OXIDATIVE DETERIORATION IN FISH AND FISHERY PRODUCTS

Part III - Progress on Investigations Concerning Reactions Resulting in Brown Discoloration

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ABSTRACT

STUDIES ARE IN PROGRESS ON THE UNDESIRABLE COLOR CHANGES, SOMETIMES FOUND IN FISH PRODUCTS, THAT ARE ASSOCIATED WITH OXIDATIVE DETERIORATION OF THE MEAT AND OIL OF THE FISH. WORK TO DATE INDICATES THAT AT LEAST THREE DIFFERENT REACTIONS CAN CAUSE SUCH PIGMENT CHANGES. METHODS OF CONTROLLING THE REACTIONS ARE NOW UNDER INVESTIGATION. A HYPOTHESIS AS TO THE MECHANISMS AND THE ROLE OF THESE DIFFERENT REACTIONS IN PRODUCING BROWN DISCOLORATION PRODUCTS IS PRESENTED.

BACKGROUND

Development of a brown color during processing or storage of fishery products is quite common. Several species of fish with white meat, upon being canned, turn to various shades of yellow to brown. Dehydrated fish, which immediately after manufacture may be of a white hue, slowly darken and eventually become a deep brown during storage. Fish meals often slowly change from an initial light brown color to a deeper brown color. Frozen whole fish frequently exhibit, at their surface, a brown discoloration in the oil that has seeped through the skin; this discoloration is known as rust.

Some of these changes in fish are ascribed to the well-known Maillard reaction in which the amino acids combine with free aldehyde groups of sugars or carbohydrate (Tarr 1950). Such reactions are common in vegetables that contain considerable quantity of carbohydrate. Fish, however, contain at most, only a few tenths of a percent of such carbohydrate, and it seems somewhat strange that these substances, which occur in trace amounts, could cause such extensive reactions as to decolorize the product completely.

Fig. 1 - Measurement of color developed during browning reaction employing a differential type color instrument.

Rusting of frozen fish generally has been ascribed to an oxidation of oil, although Brocklesby (1929) obtained evidence that nitrogenous compounds such as ammonia were somehow involved in the reaction.

Work is currently under way to investigate the mechanism of production of brown colors in fish (1) by a reaction between oxidized fish oils and proteins, (2) by oxidation or polymerization of fish oils, and (3) by a combination of these general types of reactions. The carbonyl groups in oxidized fish oil present the same opportunity for reaction with amino acids as might occur with carbohydrate, and since oils occur to a much greater extent in fish than do carbohydrates, this possibility should not be overlooked.

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EXPERIMENTAL

PROBABLE TYPES OF REACTIONS INVOLVED: In initial experiments, an attempt was made to determine, by use of model systems, whether the reaction resulting in the development of the brown color was one of oxidation or one between fish oil and protein. In these initial experiments, it was shown that emulsions of menhaden oil and protein invariably reacted to form a deep brown color so that the presence of carbohydrate definitely was not necessary. The rate of browning of emulsions prepared from menhaden oil and egg albumen, buffered at pH 7, was determined at 21.1°, 44.7°, and 55.0° C. The color of emulsions stored in Petri dishes was measured with a differential-type color instrument (fig. 1). From these data, the activation energy for the reaction between egg albumen and menhaden oil was calculated to be 19 kilogram calories per mole. This value, which lies between the values of 16 kilogram calories per mole for unsaturated fat oxidation and 30 kilogram calories per mole for carbonyl-amine browning would indicate that we are dealing with a combination of these two types of reactions.

METHOD OF MEASURING THE DEGREE OF BROWNING: In subsequent experimental work, precise measurement of the effect of a number of factors upon the degree of browning was made with the differential color instrument. Emulsions of fish oil and protein were allowed to react in Petri dishes, and the degree of browning was obtained objectively by making reflectance measurements through the bottom of the dish. The results were expressed in terms of ΔE, the deviation of a sample, in Bureau of Standards units, from its original color. To make data comparable regardless of the initial color of any individual sample, we calculated the deviation ratio, $R = \Delta E / \Delta E_{max}$, where ΔE_{max} is the distance, in Bureau of Standards units, between the initial color of a sample and pure black.

Color changes of samples were compared to those of controls by subtracting from the deviation ratio, R, of the specific sample that of the control, R_c. The value $(R - R_c)$ is a measure of the change in the color behavior of an emulsion resulting from a known difference between it and the control.

PROTEIN-OIL REACTION AND OIL-OXIDATION REACTION: Experiments were set up to investigate the effect of conditions that might favor or retard the protein-oil reaction or the oil-oxidation reaction. Thus acetylation of the protein would retard or stop the protein-oil reaction, whereas incorporation of antioxidants would retard the oil-oxidation reaction. Comparing plots of $(R - R_c)$ values against time, we found that both antioxidants (NDGA[1], BHT[2], Santoquin) and prooxidants (cupric ion, hemoglobin, oxygen) diminished the rate of browning. Increased rate of browning occurred only when the active carbonyl amine (Maillard) reaction was blocked by acetylation of the egg albumen to make the protein amine groups inaccessible or when active carbonyl groups were made unavailable by treatment with sulfite ion.

TENTATIVE HYPOTHESIS: Although this work is still in progress, a tentative hypothesis has been drawn up to account for these observations. Three different reactions--called (1), (2), and (3)--are postulated as competing to some extent for the available reactants:

(1) Active carbonyl amine browning, yielding a more lightly-colored product than that from (2).

(2) Unsaturated lipid oxypolymerization.

(3) Rapid unsaturated lipid oxidation, also yielding a more lightly colored product than that from (2).

Treatment of emulsions to block active carbonyl amine browning favors reaction (2) with resulting augmented development of color. On the other hand, antioxi-

1/ Nordihydroguaiaretic acid.
2/ Butylated hydroxyanisole.

dants block (2) and (3), whereas prooxidants divert reactants from (1) and (2); and thus both types of treatment diminish the rate of color development. It is to be noted, however, that the decrease in the rate of browning is more pronounced when caused by the antioxidants BHT and Santoquin, than when caused by the pro-oxidants.

SUMMARY

1. The browning reaction, which results in formation of rust in frozen fish and darkening during canning of certain species of fish as well as development of brown colors in fish meal and other fishery products, is being studied.

2. It has been shown that a number of different reactions are concerned in the development of these brown colors.

3. These reactions include (1) those between oil and protein at the carbonyl and amino groups, (2) oxypolymerization, and (3) oxidation of unsaturated oils.

4. Factors important in controlling these various reactions are being investigated.

5. A hypothesis concerning the role of these different reactions in the development of brown discoloration products has been formulated.

LITERATURE CITED

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FOOD PROTEIN INCREASED WITH FISH FLOUR

Adding a small amount of defatted fish flour to millet and grain sorghum results in as much as sixfold increase in the body weight of rats fed on this kind of diet, Dr. Barnett Sure, University of Arkansas, Fayetteville, reported to the American Institute of Nutrition Meeting in Chicago.

The defatted fish flour is a mixture of carp, smelts, and whiting and increases the protein efficiency of the foods as well as the body weight, he reported.

When 5-percent defatted fish flour was added to the proteins of grain sorghum, the animal's body weights increased by 644 percent and the protein efficiency ratio, which is the gain in weight per gram of protein intake, increased by 213.2 percent.

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