# Marine-Derived Fatty Acids or Fish Oils as Raw Material for Fatty Acids Manufacture

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## ABSTRACT

Fish oils, often an abundant source of $C_{20}$ and $C_{22}$ fatty acids, could supplement rapeseed oil in the manufacture of long chain saturated fatty acids. Herring oil, traditionally the fish oil of choice, is in very short supply due to depletion of fishery stocks. Menhaden oil, when made from fish caught in the Atlantic, could furnish a steady supply with long chain acids at about the 30% level. Oil made from other species such as anchovy or pilchard need further data on fatty acid content and variability. Manufacture of polyunsaturated fatty acids from fish oils is hampered by lack of suitable procedures. Potential markets for fish oil polyunsaturates especially in the pharmaceutical field seem promising.


## INTRODUCTION

Fish oils have been used to only a small extent in the past as a raw material source for the manufacture of industrial fatty acids. Certain changes in characteristics of more conventional raw material sources, especially for manufacture of long chain fatty acids, may make the use of fish oils in the future a source to be given greater consideration. This paper discusses fish oils from the standpoint of their utilization for such a purpose. Considerable emphasis is placed on background information concerning fish oils which can be applied toward selections of types of fish oil most suitable for such use.

Fish oils differ from most other natural triglycerides by having (a) a much greater number of different constituent fatty acids; (b) more longer chain fatty acids; (c) a considerable proportion of the fatty acids in a highly polyunsaturated form (up to six double bonds); and (d) abundant quantities of long chain polyunsaturates of the omega-3 type.

Fish oils are manufactured usually from whole fish, but sometimes from trimmings from fish canned or processed in some other manner. The oil is prepared along with fish meal, a dried protein product used in feeding of poultry and occasionally for other animals. Sometimes a third product, condensed fish solubles, is also prepared. The manufacturing procedure (1) consists ordinarily of cooking the fish with steam, pressing oil and cook water from the solids (press cake), drying of this press cake into fish meal, evaporating part of the water from the aqueous phase to produce the condensed fish solubles, and separating the oil from accompanying water by one or more centrifugation steps.

The oil may be sold at this stage as a crude fish oil or it may be further refined (2) by one or more such steps as winterization, degumming, bleaching, alkali treatment and deodorization.

In the United States the principal fish oil produced is made from menhaden, which abounds along the Atlantic Coast from New York southward and around into the Gulf of Mexico. Menhaden oil production makes up ca. 90% of the total U.S. fish oil output. Other species employed for fish oil manufacture in this country include tuna, anchovy and herring. The annual amount of fish oil produced in the United States, while fluctuating widely, generally amounts to around 200 million pounds. Most of the U.S.-produced fish oil, often up to 90% or more, is exported for hydrogenation for use in shortening or margarine. The small remainder goes mostly into paint and varnish manufacture. The still smaller remaining amount is largely used in the manufacture of chemicals of which saturated fatty acids are one of the main type.

The principal fish oil produced abroad is anchovy oil manufactured primarily in Peru (also Chile to a lesser extent). This industry is the largest current source of fish oil in the world. Annual production of 300 million lb. or more is not uncommon. The second largest production of foreign-made fish oil has been herring oil, but in recent years the amount produced has been markedly declining. There are many other fish oils produced abroad in small to moderate quantities including sardine oils in South Africa and Japan, saury oil in Japan, capelin oil in northern European countries, and fish liver oils, especially in Japan.

## FATTY ACID COMPOSITION OF FISH OILS

There seems to be a generally prevailing belief that a fish oil made from fish of a particular species will have a characteristic fatty acid pattern which will vary only a little from one sample to another. Actually, different batches of commercially manufactured fish oil made from the same species of fish often vary quite widely in fatty acid composition. This is the case even when the batches of oil are very large, each representing thousands or sometimes millions of individual fish. Furthermore, there is sometimes a quite significant variation in fatty acid composition of fish of the same species from year to year. These differences arise from the fact that to a very large extent, the fatty acid content of the oil of a fish depends upon the composition of the lipid in the food which the fish eat. While it is true that fish have the ability to alter fat in their food as consumed so as to lay down some fatty acids different from any in the consumed food, this effect is largely overridden by the more important direct laying down in the fish tissue of the same fatty acids present in the feed. As the food available to fish varies greatly from place to place or time to time, the fatty acid content of the oil of the fish likewise shows wide variation.

It is only within the past few years that the extremely wide variability in the fatty acid content of fish oils has been recognized at all, and many are still unaware of this situation. The literature is full of data supposedly representing the fatty acid pattern of fish oils. Yet in a very large portion of such data the analyses were carried out upon oil from only a very few individual fish. Such data are almost meaningless. Rather extensive sampling programs are needed before we can expect results which will give some idea as to the "average" fatty acid pattern and the degree of variability. Based upon data appearing in the literature, such information is available for only two species of fish, herring and menhaden.

What might be considered as average values for the contents of the most common fatty acids in menhaden oil is shown in Table I. Also shown in this table are the minimum and maximum amounts of each fatty acid as found in large commercial batches of menhaden oil for which analyses are available. These deviations show the large error that exists if one merely assumed that all commercial menhaden oil has the "average" fatty acid pattern. It points out the necessity for purchase of fish oil on the basis of a

TABLE I

Variation in Content of Principal Fatty Acids in Large Commercial Batches of Menhaden Oil, Percent of Fatty Acid

| Fatty acid | C14:0 | C15:0 and C17:0 | C16:0 | C16:1 | C18:0 | C18:1 | C18:2 | C18:3 | C18:4 | C20:1 | C20:4 | C20:5 | C22:5 | C22:6 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Minimum percent | 7 | 2 | 19 | 11 | 2 | 10 | 2 | 0.4 | 0.8 | 1.6 | 0.6 | 10 | 0.3 | 3.3 |
| Maximum percent | 16 | 4 | 24 | 18 | 3 | 23 | 3 | 1.7 | 3.6 | 2.7 | 2.1 | 15 | 2.5 | 11 |
| Average[a] | 10 | 3 | 21 | 12 | 3 | 12 | 3 | 1 | 3 | 2 | 2 | 13 | 2 | 8 |

[a]Averages were calculated from available data on analyses of large commercial batches of oil, but heavily weighted by the analyses provided by Dr. Anthony Bimbo of Zapata Haynie Co. These values represented oil composited at intervals during an entire season and from oil made at plants in different locations.

fatty acid analysis if the end use depends upon minimum amounts of given fatty acids.

Two investigations have been made of variations in fatty acids' patterns in large batches of herring oil. Ackman and Eaton (3) analyzed twelve different lots of Canadian-produced herring oil manufactured in 1964 from fish caught in the Atlantic Ocean near Halifax. Robisch and Gruger (4) measured the fatty acid content of Pacific herring oil manufactured at different seasons throughout two years. As was the case with menhaden oil, there are at times quite significant deviations between average individual fatty acid contents and those of any one batch of oil.

Aside from these studies on large batches of industrial menhaden and herring oils, there are no reliable published data which can give any meaningful idea as to average or ranges of values for any industrial fish oil made from other species. There are, indeed, a great many papers which have reported fatty acid content in numerous oils from fish of many different species. When, however, one examines the sampling procedures used to obtain the oil upon which the fatty acid content was determined, it is found that the data merely applies to that particular small sample from a relatively few fish and cannot be used to indicate what the fatty acid content of another batch of oil made from the same species might be.

An example of this dearth of information is the published data on South American anchovy oil. This oil in recent years has reached a volume which is by far the greatest of any fish oil manufactured. Yet the only published data on fatty acid content from an industrial South American anchovy oil was from a single sample of oil taken from a centrifuge on one day in one fish oil plant. Several other studies have been made upon fatty acid content in oil extracted from a few individual anchovy taken at intervals during a season. Such information, as has been indicated, is of little value. One quite good sample of industrial Mexican anchovy oil which represents fish taken over an entire production season has been analyzed, but we have no way of knowing whether the anchovy of Mexico taken thousands of miles distant have similar fatty acids patterns to those from South America.

It is quite possible, probably most likely, that the fatty acid content of other industrial fish oils has been studied and is well known within companies either who manufacture or use such fish oil.

## PRODUCTION OF LONG CHAIN SATURATED FATTY ACIDS

In the fatty acid manufacturing industry, rapeseed oil has been the usual raw material source for long chain fatty acids. In recent changes in rapeseed growing practices, genetic alteration has been made resulting in greatly reduced content of erucic acid. While this has been advantageous for many of the end uses in the nonindustrial field, this practice is raising problems for those industrial uses where very long chain fatty acids are needed. The ultimate future situation regarding continued availability of adequate amounts of high erucic acid rapeseed oil has not yet been resolved. In the meantime, the expanded use of fish oils, the only other reasonably satisfactory source of $C_{20}$ and $C_{22}$ fatty acids, should be considered.

Fish oils are used to a small extent for making saturated fatty acids. Such oils with their high content of very polyunsaturated fatty acids must be first hydrogenated to convert them to the saturated form if the usual continuous, high pressure, fat splitting techniques are to be employed. Fish oils, although they fluctuate widely in price, are usually lower in price than most other suitable oils.

## CHOICE OF MOST SUITABLE FISH OIL SPECIES FOR LONG CARBONCHAIN, SATURATED FATTY ACID PRODUCTION

The choice of which fish oil to use for making long chain saturated fatty acids will be determined primarily by the fatty acid distribution. Those species of fish oil having the highest proportion of $C_{20}$ and $C_{22}$ fatty acids will be preferred. Other factors, such as our existing knowledge of the fatty acid content of oil, its variability from lot to lot, and to some extent the continued availability of such oils, will have to be considered.

Up to the present time herring oil has been the preferred species for such use. Herring oil contains, in addition to the more usual polyunsaturated $C_{20}$ and $C_{22}$ fatty acids contained in fish oils of all species, a very significant amount of $C_{20}$ and $C_{22}$ monoenes. The presence of these monoenes raises the content of $C_{20}$ and $C_{22}$ from the range of 20 to 35% found in most other fish oils to levels usually in the range of 40 to 48% in herring oil.

Unfortunately, commercial herring oils are currently almost nonexistent, at least in pure form. North American herring oil production has almost ceased. In both Canada and the United States the available herring stocks have either disappeared, or especially in Canada, drastically declined. In Canada government regulations now stipulate that herring can no longer be reduced to oil and meal except where most of the fish is used for human food with only the trimmings available for oil production. In Northern Europe including Iceland, which has been the source of the bulk of past herring oil production on a worldwide basis, such a drastic decline in herring stocks has occurred that a ban on herring fishing for the 1979 season will probably be placed by most countries.

Furthermore, over the past several years much of the so-called herring oil is really a mixture of oil made from herring and other species. Such mixed oil may still be higher in $C_{20}$ and $C_{22}$ fatty acids than oil from other species. The content of these longer chain fatty acids, however, must vary over wide limits depending upon the proportion of herring in the mixed oil and upon the content of $C_{20}$ and $C_{22}$ fatty acid in the other species of fish which are rendered together with the herring. Capelin, one of these species, has a high proportion of $C_{20}$ and $C_{22}$

fatty acids; several other species, however, are being used, about which there is little or no information regarding their content of the long chain fatty acids.

If herring oil is not available in sufficient quantity to furnish a raw material for long chain fatty acid manufacture, a choice among other available oils is a difficult one until more is known about the content and variability of $C_{20}$ and $C_{22}$ fatty acids in the various oils. In most other oils the proportion of $C_{20}$ and $C_{22}$ fatty acids is apt to be only at levels between 20 and 35%. Among all the available commercial fish oils other than herring, published data on such levels is sufficient only for menhaden oil. The content of $C_{20}$ and $C_{22}$ fatty acids from oil made from the Atlantic-caught fish averages ca. 30%, while that made from Gulf of Mexico-caught menhaden averages ca. 25% (Table II). Unlike the production of fish oil of other species such as herring and pilchard, the production of menhaden oil has for many decades remained reasonably stable so that if a content of the $C_{20}$ and $C_{22}$ fatty acids of ca. 30% is adequate, under the present lack of knowledge of the fatty acid composition of other fish oils, menhaden would be the best substitute for herring oil for this purpose.

Other oils for which present information is inadequate but which should be investigated include anchovy, pilchard, and tuna. The anchovy oil made primarily in South America, largely in Peru, has shown wide variation in production levels, even though in the past two decades its volume of production has been greater than that of any other fish oil. In 1977 such a low production was achieved that it appeared that the industry might decline to one of very minor importance, but greatly increased production in 1978 gives an optimistic view that the fishery is reviving. Only the fatty acid analysis of a single batch of commercial, South American anchovy oil has been published. This lot of anchovy oil contained 32% $C_{20}$ and $C_{22}$ fatty acids. A much greater number of analyses of different batches of commercial anchovy oil must be available before we can have any good idea whether such a value is typical.

Likewise, only a very few fatty acid analyses, in most cases of rather small batches of pilchard oil, have been published. These show no agreement as to what might be expected, values ranging for $C_{20}$ and $C_{22}$ totals from less than 30% to over 50%. Tuna oil likewise has little published information on its long chain fatty acid content. Although the limited information on tuna oil that is available might indicate that these fatty acids may average 35%, the tuna oil is prepared in such a manner that it is the most difficult of all commercial fish oil to refine and, even in its best refined form, probably would contain too many impurities for it to be considered as a raw material for fatty acid production.

TABLE II

Content of $C_{20}$ and $C_{22}$ Fatty Acids in Menhaden Oil[a]
Percent $C_{20}$ and $C_{22}$ Fatty Acids

| Year | Menhaden oil from fish caught in Atlantic | Menhaden oil from fish caught in Gulf of Mexico |
|---|---|---|
| 1976 | 30 | 24 |
| 1977 | 31 | 24 |
| 1978 | 28 | 27 |
| Three year average | 30 | 25 |

[a]These data were provided by Anthony Bimbo, Director of Research, Zapata Haynie Corp. The samples in each case are from production in several plants taken at intervals throughout the season. These data give excellent average figures for the fatty acid contents during the years reported.

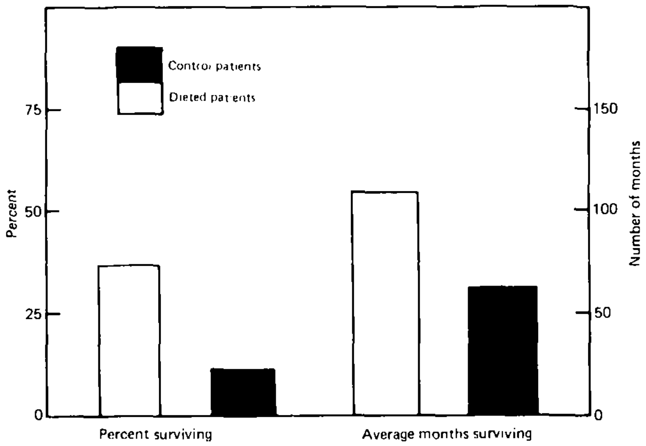


FIG. 1. The proportion of patients (some on a special diet in which seafood was the principal source of polyunsaturates) surviving over a 16 to 19 year period. The average number of months of survival is also shown. The data cover 80 individuals on the special diet and 126 who followed their usual eating habits. All patients in the experiment had suffered a heart incident before the experiment began.

## PRODUCTION OF POLYUNSATURATED FATTY ACIDS FROM FISH OILS

Production methods for polyunsaturated fatty acids from fish oils involve techniques for which research has not yet provided fully satisfactory procedures. A method described in 1902 (5) for enzymatic splitting of polyunsaturated fats by means of enzymes from castor beans was used to a limited extent in past years. It has several disadvantages, principally that the splitting is incomplete. Whether such a method could be improved by further research is uncertain. Lack of a suitable method for this purpose has prevented the unique polyunsaturated characteristics of fish oil fatty acids from achieving several potentially important applications.

Fish oil triglycerides have been fractionated without fat splitting by use of molecular distillation. During the 1960s at the Seattle Fishery Technological Laboratory many tons of menhaden oil triglycerides were molecularly distilled and distributed to medical institutes for testing in various pharmaceutical uses (5). At first this distillation was made in one step for producing a tasteless product for human feeding studies. It was also found that by collecting different fractions during the distillation, different degrees of unsaturation of the resulting triglycerides could be achieved (6). Many hundreds of pounds of the last distilled fraction of very high iodine value were likewise distributed for medical research. This fraction contained ca. 50% of docosohexaenoic acid.

If fish oil polyunsaturates are to be produced, it might be preferable to prepare first by molecular distillation the corresponding concentrated polyunsaturated triglyceride fractions. If upon testing these seemed to be as marketable for potential use as is presently tentatively indicated, then it would be time to carry out the probably difficult and extensive research needed to develop means for producing the polyunsaturated fatty acids from the fish oil.

## POTENTIAL USES FOR FISH OIL POLYUNSATURATED FATTY ACIDS

If polyunsaturated fish oil fatty acids could be readily produced, there are several potential markets for such products which depend upon the unique presence of both the highly polyunsaturated fatty acids with five and six double bonds and upon the presence of a considerable proportion of omega-3 types of fatty acids. Such applications are possible in both industrial and pharmaceutical areas. One such potential application is in pharmaceuticals.

During the early 1960s attempts were made to market a pharmaceutical product consisting of fractionated fish oil triglycerides and fatty acids for treatment of heart patients for reduction of serum cholesterol. This attempt was premature because most of the evidence that such fatty acids were effective was based upon rat-feeding tests and with only a very few extremely short term human feeding tests at that time having been made. Since then, at least one very long term dietary test has been carried out by a heart specialist who advised his patients who had suffered a heart attack to go on a diet with high fat seafood consumed several times per week. This physican succeeded in getting a portion of his patients to follow the diet for up to nineteen years and with very dramatic results (7). Of the 80 patients who adhered to the diet, 51 (57%) were alive after the 16 to 19 years of the test. In contrast, only 10 of the 116 (9%) undieted patients survived. Also, the average months of remaining life of those dying from subsequent heart attacks was 109 months for the dieted patients as compared to only 58 months for those not dieted. These impressive results would indicate there could be a demand for fish oil polyunsaturated fatty acids as a pharmaceutical which could replace the more troublesome dietary regime and extend the life of patients unwilling to follow the rigid diet.

Other possible pharmaceutical applications for polyunsaturated fish oil fatty acids include use for multiple sclerosis (8) and for gall stone treatment (9). There also might be considerable use made of highly polyunsaturated, omega-3 fatty acids in the industrial field as a starting point for chemical synthesis of a variety of substances.

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# Nitrogen Derivatives (Amides, Diamides, Nitriles, Primary Amines and Oxides)


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## ABSTRACT

Without a doubt the nitrogen derivatives are the most broadly diversified family of fatty acid derivatives. Today they account collectively for perhaps 400 million pounds of products per year in the USA alone. Although fatty amides may be produced by a large number of synthetic routes, industrially only two are of any commercial importance. Diamides are the difunctional analogs of simple amides, and a typical one that is in medium scale production volume is ethylene bis(stearamide). Industrially, the production of fatty nitriles in the fatty acid derivative industry is exclusively by ammonolysis of fatty acids at temperatures somewhat above those required to produce amides, or roughly, 300-320 C. Both vapor phase catalytic and liquid phase ammonolysis processes may be employed. Nitriles have limited uses as such, but find their utility as fatty derivative intermediates only. The primary amines, $RNH_2$, are produced industrially by the catalytic hydrogenation of nitriles. The general conditions for the conversion of nitriles to primary amines with a minimum content of secondary or tertiary amines is with nickel catalyst using an excess of ammonia at relatively low temperatures (130-140 C). Amine oxides are derived from tertiary amines by a controlled reaction with hydrogen peroxide. In addition to tertiary amines, the monoalkyl diethoxylated amines can be considered as in the same class. These are made by the addition of ethylene oxide to primary amine. Two moles of ethylene oxide can be added without catalyst. Additional ethoxylation does require a basic catalyst. These amines, besides having end uses of their own, can be converted to amine oxides or can be converted to ethoxylated quaternary ammonium salts.


## AMIDES

Primary amides of fatty acids can be regarded as simple substitutes of the hydroxyl of the carboxyl group with an amino function. Simple amides have strong association because of hydrogen bonding, which leads to relatively high melting points for fatty acid derivatives and low solubilities in most solvents. All fatty amides are essentially insoluble in water. In polar solvents solubility decreases with increasing chain lengths, and above dodecanamide it is low in all solvents. Fatty amides have good stability towards air oxidation, heat and dilute acids or bases. The stability is, of course, affected by the degree of unsaturation in the alkyl chain.

### Manufacture

Most simple amides of fatty acids are prepared by the reaction of the appropriate fatty acid with anhydrous ammonia in a batch process:

$$R\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}OH + NH_3 \rightarrow R\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}O\text{-}NH_4 \rightarrow R\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}NH_2 + H_2O$$

The reaction is conducted at 180-200 C under slight pressure (50-100 psi) for 10-20 hr. Pressure is maintained by the rate of addition of ammonia and the water of reaction is removed continuously. The effluent stream is collected and the ammonia portion is recovered and can be recycled. While most simple amides are made by this procedure, the starting material can be an ester. Various catalysts have been employed in the manufacture of amides. Among them are boric acid (1), $Al_2O_3$ (2), and zinc alkoxides (3).

If the use of ammonia is not convenient, it is possible to prepare simple amides by reacting urea with a fatty acid in a sealed vessel at 170-240 C for 2 hr at elevated temperatures (4). Other methods reported in the literature for the