

# Flavors and Odors of Fish Oils

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## ABSTRACT

Off odors and flavors in fish oils arise from contamination from metabolites, from the spoilage of fish protein, or from oxidation products of the oil itself. The resulting odors and flavors can render the oil less desirable for many applications. Odors or flavors in the flesh of animals or poultry fed fish oil come more from the polyunsaturated nature of the fish oil than from the oxidation products or flavor and odor of the oil that is fed. Odors and flavors can be removed by refining methods or in some cases, masked by use of certain additives.

## INTRODUCTION

At an earlier era, the flavor of fish oil was a more important consideration than it is today. When fish liver oils were the chief source of vitamin A and an important one for vitamin D, it was necessary to provide these oils in a form in which the flavor was of a high enough standard to meet requirements for human consumption. Today, fish oils are used, especially in the United States, largely in a way in which flavor is of secondary importance. Because of this situation, much less research has been carried out on the flavor chemistry of fish oils than with most other oil products. While a few investigations have been made on oxidation products occurring in fish oils (13,14), in most cases either little or no attempt has been made to correlate their content with the odor and flavor, or, at most, only an approximation has been observed as to correlation of the overall odor or flavor of the oils with the occurrence of the mixed carbonyls or other oxidation products. We know that flavors of fish oils are of different types depending upon the nature of the deterioration, and a tremendous gap in our knowledge occurs when it comes to correlation of components of the oil with different types of flavors or odors.

The changes in odors and flavors of fish oils while the oil remains within the fish are important for our consideration here. These changes are preliminary steps leading to what may happen to reduce quality of the oil flavor after the oil has been extracted and also relate to the flavor of fish for human consumption where quite frequently, the principal cause of the flavor of the fish is determined by the flavor of the oil it contains. Thus much of the flavor and hence the quality of fresh, especially frozen, and sometimes other preserved fish is dependent upon factors governing the condition of the oil while it is in the fish flesh.

Another situation relates to the flavor problems when fish oil is fed to animals or poultry where what is of major importance is whether the flavor of the fish oil affects the flavor of the meat or of the eggs (8). Still another situation concerns primarily the odor rather than the flavor. When fish oils are used in many industrial applications, it is the "fishy" odor rather than any flavor problem which is of greatest concern.

## SOURCES OF ODORS AND FLAVORS IN FISH OILS

The oil contained in the different species of fish possesses a flavor which is usually quite characteristic of the particular species (11). This is true at least for those species containing appreciable oil content. Herring and herring-like

fishes, for example, have a type of flavor associated with these species which is entirely different from the flavor of salmon. In each of such instances, the primary flavor of the species is that either of the fish oil itself, or at least some component primarily contained within the oil. In our laboratory, we have noted that this flavor component is highly labile and rapidly destroyed when the oil is exposed to even very low levels of oxygen for a relatively short time, and even at very low temperatures. We have shown (7) that the naturally occurring flavor component characteristic of menhaden oil is similar to that of *cis*-3-hexen-1-ol which has a flavor similar to that of grass and is spoken of as a green flavor.

The presence of these highly labile, naturally occurring components characterize the oil only during early stages of storage. Soon the flavor of a fish oil, or of the fish containing it, is determined by deterioration odors or flavors which more or less completely obscure the naturally occurring flavors and odors which are then constantly diminishing in intensity. These deterioration odors can arise from bacterial spoilage of the fish. When the oil is extracted from the fish, a part of the odorific components will be partitioned into the oil phase. One can often recognize the odor or flavor of amines or sulfur containing compounds in extracted fish oil made from even only slightly spoiled fish.

After extraction, unless the oil is quite completely protected against oxidation, various carbonyl compounds will form to produce typical oxidative rancidity odors and flavors when oxidation has occurred to any considerable extent. These odors and flavors of fish oils are of the type also characteristic of many oxidized vegetable oils including especially those having odors and flavors of a bitter character with considerable acrid aftertaste.

At the very early stages of oxidation, the odor and flavor may be quite different, being reminiscent of that of a good grade of cod liver oil. These early oxidation types of flavor or odor are generally described as fishy. There is considerable doubt (10) as to whether this early oxidative "fishiness" comes from specific pure oxidation of the  $\omega$ -3 types of polyunsaturated fatty acids prevalent in fish oils or whether, as first proposed by Davies and Gill (3), this fishiness involves both oxidation and some participation of tertiary amines (probably trimethylamine).

## ODOR AND FLAVOR OF OIL OF FRESH AND FROZEN FISH

When stored, iced fish results primarily in bacterial spoilage deterioration. Changes in the oil proceed so much slower that the bacterial deterioration metabolites obscure the changes brought about by the very early alteration of the oil. In frozen fatty fish, where bacterial spoilage is arrested, the principal changes in flavor and odor result from alteration in lipid components. For example, during cold storage frozen silver salmon (*Oncorhynchus kisutch*) follows a pattern of flavor alterations in which, initially, changes are noted only in the dark flesh (where hematin compounds act as prooxidants to accelerate oxidation). The natural salmon flavors first fade away, then "fishy" flavors develop. This stage is followed by development of the typical rancidity which eventually becomes evident even in the light (pink) flesh of the frozen fish.

## EXTRACTED OILS

### Introduction

The types of flavors and odors which are produced in

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fish oils that have been extracted from fish are apt to be somewhat different from those which form while the oil still remains in the tissue. Not only are there no tissue constituents in the oil to contribute spoilage products to affect flavor, but also the mode of oxidation is apt to be quite different. Oil occurring in fish tissue oxidizes differently depending upon such factors as the way it is contained in the tissue and the presence or absence of prooxidants such as hematin compounds. Extracted oil not only does not have these variable conditions, but also may be stored in ways which greatly limit access to oxygen and hence result in reduced rancidity formation. On the other hand, once the oil is put to some end use, oxidation or other changes can take place in many ways depending on the particular end use.

Only a very small part of the fish oil production is used directly in human food and when this is done, a considerable problem occurs with flavors. The most frequent use of extracted fish oils on a worldwide basis is for hydrogenation for edible use. Although hydrogenated fish oils are practically flavorless when first produced, there are some flavor reversion problems. Much of the United States production of fish oils goes into nonfood, industrial applications which present no flavor problems at all, but which may give the end product an undesirable fishy odor. The problem of fish oils fed to animals or birds in which they impart a fishy flavor to the resulting meat or egg products is a quite different situation, which will be discussed at some length. Finally, in some situations, fish oil flavor problems can be overcome by suitable refining techniques or by masking the flavors by addition of other flavors.

#### Flavor Changes in Extracted Fish Oils

Very few studies have been made on flavor changes in stored, extracted fish oils. Stansby and Jellinek (12) showed that the characteristic flavor of fresh, highly refined (clay-bleached and molecularly distilled with discarding of the first 8% of distillate) menhaden oil is a "green," grass-like flavor similar to that of *cis* 3-hexen-1-ol. Upon standing exposed to air and light in a thin layer in a petri dish at 24 C, the flavor first intensified, reaching a maximum green flavor after two days. After three days storage, the green flavor had diminished and was largely replaced by a fishy type of flavor. After four days of storage, the intensity of fishiness had diminished considerably and a typical rancid flavor was beginning to develop. After five days of storage, the flavor was quite rancid with other types of flavor absent.

General experience with such extracted fish oils as herring, pilchard and salmon indicates that this same pattern of flavor change occurs during storage of oil if any air is present to produce oxidation. First, the natural flavor of the oil may intensify at very early storage periods, but it is highly unstable and soon rapidly diminishes. Usually by the time that the first traces of deterioration odors and flavors appear, most, often all, of the natural flavor is gone. The first type of new flavor to appear, usually only for a short transitory period, is the fishy type reminiscent of that of a good grade of cod liver oil. This flavor is soon obscured by a rancid type, similar but not identical to that of oxidized vegetable oils. The rancid flavor usually is faint at first and as oxidation continues, the flavor is persistent as evidenced by a prolonged aftertaste. Finally, after extensive oxidation, the initial flavor of the oil is a sharp, bitter one of a disagreeable nature, similar in most respects to that of other rancid oils.

When commercial fish oil is held after manufacture in large, well filled storage tanks—often of capacities of 50,000 to 750,000 gallons, the ratio of air to oil is so low that very little change occurs so long as the oil remains in the original storage tank. This does not, however, mean that

the oil is of good flavor. Most industrial fish oil, unless given very special refining treatment, will have considerable odor and flavor derived from spoilage products present in the fish when it was rendered. These odors and flavors will range from a vague indefinable type, which usually occurs even in oils given the customary refining steps (alkali refining, bleaching and steam deodorizing), to an extremely unpleasant spoilage odor and flavor, characteristic of unrefined fish oil made from spoiled fish.

#### Flavor Problems in Food Uses

About the only existing commercial use of fish oils in the United States directly for human food is the practice of preparing oil from salmon trimmings for adding back to canned salmon. This practice is carried out so that salmon caught near the end of the season when the natural oil content is very low can have the free oil content of the canned product increased to about the average level maintained throughout most of the season. Trimmings from only edible parts of the fish such as tail pieces, too small for canning, are used to prepare the oil which is produced by simple steam cooking of the fish with water which releases the oil so that it can be recovered by centrifuging. The finished oil is placed in 5 gal metal cans which are completely filled with hot oil and the lids attached immediately which keeps out air. The cans are stored at refrigerated temperatures until needed. Unless absolutely fresh salmon trimmings are used, off flavors resulting from spoilage can result. Storage of partly filled cans quickly results in oxidation and rancid flavors. Any such off flavor development can ruin the salmon pack to which the oil is added. Storage of the oil for more than a few months even without access to air and even at low temperature can result in flavor reversion.

Fish oil has been used in clinical research on cholesterol depression action of polyunsaturates. Problems of oxidation with resulting rancidity are best overcome by storage of just enough oil for a single dose in tightly filled, sealed containers. Alternately, use of flavoring compounds such as oil of wintergreen (see subsequent section on masking of flavors) can effectively mask rancidity development at moderate levels of off flavor.

The much more frequent use of fish oils for edible purposes involves their incorporation in the hydrogenated form into margarine or shortening. Hydrogenated fish oils are never added to margarine in the United States because current standards of identity do not provide for the use of fish oils. Hydrogenated fish oils are seldom added to shortenings in this country because most fish oils are not produced here in plants having minimum food sanitation standards. The practice of using hydrogenated fish oil in both margarine and shortening, however, is widespread in Canada, Europe and elsewhere.

The process of hydrogenation removes most odors and flavors so that in addition to providing a hardened fat of proper texture for incorporation into margarine or shortening, the hydrogenation process is a very effective deodorization procedure. Although the flavor of the hardened fish oil is quite tasteless immediately after the hydrogenation process is complete, flavor reversion takes place so that soon thereafter some flavor is present. The reversion occurs within only a very few hours in the presence of light, somewhat slower in the dark. The flavor which develops is not at all the same as that of the oil before hydrogenation but rather is that of most other hydrogenated oils of a type described as a "cardboard" or "hardened" type of flavor. According to Hannewijk (6) this flavor is correlated with the content of certain "bound aldehydes" which rise to 200 to 300 ppm within two months after hydrogenation. Some of these bound aldehydes have very low threshold levels, e.g., 6 *trans* nonenal which can be detected at a level of 0.0003 ppm.

### Flavor Problems in Feed Uses

Fat deposits in all monogastric animals are affected to a large extent by the type of fat in the diet. When fish oil is one component of the diet, the type of polyunsaturates found in fish are assimilated and deposited in the adipose tissue of the animal or bird consuming the diet. It has long been observed that this situation may result in the flesh acquiring a fishy flavor. Chickens and especially turkeys are subject to this possibility even when the content of fish oil in the diet is quite low (1% or even less). The same situation has been noted many times in pork from pigs fed fish oil. It does not matter a great deal whether the fish oil fed was fresh, unoxidized oil or whether it was rancid and oxidized. As a matter of fact, badly oxidized, extremely rancid fish oil gives less of a problem than does fresh oil. The explanation is probably that in the badly oxidized fish oil, much of the most highly polyunsaturated fatty acids have been destroyed and that the monoenes and saturates which then predominate give very little problem. It is most likely that it is the stability, not the taste of the freshly laid down fish oil fatty acids in the tissue of the animal or bird, which is critical. The polyunsaturated fatty acids when first deposited in the tissue are doubtlessly tasteless or nearly so. They are, however, highly labile so that merely a short handling period plus the cooking process are sufficient to cause sufficient oxidation to alter the flavor.

In cases where flesh from animals or birds fed fish oil result in a fishy flavor, the problem can be overcome by either keeping the fish oil at a sufficiently low level, or, in some cases, by removing fish oil from the diet a few weeks before slaughter. The safe level for fish oil in a diet varies with the species of animal or bird being fed as well as with the degree of unsaturation of the fish oil. Turkeys are perhaps the most sensitive to this effect and may develop fishiness when fish oil as low as 0.4% of the diet (9) is used. Chickens usually can utilize 1% to 2% fish oil without any fishy flavor problems. Anglemeir and Oldfield (1), who found that as little as 2.75% of pilchard oil in the diet of pigs resulted in fishy flavored pork, were able to overcome this problem by using polymerized pilchard oil but at the expense of a decreased growth rate.

### Odor Problems in Industrial Uses of Fish Oils

Whereas flavors are more important than odors for use of fish oils for edible or feed applications, the reverse is true for most other industrial applications. Using modern refining techniques, it is easy to produce a fish oil having little or no objectionable odor. During subsequent use of the fish oil, however, only a small exposure to air may result in sufficient oxidation to cause return of enough fishy odor to be of nuisance value. Where the end use of the fish oil requires extensive oxidation, the odor problem may become intolerable barring the use of fish oil unless modification of the oil can be effected so as to sufficiently reduce the odor problem.

With many products incorporating fish oil, a faint fishy odor may be perceived. At low levels, such odors may not be particularly objectionable. They may in fact be so associated with the product as to be an asset. Leather used for shoes is generally tanned by a process employing fish oil, and it leaves a very faint fishy odor in the leather. Buyers of shoes associate this odor with that of new shoes and do not recognize it as a fishy odor. When a modified, less fishy smelling fish oil was offered for sale to shoe leather tanners, they rejected it because buyers of new shoes made from leather processed in this way missed the familiar odor they associated with new shoes (11).

The use of fish oil in paint or varnish represents an extreme case where the end use of the product requires very extensive oxidation in order to achieve the desired effect. During formation of a paint film over a period of

several days, if unmodified fish oil is employed in the paint, no matter how carefully refined was the fish oil and how completely odorless it was initially, it will inevitably develop extensive, objectionable fishy or rancid odors during the drying process. This may be tolerable in a paint used for outside applications where the odor is dissipated by winds. When such paint is applied to indoor applications, the odors accumulate so that such paints made from unmodified fish oil may be unsuitable for use.

Modern usage of fish oils in paints employs fish oil derivatives such as alkyd resins or cyclopentadiene treatment which effectively removes this odor problem (4). Even the much simpler modifications such as the production of blown fish oil (partial oxidation) or heat bodying (polymerization) greatly reduce the odor problems of fish oil usage in paints.

### Removal of Fish Oil Flavors

Off flavors and odors are ordinarily diminished or removed from fish oils for commercial applications by vacuum steam distillation deodorization, by bleaching processes, by molecular distillation, by hydrogenation, or by a combination of these procedures. Chang (2) gives considerable detail on some of these procedures.

For the best flavor such as might be needed for a fish oil to be added to a canned fishery product, the most suitable procedure is to prepare the oil from very fresh raw material so as to obtain an oil of such quality that no further processing is necessary. If a commercial fish oil is to be the product from which flavor and odor is to be removed, several processing steps are usually needed and, at best, the production of an oil having high flavor quality is a difficult matter.

One of the most effective methods for removing flavor of fish oils is hydrogenation which not only eliminates most flavors but also stabilizes the oil against subsequent oxidative deterioration. The end product, however, is not an oil but rather a solid fat so that this method is restricted to use for material going into products such as shortening or margarine. Even hydrogenated fish oils have to be given a posthydrogenation treatment to eliminate hardening flavor and to remove traces of catalyst. A combination of heat treatment with alkali, bleaching and steam deodorization is often used.

For preparing a special fish oil having a relatively good grade of flavor suitable for human consumption, a method (5) involving clay-bleaching followed by molecular distillation gives good results. The first 8% (forerun) of the molecular distillation must be removed since it contains most of the flavor compounds. To produce an oil having maximum quality, the product resulting from clay-bleaching and molecular distillation can be given an additional silica gel bleaching as described by Stansby and Jellinek (12).

### Masking of Fish Oil Flavors

Off odors, which although initially absent from fish oil after refining but which form during use through incidental mild oxidation, can sometimes be very effectively masked by addition of suitable flavor compounds which seem to replace the rancid or fishy odors. The widespread use of peppermint or orange flavor in cod liver oil to disguise the fishy flavor of cod or other fish liver oil is an example of this masking effect. Jellinek and Stansby (7) examined several hundred such flavor materials when used in this way. Among the most effective found were root beer extract and wintergreen extract (wintergreen is the main flavor component of root beer). Fish oil and fish oil emulsions flavored with root beer extract at a level of one part per volume per 400 parts by volume of oil showed little or no fishy flavor after six weeks exposure in tubes

open to the air at 24 C. Control samples held without added flavor under identical conditions were, after such a storage period, intensely fishy and rancid and of quite an objectionable flavor. Other flavors which gave nearly as good a masking effect included extract of wild cherry and oil of wintergreen (methyl salicylate).

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