed in $\frac{1}{2}$-pound tin cans and frozen. The waste from each lot of fish was composited and treated in the same manner as the fillets. The samples were stored at 0° F. until the analyses were run. The samples were then thawed, again thoroughly mixed, and finally weighed for the determinations.

SHEEPSHEAD SELECTED FOR THOROUGH COVERAGE

Attempts to determine the variation within a species are an important part of this project on composition. It was not possible to follow through on all species a series on the effect of location of catch, seasonal variation, and yearly variation. In attempts to select a species for a thorough study, sheepshead (Aplodinotus grunniens) appeared to be an excellent choice. More markets are needed for sheepshead, and they are extensively distributed, being found from Guatemala to Alberta, Canada, and from the Rocky Mountains to the Appalachians. They are caught in commercially-important quantities in the Great Lakes, smaller lakes, and rivers.

OIL CONTENT: The greatest variation in the composition of sheepshead appeared to be in the oil content. The oil analyses reported in table 1 show that a wide range usually occurred even among the fish found in a single lot caught at the same time in the same location; if all lots are considered, the oil content varied somewhat more widely, the content ranging from 0.72 percent to 20.36 percent. Even the averages for the various batches ranged from 1.04 percent to 11.53 percent.

If only 16 sheepshead (a much larger sample than that for most values reported in the literature) from Clearwater Lake, Minn., had been used as representative of all sheepshead, the oil content would have been reported as ranging from 0.72 to 1.67 percent and as averaging 1.04 percent. Sheepshead would then have been considered a non-oily fish. If only sheepshead had been used from another small lake, Lake Kegonsa in Wisconsin, the oil would have been reported as ranging from 2.00 to 8.84 percent and as averaging 4.89 percent. Sheepshead would then have been considered as intermediate in oil content. However, if 16 samples of sheepshead from the Mississippi River had been taken in June 1954, values from 3.57 to 14.20 percent and averaging 8.78 percent would have been found. Then sheepshead would have been classified as an oily fish. This is an example of the danger of analyzing one fish, or even one large lot of fish from the same source, and reporting that the values obtained are representative for that species.

In considering location, it is interesting to note that the sheepshead caught in the Mississippi River apparently contain the most oil and that those from the small lakes apparently contain less oil than do those from either Lake Erie or the Mississippi River.

The effect of season on the oil content is not as clearcut as is the effect of location. Although apparently some variation occurs due to season, more samples taken during different times of the year must be analyzed before a definite statement can be made. It is also interesting to note that comparatively little variation occurs among the samples obtained in successive years from the same site on the Mississippi River.

PROTEIN, ASH, AND MOISTURE CONTENT: As already indicated, the range in oil content was by far the greatest variation found in any of the constituents for which an analysis was made in the sheepshead. In this same group of samples, the protein content ranged from 14.5 to 19.9 percent, and the ash content ranged from 0.87 to 1.29 percent. Since the moisture content is related to oil content, a greater variation occurred. The range was from 66.8 to 84.8 percent. The variations and the wide range occurring in sheepshead serve to emphasize the importance of not considering the composition of a species of fish to be established by the analyses of a few fish caught at the same time.

MISCELLANEOUS FRESH-WATER FISH

In addition to the more thorough study that is being conducted on sheepshead, 16 other species have been analyzed for their proximate composition. The analysis of one species of fish gave spectacular results. Siscowets lake trout (Cristivomer

namaycush siscowet) had an exceedingly high-oil, low-protein, and low-moisture content. The range of oil content of 15 fish was from 6.7 percent to 64.2 percent. The protein ranged from 5.9 to 17.8 percent, and the moisture content ranged from 27.8 percent to 74.8 percent. All of these fish were caught in Lake Superior in September, and therefore the variation is due, not to seasonal or geographical factors, but to individual differences.

There is much interest in increasing the utilization of lake herring. We have analyzed one lot of this species and have more from various areas to analyze. One observation that may be made is that, although the name "herring" referring to salt-water fish makes one think of an oily fish, lake herring apparently have a low oil content. In the lot analyzed, the oil ranged from only 0.86 percent to 2.87 percent.

Many species of fresh-water fish, both commercially-important and "trash" or noncommercial fish, are yet to be analyzed, and additional batches of the species that have been tested must be analyzed before values for composition can be established.

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LAKE HERRING SAMPLES COLLECTED FOR COLD-STORAGE STUDIES

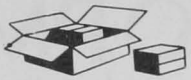
The program in collaboration with The Refrigeration Research Foundation at the Service's Seattle Fishery Technological Laboratory includes work on the cold-storage life of fresh-water fish. One important fresh-water species with which some difficulty in holding in the frozen state has occurred is lake herring. During November 1955, the Seattle Laboratory procured and put up samples of this species from three runs in the Great Lakes. These fish are caught in large quantities during a brief period in late November and early December. Two important runs of fish occur in Lake Superior and one in Lake Huron. In Lake Superior, one occurs adjacent to Duluth, the other along the north shore of the lake. The fish taken in the three runs are somewhat different and may have differing storage life. Samples of all three runs were taken, processed, frozen in different ways, and transferred to Seattle where storage tests will be run at suitable intervals.

WEIGHT LOSS FOR FISH STICKS STORED AT 0° TO 5° F.

The changes in weight which occurred in 7 different commercial packs of fish sticks, under several different storage conditions, were observed and recorded over a period of 8 months. One storage series consisted of 3 weighed packages of each of 7 commercial brands stored under theoretically optimum conditions. The packages were sealed in master cartons, and placed inside a large wooden box in a still-air cold-storage (0° to 5° F.) room.

In the course of the study, all packs stored under these conditions, with one exception, lost approximately 1.2 percent of their respective initial weights. These

packs were packaged in a waxed chipboard container with a glassine laminate and overwrapped with a microcrystalline wax paper. The exception, which lost approximately 4.1 percent of its initial weight, differed only in that the waxed chipboard container did not have a glassine laminate. It would seem that the laminate, in addition to preventing staining of the chipboard container by the oil in the fish sticks, may also afford some protection from dehydration during storage.



CRAB MEAT FEDERAL SPECIFICATIONS

Federal specification PP-C-651 (Crab Meat: Canned) was revised in view of comments from industry and interested Federal agencies. The revised draft was submitted to General Services Administration for issue as an "Interim specification." The specification was developed by the U. S. Fish and Wildlife Service and the Quartermaster Corps Food and Container Institute for the Armed Forces, based upon currently available technical information. It will be recommended that Federal agencies use it in procurement and recommend changes if necessary. The Interim specification is subject to modification.

Interim specification PP-C-00656a (Crab Meat, Cooked: Chilled and Frozen) was revised in view of industry and Federal agency comments, and submitted to General Services Administration for promulgation into a Federal Specification.

PREPARATION OF MULLET ROE

Dried mullet roe is prepared to a limited extent along the southeastern coast of the United States, from North Carolina to Florida. The unbroken roe bags are placed in tubs where they are either sprinkled with salt or soaked in strong brine. About 5 quarts of salt are added to each 100 pounds of roe. Too much salt will cause the egg sacks to break. After the roes have remained in the brine for 10 to 12 hours, they are drained and spread on boards in the sun to dry. They are taken in each night to prevent their becoming wet by dew. During fair weather the drying process requires about a week. The finished product varies in color from a yellowish brown to a dark-red.

When the drying process is completed, the roe may be dipped in a mixture of melted beeswax and paraffin and held for a considerable period of time at room temperature. It can be kept for much longer periods under refrigeration at 40° to 50° F. The mixture of 50-percent wax and 50-percent paraffin prevents further loss of moisture in the preserved roe. In some cases this product has been smoked with a cool smoke immediately after brining. Only a very light smoke is used for approximately 30 minutes at just sufficient heat to burn the sawdust. This adds to the keeping quality and flavor of the final product.

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