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CHEMICAL AND ENZYMATIC HYDROLYSIS OF FISH SCALES

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INTRODUCTION

Fish scales, a byproduct of the fish-processing industry, normally are wasted. Their only commercial use at this time is in the preparation of pearl essence from scales of some species such as herring. The scales, which are removed mechanically from the fish, are washed away by jets of water, and eventually find their way to the harbor, where unless tidal flows are strong they settle to the bottom and become a potential nuisance.

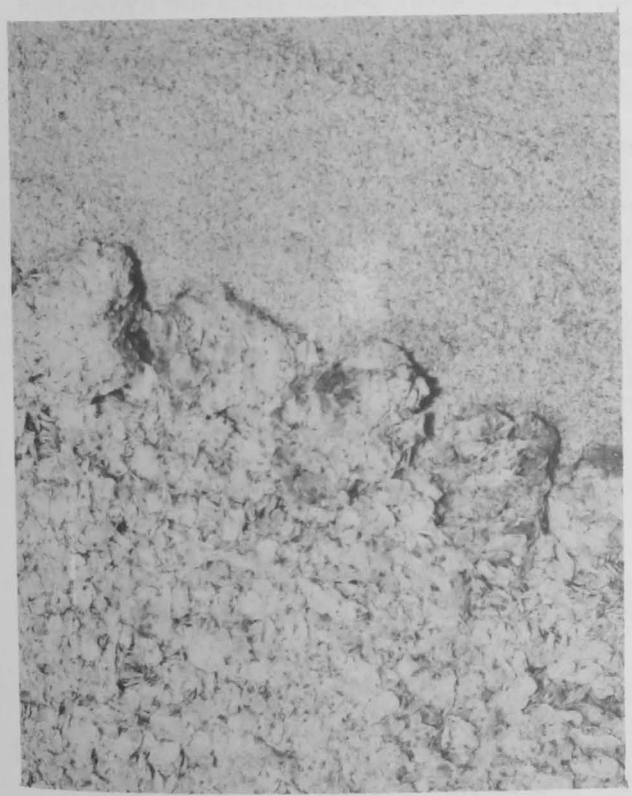

FIG. 1 - GROUND AND WHOLE POLLOCK FISH SCALES.

Attempts to process the scales in fish-meal driers have been only partially successful. The scales mass in large balls which are difficult to dry, stick to the equipment, and clog the driers; and some scales are drawn up the exhaust stack. Attempts have been made to find other uses for the scales but apparently without success.

This general project is designed to attack the problem of scale disposal by determining if the scales may have value as a source of protein in the diets of farm animals.

There is some reluctance on the part of the fish-meal manufacturers to handle the abrasive raw scales, owing to their poor grinding properties. A more suitable form for commercial handling therefore is to be desired. For this reason, the study reported here concerns an investigation of the optimum conditions of hydrolyzing the scales of ocean perch (Sebastes marinus) for use in animal feeding. Hydrolysis also may alter the nitrogen compounds in the scales physically into a more palatable form and perhaps chemically into a more available form.

* THE RESEARCH REPORTED IN THIS PAPER WAS CONDUCTED BY THE UNIVERSITY OF MASSACHUSETTS UNDER A CONTRACT WITH THE U. S. FISH AND WILDLIFE SERVICE. IT WAS FINANCED BY FUNDS MADE AVAILABLE UNDER PROVISIONS OF PUBLIC LAW 466, 83RD CONGRESS, APPROVED JULY 1, 1954, GENERALLY TERMED THE SALTONSTALL-KENNEDY ACT. THE RESEARCH WAS UNDER THE GENERAL SUPERVISION OF THE STAFF OF THE FISHERY TECHNOLOGICAL LABORATORY, EAST BOSTON, MASS. THEY ALSO AIDED THE CONTRACTOR IN OBTAINING SUPPLIES OF FISH SCALES AS NEEDED THROUGHOUT THE STUDY. THIS ARTICLE WAS PREPARED BY DONALD G. SNYDER, BIOCHEMIST, FISHERY TECHNOLOGICAL LABORATORY, COLLEGE PARK, MD., FROM PROJECT REPORTS SUBMITTED BY THE CONTRACTOR TO THE U. S. FISH AND WILDLIFE SERVICE.

EXPERIMENTAL AND RESULTS

Seven 5-gram samples of dried scales from ocean perch were hydrolyzed by refluxing them for 10 hours in 250 milliliters of the following solutions: (a) water, (b) 10- and 5-percent sodium hydroxide, (c) 33- and 5-percent sulfuric acid, (d) sodium hydroxide solution at pH 9.7, and (e) sulfuric acid solution at pH 3.8. The extent of hydrolysis, as measured by percentage reduction in amount of insoluble solids, was 52.4, 57.8, 50.8, 52.4, 57.2, 47.6, and 48.4 percent, respectively.

Since these acid-base hydrolysates resulted in yields of only about 50 percent, an investigation into the value of enzymatically hydrolyzing the scales was suggested. Five grams of scales was added to 250 milliliters of a 0.20-percent solution of pepsin adjusted to pH 1.7 with hydrochloric acid. The mixture was placed in an incubator for approximately 20 hours at 37° C. This treatment resulted in 98.5-percent hydrolysis.

Since this treatment produced nearly completed hydrolysis, it was desirable to investigate what ratio of scales to pepsin was best for optimum hydrolysis with minimum amount of liquid. Five grams of scales was added to 250 milliliters of a 0.1-percent solution of pepsin in 0.1 N hydrochloric acid; 100 milliliters of a 0.2-percent solution of pepsin in 0.1 N hydrochloric acid; and 50 milliliters of a 0.2-percent solution of pepsin in 0.1 N hydrochloric acid. Each mixture was placed in an incubator for approximately 20 hours at 37° C., after which time the hydrolysis was 96.6, 97.6, and 80.0 percent complete, respectively. From these data, it was evident that the best solution to use would be 100 milliliters of a 0.2-percent pepsin solution in 0.1 N hydrochloric acid containing 5 grams of scales.

Initially, some concern was shown because of the large amount of sodium hydroxide needed to neutralize the hydrochloric acid. This requirement would result in a dried hydrolysate containing relatively large concentrations of sodium chloride, which might possibly affect the palatability of the scale hydrolysate and, thereby, the nutritive value.

Three hydrolysates were prepared in order to determine the final salt content: the first was unadjusted; the second, partially neutralized to pH 4.5; and the third; neutralized to pH 7.0. The percentages of sodium chloride (calculated from sodium content), of crude protein, and of ash were 2.89, 38.6 and 39.7; 4.14, 35.6 and 44.6; and 5.42, 33.3 and 59.4, respectively. It was thought that the most satisfactory hydrolysate might be the one neutralized to pH 4.5 since it was lower in acidity than the unadjusted hydrolysate and lower in salt content than the fully neutralized material. Subsequent investigation showed, however, that this hydrolysate was the least desirable, owing (1) to its highly hygroscopic nature, which made drying difficult, and (2) to the odors formed during further processing. As a result, the completely neutralized hydrolysate was deemed most desirable. This hydrolysate was not hygroscopic and was easily ground.

Since a less expensive economic proteolytic reagent than reagent-grade pepsin was desirable, the effectiveness of Proteose 15[1/] for hydrolyzing fish scales was investigated. Proteose 15 is a purified form of Rohm and Haas Rhozyme B-6, which currently is used to facilitate the concentration of fish solubles. The optimum pH for Proteose 15 is reported as being 7. Digestion at this pH would eliminate the need for acidification and neutralization with resultant formation of salt.

Five-gram samples of scales were hydrolyzed in 100-milliliter solutions of various concentrations ranging from 0.2 to 1.0 percent of Proteose 15 adjusted from pH 2.1 to 7.0. These mixtures were placed in an oven at 60° C. (the reported optimum temperature for proteose 15 hydrolysis) overnight, and one mixture, which served as a control, was incubated at 37° C. overnight. Visual examination of these mixtures showed that the hydrolysis was quite incomplete.

1/ MANUFACTURED FOR ROHM AND HAAS CO., PHILADELPHIA, PA.

The results indicated that the best solution would be 100 milliliters of a 0.2-percent pepsin solution containing 5 grams of scales. Use of this solution resulted in 98-percent hydrolysis. At completion of hydrolysis, the solution was filtered, and the filtrate neutralized with sodium hydroxide. The water then was evaporated, the hydrolysate was dried, and not being hygroscopic, was ground easily. The resulting material was a fine, soft, white powder, for which the percentage analyses were as follows: moisture 1.8; crude protein, 34.0; calcium, 10.5; phosphorous, 5.5; sodium, 1.2; sodium chloride, 3.1; potassium, 0.2; and ash, 60.1. In addition, the scales contained 0.177 milligrams of riboflavin and 0.2 micrograms of cyanocobalamin per 100 grams of hydrolysate.

SUMMARY AND CONCLUSION

The yield from the hydrolysis of scales from ocean perch was only about 50 percent when the scales were hydrolyzed in water and in different concentrations of sodium hydroxide and sulfuric acid. The scales were 98.6 percent hydrolyzed, however, when 5 grams of scales was added to 250 milliliters of a 0.2-percent solution of pepsin adjusted to pH 1.7 with hydrochloric acid and incubated for 20 hours at 37° C. This extent of hydrolysis was not affected when the volume was reduced to 100 milliliters of the 0.2-percent solution of pepsin.

A need for complete neutralization of the hydrolysates was indicated when they tended to resist dehydration and produced repulsive odors. The completely neutralized hydrolysate was not hygroscopic and was easily pulverized. Hydrolysis of the scales under different conditions with Proteose 15 was found to be very incomplete.

This study indicates that the best method of preparing scale hydrolysates in small amounts is to place 5 grams of scales in 100 milliliters of a 0.2-percent pepsin solution adjusted to pH 1.7, and to incubate for 20 hours at 37° C. This method results in about 98-percent hydrolysis. After hydrolysis, the solution is filtered, and the filtrate is neutralized with sodium hydroxide. The water then is boiled off, and the hydrolysate is dried and pulverized. The resulting material is a fine, soft, white powder. Sufficient quantities of fish-scale hydrolysates will be prepared in this manner for use in future animal-feeding tests. In these tests the biological value of the hydrolyzed scales will be compared with that of the raw scales.

PACKAGED FROZEN OYSTERS

Research has shown that frozen oysters packaged unglazed but overwrapped have a storage life of about 6 months. Frozen oysters glazed with water and with weak brine were still acceptable after 8 months. The best frozen stored oysters were those which had been packed in a tin under an 18-inch vacuum.

--Southern Fisherman, April 1956.