OXIDATIVE DETERIORATION IN FISH AND FISHERY PRODUCTS

Part IV - Progress on Studies Concerning Oxidation of Extracted Oils

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ABSTRACT

Studies are being made to determine the mechanism of oxidative deterioration prevailing in extracted fish oils. Initial studies were made to determine the tocopherol (a naturally-occurring antioxidant) content in oils extracted from 10 different species of fish. The stability of the tested oils was greater in oils containing a higher tocopherol content and lower in oils containing higher iodine numbers.

INTRODUCTION

In previous papers in this series, results obtained when oil, located in fish tissue or fish meal, oxidizes have been described. When oil is extracted from fish tissue (either commercially or under laboratory conditions), however, the resulting oil may behave quite differently from the way that it does while it is still in the tissue. The extracted oil is no longer in contact with such tissue constituents as protein and hematin compounds, which can play a profound role in modifying the oxidation process. In addition, the heating of the oil during processing may destroy other antioxidants or pro-oxidants that might have altered the oxidation pattern if the oil had remained in the tissue. A program therefore has been started to investigate the oxidation of extracted fish oils, and some preliminary results are described in this report.

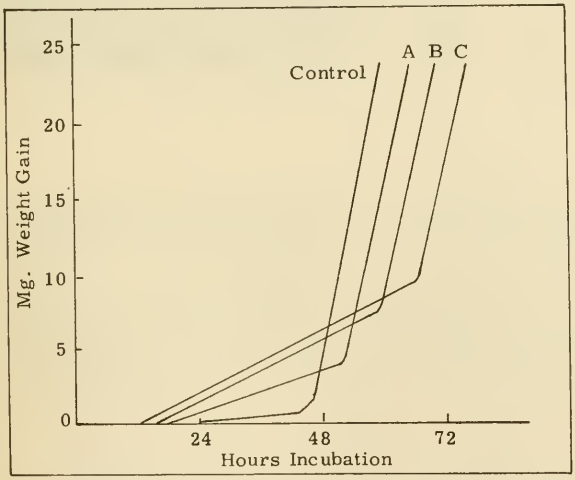

Fig. 1 - Effect of different levels of alpha-tocopherol on the induction period of pink salmon oil. (Incubation in 50 ml. beakers.)
A = 0.1 percent
B = 0.3 percent } alpha-tocopherol
C = 0.5 percent

This phase of the program is being undertaken primarily to obtain a better understanding of the oxidation of commercially-produced fish oils. Some work, however, is included on noncommercial oils extracted in the laboratory from species of fish not generally used for commercial fish-oil production. Information on the chemical behavior of such extracted oils, when combined with that on the behavior of these oils when still in the fish tissue, will give us a better insight into the role of the biocatalysts present in the tissues on the course of oxidation of all fish oils.

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Work undertaken so far on extracted oils has dealt with the following: (1) a survey of some fish oils in which their stability was compared with their iodine numbers and their contents of naturally occurring tocopherols and (2) the further elucidation of details on the role of naturally-occurring tocopherols in retarding oxidation of fish.

OXIDATION RATE OF EXTRACTED FISH OILS

The rate of oxidation of commercially-prepared tuna, menhaden, sardine, pink salmon, and herring oils was compared in a Warburg apparatus at 37° C. After 1 hour, the tuna oil had adsorbed 94 microliters of oxygen per gram as compared to 67 microliters for menhaden oil and 46 and 27 for two different batches of sardine (pilchard) oil. Neither pink salmon nor herring oils absorbed any oxygen under these conditions.

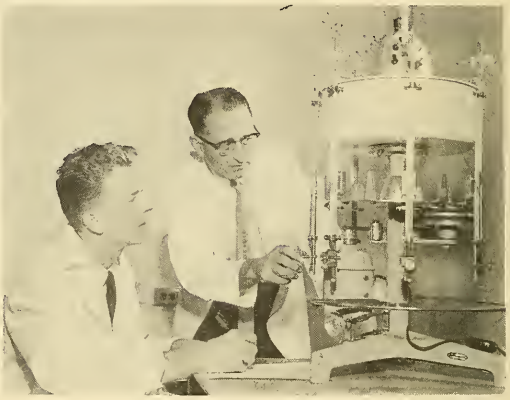

Fig. 2 - Operation of Warburg equipment for measurement of oxygen uptake by fish oils.

A number of fish samples were treated to extract the oil on a laboratory scale by (1) blending in a Waring Blendor with water and ethyl ether, (2) separating out the ether phase in a centrifuge, and (3) evaporating the ether phase under an atmosphere of nitrogen. The resulting oil was stored under nitrogen in a refrigerator until needed. The oils were analyzed in the form as prepared and also after extended oxidation, which was carried out by storage of 10 grams of oil in a 9-centimeter petri dish at 91° F. for 70 hours. Oxidation rate in a Warburg apparatus at 37° C. and total tocopherol content were determined, with the results given in table 1. There was (1) a general increase in oxidation rate after prolonged oxidation (the sheepshead oil was an exception) and (2) a decrease in tocopherol content.

Table 1 - Properties of Extracted Oils

Oil	Rate of Oxidation		Total Tocopherol Content	
	Oil		Oil	
	Original	Oxidized	Original	Oxidized
	μ l. Oxygen Per Hr. Per Gram		μ g. Per Gram of Oil	
Sheepshead	279	194	27	3
Mountain trout	14	36	46	35
Pink salmon	7	40	101	0
Lake chub	4	39	297	58
Commercial tuna 1/	113	188	112	43

1/ Species unknown, probably mixed skipjack and yellowfin.

Table 2 - Comparison of Stability of Fish Oils with Iodine Number and Tocopherol Content

Oil	Induction Period at 50° C.	Iodine No.	Tocopherol Content
	Hours		Mg./Kg.
Sardine	6	199	40
Menhaden	9	167	66
Tuna	36	185	159
Herring	45	142	142
Pink salmon	48	164	217
Whale	93	161	198
Sablefish	136	99	628

TOCOPHEROLS AND FISH-OIL STABILITY

Preliminary experiments indicated an inverse correlation between the rate of autoxidation of various fish oils and their content of tocopherols (table 2). It was

Table 3 - Protection Afforded Pink Salmon Oil by Various Antioxidants

Antioxidant		Time Needed for Oil to Gain 1 Percent in Weight
Kind	Amount	
	Percent	Day
None (control)	-	1.5
2,2'-methylenebis (4-methyl-6-tertiary-butylphenol	-	
	0.5	1/ 95
5-ethoxy, 2-2-4-trmethyl-dihydroquinoline	0.1	8
	0.5	87

1/ This 1-gram sample had gained a total of 5.0 mg. in weight and was still fresh when the test was discontinued.

observed that treatments tending to destroy the tocopherols also accelerated autoxidation, which is in accord with the theory that tocopherols play an important role in the relative stability of the fish oils. Successively larger additions of tocopherols to fish oils, however, increased the rates of the initial oxygen absorption. It has been reported previously that, at certain higher concentrations, tocopherols may become pro-oxidants. We do not know what this concentration is for the various fish oils, but increasing concentrations of alpha-tocopherol, gamma-tocopherol, and mixtures of the two did not give proportionate decreases in the autoxidation of several of the fish-oil samples tested. This aspect is being studied further.

To investigate the effect of alpha-tocopherol upon "stable" fish oils, that is, those still in their induction periods, some method was desired that would obviate certain difficulties associated with long-term Warburg experiments. The method used consisted of recording the increase in weight, due to oxygen absorption, of a fish oil during a period of exposure to air in a forced-draft oven at 50° C. In these experiments, 1-gram samples of oil plus the appropriate level of antioxidant were weighed into small beakers, and the beakers were placed in the oven. At intervals, the beakers with their contents were removed and then allowed to cool at room temperature for one-half hour before being weighed. Figure 1 illustrates what effect different levels of alpha-tocopherol have upon the induction period of pink salmon oil. Increases in the tocopherol level of the oil exert a definite although minor effect upon the stability of the oil.

COMMERCIAL ANTIOXIDANTS AND PINK SALMON-OIL STABILITY

Two synthetic antioxidants in relatively large amounts (5-ethoxy, 2-2-4-trimethyl-dihydroquinoline, and 2,2'-methylenebis (4-methyl-6-tertiary-butylphenol) gave excellent protection to pink salmon oil as measured by the weight-gain method (table 3). The former is not presently permitted by the U. S. Food and Drug Administration to be used in contact with foods.

SUMMARY

1. The tocopherol content of a group of fish oils varied from about 40 micrograms per gram of oil for sardine oil to 630 micrograms per gram of oil for sablefish oil.

2. The induction period of the oils tested was roughly proportional to the tocopherol content and roughly inversely proportional to the iodine number.