Oxidative Deterioration in Fish and Fishery Products

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A RESEARCH PROGRAM on oxidation of fish and fish products is being supported by Saltonstall-Kennedy funds at the Davis and Berkeley Campuses of the University of California. The following is a report of work now being done by W. D. Brown, E. Einset, W. Venolia, A. L. Tappel, and H. S. Olcott.

Fish oils are particularly susceptible to oxidative deterioration due at least in part to the high degree of unsaturation of the fatty acids. In frozen fish products, oxidation leads to deterioration in flavor and color; in fish meals the oxidation of oils may be responsible for changes in nutritional value; in fish oils, the oxidation leads to rancidity with subsequent loss of value. In order to develop methods for controlling these unwanted reactions, it is necessary to understand the various factors involved.

Hematin compounds, such as the pigments of blood or muscle, accelerate the oxidation of systems containing unsaturated fatty acids. Studies on the amount of hematin compounds in fish and their effect in accelerating the rate of oxidation of emulsions containing fish oils suggest that they are important catalysts for oxidation of fish lipids. They are in fact probably the most important pro-catalysts in fish, since no evidence has been found that fat oxidation-promoting enzymes, such as lipoxidases, occur.

Tocopherols (vitamin E) inhibit the auto-oxidation of fish oils and also the hematin-catalyzed oxidation. No detailed study has been reported on the occurrence of these substances in fish or in fish oils. Such determinations are now being made. The data indicate that fish oils contain variable amounts of tocopherols and that the tocopherols contribute to the stability of the oils as measured by the length of the induction period (length of time until the fat begins to oxidize rapidly). In general, of two oils of similar iodine number, the one with the higher tocopherol content appears to be the more stable. On the other hand, the few exceptions which have been observed suggest that other anti- or pro-oxygenic factors may be present in some fish oils. The sable fish yielded the most stable fish oil encountered as yet—one which had both a low iodine number, 100, and a high tocopherol content (625 mg/100 gm). Experiments to determine the relative antioxidant effectiveness of the seven different naturally occurring tocopherols, and their occurrence in marine products are in progress.

Studies of the interaction of mixtures of different type antioxidants have revealed that under some circumstances synergism is very marked. Hematin-catalyzed unsaturated fatty acid oxidation, for example, is slowed down by tocopherol and ascorbic acid separately, but practically stopped by mixtures. Not sufficient is known about the numerous possible combinations to predict the most effective mixtures for the different products.

Of a number of commercial antioxidants assayed both in oils and in meals, 6-ethoxy,-2,2,4 trimethyl, 1,2-dihydroquinoline (Santoquin) was the most effective. In fish oil, for example, Santoquin appeared to be 5 to 10 times more effective than BHA (butylated hydroxyanisole) or BHT (butylated hydroxy-toluene), under the conditions used for the assay (50°C). The use of Santoquin has not yet been sanctioned as an additive for feeds or foods.

"Green" tuna, a color problem which occasionally is a serious cause for rejection, appears to be an oxidative phenomenon. With the use of spectrophomometric methods it has been shown that the pink color of cooked tuna flesh is due to the presence of *hemochromes* derived from myoglobin or hemoglobin in the raw tissue. The hemochromes are probably denatured globin hemochromes in which nicotinamide may play an important role. Oxidation leads to the formation of *hemichromes* which are tan. These can be reduced by simple reducing agents to the hemochromes. The "green" of off-color tuna is at least in part *hemichrome* since "green" tuna samples can be reduced to pink under appropriate conditions.

Royal Red Shrimp—A New South Atlantic Resource

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FOLLOWING THE 1955 FALL meeting of the Fishery Advisory Committee favorable consideration was given to an industry-sponsored request for shrimp exploration off the south Atlantic coast. A sum of $60,000 was allocated from Saltonstall-Kennedy funds to be used for chartering a vessel suitable for exploratory work, hiring a crew, and providing the necessary gear and operating funds. This sum was sufficient to carry out a short range program, lasting through June, 1956. The programming was carried out under the supervision of the Service's Gulf Exploratory Fishing office.

While steps were being taken to obtain and rig a vessel, a comprehensive review of previous offshore investigations in the area under consideration was undertaken, both by reviewing the meager literature, the rather extensive unpublished station records from previous Service work in this region, and State reports on localized projects, and by personally interviewing large numbers of fishermen and fleet owners that fish the south Atlantic coast the year around.

It was found that previous work had extensively covered the continental shelf out to 100 fathoms without extending the known shrimping areas or, with the exception of finding scattered, small rock shrimp (*Sicyonia brevirostris*) beds, had not succeeded in locating new species for possible commercial exploitation. Other points of interest were that commercially valuable stocks of fish were disappointingly small or absent and that practically all previous exploratory work had been accomplished in the winter and spring, with little summer or fall coverage.

On the encouraging side, examination of the depth-temperature data collected in recent years by the Service's M/V *T. N. Gill* between Cape Canaveral and Cape Hatteras revealed several areas having depth-temperature patterns very similar to those in the Gulf of Mexico red shrimp grounds. A few bottom samples from these depths were similar to the red shrimp bottom off Dry Tortugas. Further, it was found that scattered individual specimens of red shrimp (*Hymenopenaeus robustus*) had been collected many years ago along the east coast as far north as Georges Bank, which suggested that this species might be found in greater concentrations. Therefore, with only four months time to carry out the program, deep water exploratory coverage was given primary emphasis. To