Variability of the composition of fish oils: significance for the diet

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Photosynthesis by most algae and phytoplankton is associated with the production of n-3 polyunsaturated fatty acids (PUFA). These acids, members of the α-linolenic family, eventually pass through the food web and are incorporated into fish lipids and, thus, form an integral part of our diet either through consumption of fish, fish oils or the flesh of terrestrial animals subjected to a diet containing fish or fish products. Our consumption of fish has a long history. In palaeolithic times, man was already enjoying crustaceans and mollusces while fossilized remains of hand-caught fish date back 380 000 years. Methods of preservation, including smoking and drying, were developed thus allowing increased utilization of this food. Since the forging of a link between the consumption of n-3 fatty acids and benefits to health, many detailed studies have been carried out to investigate the influence of fish oils on various physiological processes. The term fish oil, used generically, embraces a complex matrix of components in which there are differences in composition depending on the species of fish from which the oil is obtained. This overview attempts to provide an insight into the range of molecular species present in fish oils and to emphasize the importance of characterizing the composition of products used in feeding trials and physiological studies.

NA MARA (OF THE SEA)

Oceans and seas cover more than seven-tenths of the earth’s surface, providing a habitat for over 60 000 different species of fish, crustaceans and mollusces. Many of these are edible. Fish and shellfish were one of primitive man’s main foods in his earliest days as a food gatherer (Connell & Hardy, 1982) although, in Scotland, the early inhabitants were not great fish-eaters and did not exhibit any marked seafaring tendency (Hope, 1987). Our ancestors did enjoy shellfish such as mussels, whelks and limpets but, apart from the occasional stranded whale or seal, this represented the limit of the Scottish marine diet. The introduction of small boats permitted the capture of ling and cod but the arrival of the Vikings with their large sea-going boats in the 8th century, introduced the Scots in the North and West to the bountiful supply of herring which were present in the seas around Scotland. Furthermore, the introduction of Roman Catholicism meant that fish was the chief permitted protein during Lent and at other times (Hope, 1987). Thus, commercial fishing soon became both necessary and profitable.

A major difficulty encountered with fish as a food is that it is highly perishable and rapidly spoils immediately after catching (Kelman, 1982). Thus, some means of preservation must be employed to counteract bacterial and oxidative spoilage. Demersal species including Atlantic cod (Gadus morhua) and haddock (Melanogrammus aeglefinus) together with flatfish, dogfish and others live on or near the sea bed. These fish tend to have a low fat content in the flesh (<20 mg/g), the bulk of the lipid being phospholipid (Bligh & Scott, 1966; Jangaard et al. 1967). As such, they lend themselves
to a simple and effective cure merely by salting and drying in the sun and wind, yielding a bread substitute. Pelagic species, shoaling fish living in midwaters, include Atlantic herring (*Clupea harengus*) and mackerel (*Scomber scombrus*). These fish store most of their lipid in the flesh and under the skin (Love, 1982). Consequently, if simply hung up to dry, the flesh rapidly deteriorates due to oxidation of the highly unsaturated lipids. This problem was resolved in the 14th century with the introduction of a ‘new process’, the gutted and rinsed fish were packed in layers, interspersed with coarse salt, in barrels.

The historical consumption of fish in Scotland varied considerably according to location and availability. Cod, haddock and plaice were prominent in the diet of coastal areas while salmon and trout made a significant contribution to the diet in many inland areas (Steven, 1985). In the Northern Isles and the Hebrides coal-fish or saithe (*Pollachius virens*) were an important component of the diet while the liver oil was used as a fuel for lamps. Part of the staple winter and spring diet of the Shetlanders was dried saithe, cod and haddock, while shellfish boiled in milk was a nutritious stand-by. On the West Coast, herring was the most important fish, herring boiled over potatoes being considered very nutritious. Red herrings was a popular product in England. This heavily salted, hard-smoked product became popular during the 14th century but, in more recent times, mildly smoked products including the succulent ‘Scots’ kipper have become more popular, although the term ‘kipper’ initially referred to salmon (Cutting, 1955; Steven, 1985).

In the early 19th century, canning of fish products was introduced and canned fish became as much a standard item of the diet as pickled herring and dried-salted cod would have been in former times (Cutting, 1955).

In modern times, freezing has developed as a popular method of preserving fish. This technique, when successfully carried out, has the advantage of permitting the preservation of the fish, as it were, in the fresh state. A consequence of this is that dried fish or even pickled fish are no longer major products consumed in this country.

The present day UK trade in fish products is illustrated by examining the UK import and export figures for the seven fishery commodity groups (Table 1). Chilled, fresh or frozen fish represent the major fishery commodity with respect to both import and

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**Table 1. UK imports and exports by fishery commodity groups***

<table>
<thead>
<tr>
<th>Commodity group</th>
<th>Import (tonnes)</th>
<th>Export (tonnes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fish, fresh, chilled, frozen</td>
<td>279 796</td>
<td>302 316</td>
</tr>
<tr>
<td>Fish, dried, salted, smoked</td>
<td>2 879</td>
<td>3 842</td>
</tr>
<tr>
<td>Crustaceans† and molluscs‡</td>
<td>34 797</td>
<td>34 213</td>
</tr>
<tr>
<td>Fish, canned</td>
<td>133 528</td>
<td>126 733</td>
</tr>
<tr>
<td>Crustaceans and molluscs, canned</td>
<td>29 626</td>
<td>30 243</td>
</tr>
<tr>
<td>Oils</td>
<td>177 875</td>
<td>161 818</td>
</tr>
<tr>
<td>Meals</td>
<td>266 498</td>
<td>275 375</td>
</tr>
<tr>
<td>Total value (1000 US$)</td>
<td>1 627 924</td>
<td>1 911 161</td>
</tr>
</tbody>
</table>

* Food and Agriculture Organization (1992).
† Includes crabs, lobsters, prawns, shrimps and crayfish.
‡ Includes mussels, oysters, scallops, squid and octopus.
export, but substantial quantities of canned fish, fish oils and fish meals are imported by
the UK (Food and Agriculture Organization, 1992).

During 1991 about 488 878 tonnes of sea fish, excluding shellfish and livers, were
landed in the UK, a substantial amount (83%) being caught in the North Sea or off the
West Coast of Scotland. The bulk of sea fish (79%) was landed at Scottish ports where
the percentage accounted for by pelagic species was slightly greater than that for
demersal. Mackerel was landed in the greatest quantity in 1991 (124 955 tonnes)
followed by herring (93 298 tonnes; Sea Fish Industry Authority, 1992).

THE SOURCE AND NATURE OF FISH OILS

Although water and protein are major components of fish flesh, fish oils, specifically cod
liver oil, have long been held in high regard as being nutritionally beneficial (Bull, 1899).
Since the early 1970s, there has been an intense scientific interest in the health benefits of
fish and fish oils stimulated by the work of Dyerberg and co-workers on the incidence of
coronary heart disease in native Greenland Eskimos (Dyerberg et al. 1975, 1978;
Dyerberg & Bang, 1979; Dyerberg & Jorgensen, 1982).

Fish lipids are different from those of terrestrial origin in that the major unsaturated
fatty acids belong to the n-3 family (Exler et al. 1975; Herold & Kinsella, 1986;
Ballard-Barbash & Callaway, 1987). These long, straight-chain molecules contain a
series of cis double bonds, the first of which is between C-3 and C-4 counting from the
methyl- or ω-C. The fatty acids which have attracted most attention are cis-5,8,11,14,17-
eicosapentaenoic acid (EPA; timnodonic acid) and cis-4,7,10,13,16,19-docosahexaenoic
acid (DHA) (Payan et al. 1986; Kinsella, 1987; Hirai et al. 1989; Yerram & Spector,
1989). Fish and fish dishes provide 14% of the average daily intake of n-3 fatty acids
(Gregory et al. 1990). Other major sources include cereal products (17%), meat (19%)
and vegetables (22%). Consumption of fish should help people to obtain the rec-
commended provision of 7-5% of total energy by cis-PUFA (British Nutrition Founda-
tion, 1992) but EPA and DHA can be consumed via fish oils.

The largest source of fish oils is that of body oils from pelagic species; 1 368 145 tonnes
were produced in 1990 (Food and Agriculture Organization, 1992) corresponding to
97-9% of total fish oil production. Fish liver oils accounted for 1-7%, the remainder
coming from marine mammals, squid and various other species. The major fish
oil-producing species include anchovy (Engraulis spp.), capelin (Mallotus villosus),
herring (Clupea spp.), horse mackerel (Trachurus spp.), menhaden (Brevoortia spp.),
mackerel (Scomber spp), Norway pout (Trisopterus esmarkii), sand eel (Ammodytes
tobianus), sprat (Clupea spratus), Sardinops spp. and others. Capelin and herring are
found in polar or boreal waters, but the really large pelagic resources are found in
temperate or subtropical waters. However, a very high proportion of the total catch of
pelagic fish is taken over a very small proportion of the earth’s surface, much of it close to

Japan is the largest single producer of fish oils and fats, averaging 29% of total world
production from 1988 to 1990, inclusive. There is little difference in the average
production in Asia (31.7%) and South America (30.4%) over the same period (Food and
Agriculture Organization, 1992). Production in Europe is dominated by Denmark,
Norway and Iceland, with the United Kingdom contributing only 0.5% to total world
production.
In Europe, fish body oils are produced either from small fish such as sprat or sand eel or from larger fish such as herring when there is excess, or from fish offal (Windsor, 1982; Young, 1982). Fish meal and fish oil are generally made at the same time, fish oil being a byproduct of the meal industry. The most important factor in the production of a high-quality crude fish oil is the condition of the raw material at the start of processing. Prompt handling of the fish and fish offal is critical. The raw material is first cooked, for 15 min at 90°C, to facilitate coagulation of the proteins, sterilization and separation of oil. The cooked fish is then conveyed through a perforated tube whilst being subjected to increasing pressure, normally by means of a tapered shaft on a screw conveyor. The oil and water mixture, known as press liquor, passes through the perforations while the solid, known as press cake, emerges from the end of the press. After screening to remove coarse pieces of solid material, the press liquor is centrifuged, in desludging or self-cleaning centrifuges, to separate the oil from the water. The fish oil is further refined by washing with water (100 ml/l oil) at 90–95°C followed by centrifugal separation. At this stage the crude fish oil still contains a number of impurities. These include moisture, rust, dirt, proteins, free fatty acids, mono- and diacylglycerols, enzymes, soaps, trace metals such as Cu and Fe which promote oxidation, oxidation products, pigments, phosphatides, hydrocarbons, terpenes, resins, sterols, waxes, sugars and compounds containing S, N and halogens (Young, 1982, 1985, 1986). The impurities arise as a result of the natural phenomena of season, geographical location (giving rise to marine pollutants in the oil) and food, together with the freshness of the fish at time of extraction, and efficiency of the extraction process. Thus, the essentially 900–950 g triacylglycerol/kg oil (Young, 1986; Urdahl, 1992) is further refined as detailed in Table 2. The final product will still be subject to post-processing oxidation. The nature and concentration of the oxidation products will vary with time and are critically dependent on how well the oil is stored.

In the past, fish oils have been used for tanning, as water repellents, lubricants, plasticizers, corrosion inhibitors and as a fuel (Windsor, 1982). In excess of 95% of fish oil produced is now used for human food (Young, 1986). The oils are hydrogenated following refining to produce a solidified fat for use in margarines and shortenings. Total hydrogenation results in a product devoid of the vital n-3 PUFA and associated triacylglycerols containing the highly unsaturated molecules (Fig. 1). If, however, the oil is not hydrogenated, its composition and that of virtually all fish oils, can be described by reference to eight fatty acids: tetradecanoic acid (14:0, myristic acid), hexadecanoic acid (16:0, palmitic acid), cis-9-hexadecenoic acid (16:1 (n-7), palmitoleic acid), cis-9-octadecenoic acid (18:1 (n-9), oleic acid), cis-9-eicosenoic acid (20:1 (n-11), gadoleic acid), cis-11-docosenoic acid (22:1 (n-11), cetoleic acid), EPA and DHA (Fig. 2). The fatty acid composition of fish oils is further complicated by the presence of lesser amounts of pentadecanoic acid (15:0), hexadecadienoic acid (16:2), hexadecatrienoic acid (16:3), hexadecatetraenoic acid (16:4), octadecanoic acid (18:0, stearic acid), cis-11-octadecenoic acid (18:1 (n-7), asclepic acid), cis-9,12-octadecadienoic acid (18:2 (n-6), linoleic acid), cis-9,12,15-octadecatrienoic acid (18:3 (n-3), α-linolenic acid) cis-6,9,12,15-octadecatetraenoic acid (18:4 (n-3), moroctic acid), eicosanoic acid (20:0, arachidonic acid), cis-11-eicosanoic acid (20:1 (n-9)), cis-5,8,11,14-eicosatetraenoic acid (20:4 (n-6), arachidonic acid), cis-8,11,14,17-eicosatetraenoic acid (20:4 (n-3)), and cis-7,10,13,16,19-docosapentaenoic acid (22:5 (n-3), clupanodonic acid). Furthermore, there are trace quantities of the odd carbon number fatty acids heptadecanoic (17:0) and
Table 2. Unit processes utilized in the refining of crude fish oils (after Young, 1982, 1985)

<table>
<thead>
<tr>
<th>Stage</th>
<th>Procedure</th>
<th>Impurities reduced or removed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crude oil storage</td>
<td>Oil left in tanks to settle. Good oil drawn off the top</td>
<td>Oil insolubles</td>
</tr>
<tr>
<td>Degumming</td>
<td>Treatment with phosphoric acid (800–850 ml/l) at 90°</td>
<td>Phospholipids, sugars, resins, proteinaceous compounds, trace metals and others</td>
</tr>
<tr>
<td>Neutralization</td>
<td>Treatment of hot oil (90–95°) with sodium hydroxide (4 mol/l)</td>
<td>Fatty acids, pigments, oil insolubles, water solubles</td>
</tr>
<tr>
<td>Washing</td>
<td>Treatment with soft water (&lt;50 µg/g hardness expressed as CaO) at 90–95°</td>
<td>Soaps</td>
</tr>
<tr>
<td></td>
<td>Phosphoric or citric acid may be added to the final wash water</td>
<td></td>
</tr>
<tr>
<td>Drying</td>
<td>Heated to 90° under vacuum with rapid agitation</td>
<td>Water</td>
</tr>
<tr>
<td>Bleaching</td>
<td>Treatment with activated clays (2–300 g/kg) under vacuum at 90–110°</td>
<td>Pigments, oxidation products (aldehydes and ketones), trace metals, trace soaps</td>
</tr>
<tr>
<td>Filtration</td>
<td>Various designs of filters</td>
<td>Spent bleaching earths</td>
</tr>
<tr>
<td>Deodorization</td>
<td>Steam distillation under vacuum</td>
<td>Fatty acids, mono- and diacylglycerols, aldehydes, ketones, hydrocarbons, sulphur compounds, pigment decomposition products</td>
</tr>
</tbody>
</table>

Fig. 1. Silver ion HPLC of the triacylglycerols from a Norwegian fish oil (A) and the hardened derivative (B). The oils (120 mg) were dissolved in 1,2-dichloroethane (10 ml). Injections (50 µl, 600 µg) were performed automatically to ensure reproducible reconditioning of the Nucleosil SSA column. Detection was by means of a light scattering detector (McGill & Moffat, 1992). The original fish oil contained trisaturated triacylglycerols (retention time (RT) 3 min) and those with one or two monoenoic acids per molecule (RT 8 and 11 min respectively). Triacylglycerols containing three monoenoic acids (MMM) precede those with di-, tri- and more highly unsaturated fatty acids. Very highly unsaturated molecules (greater than twelve double bonds) are within the last group of peaks of chromatogram A. The peak at 4.7 min in the hardened Norwegian oil profile arises from triacylglycerols substituted by trans-acids.
Fig. 2. Fatty acid profiles for herring (*Clupea harengus*), mackerel (*Scomber scombrus*) and capelin (*Mallotus villosus*) body oils. The methyl esters were prepared and analysed as described by Moffat *et al.* (1991). The combined levels of cis-5,8,11,14,17-eicosapentaenoic acid (EPA) and cis-4,7,10,13,16,19-docosahexaenoic acid (DHA) is 196, 195 and 124 mg/g fatty acids for herring, mackerel and capelin respectively. Other PUFA present include 18:3 (n-3), 18:4 (n-3), 20:4 (n-3 and n-6) and 22:5 (n-3). These oils contain significant amounts of 20:1 and 22:1. Values in parentheses are levels for individual fatty acids expressed as mg/g fatty acids. FID, Flame ionization detector.
Fig. 3. Fatty acid profiles for menhaden (Brevoortia spp.) oil and Indian oil sardine (Sardinella longiceps). The combined amounts of cis-5,8,11,14,17-eicosapentaenoic acid (EPA) and cis-4,7,10,13,16,19-docosahexaenoic acid (DHA) is 236 and 269 mg/g fatty acids respectively. These fish oils contain only small amounts of 20:1 and only traces of 22:1. Values in parentheses are levels for individual fatty acids expressed as mg/g fatty acids. FID, Flame ionization detector.

heptadecenoic (17:1) acid together with methyl-branched fatty acids (Ackman, 1980; Adolf & Emken, 1985; Ratnayake et al. 1989). The wider range of fatty acids found in fish relative to land animals arises because fish absorb and assimilate the wide range of fatty acids in their food. Pelagic species feed on the numerous floating populations of plankton species which contain significant concentrations of EPA and DHA. Fish can synthesize fatty acids de novo, but another source of 20:1 and 22:1 is thought to be the oxidation of the corresponding long-chain alcohols in the dietary copepod wax esters (Ratnayake & Ackman, 1979a,b). Thus, pelagic species, including herring which feed on the copepods, show large quantities of 20:1 (96–200 mg/g fatty acids) and 22:1 (150–320 mg/g fatty acids) in their depot triacylglycerols (Fig. 2). Mackerel and capelin oil are also high in 20:1 and 22:1 and contain reasonable quantities of EPA and DHA (Fig. 2).

In contrast, menhaden (B. patronus and B. tyrannus) which is also planktivorous (Ackman, 1989) and Indian oil sardine (Sardinella longiceps), both species which are found in much warmer waters, have an equivalent range of fatty acids in their oils (Fig. 3), but 20:1 and 22:1 are minor constituents or absent (Ackman, 1980; Grundy, 1986). Although not regarded as a classical division, it is convenient to subdivide fish oils into those containing significant amounts of 20:1 and 22:1 and those with only trace quantities of these fatty acids. Thus, a major interspecies variation is immediately apparent.
Table 3. Fatty acid composition of Atlantic herring (Clupea harengus) oils and cod (Gadus morhua) liver oils (after Ackman & Eaton, 1966 and Jangaard et al. 1967 respectively)

<table>
<thead>
<tr>
<th>Fatty acid</th>
<th>Herring oils (range of twelve)</th>
<th>Cod liver oils*</th>
</tr>
</thead>
<tbody>
<tr>
<td>14:0</td>
<td>46–84</td>
<td>15–48</td>
</tr>
<tr>
<td>16:0</td>
<td>101–150</td>
<td>110–188</td>
</tr>
<tr>
<td>18:0</td>
<td>7–21</td>
<td>17–45</td>
</tr>
<tr>
<td>16:1</td>
<td>63–120</td>
<td>68–119</td>
</tr>
<tr>
<td>18:1</td>
<td>93–214</td>
<td>171–314</td>
</tr>
<tr>
<td>20:1</td>
<td>110–199</td>
<td>40–146</td>
</tr>
<tr>
<td>22:1</td>
<td>148–306</td>
<td>8–123</td>
</tr>
<tr>
<td>18:2 (n-6)</td>
<td>6–29</td>
<td>8–21</td>
</tr>
<tr>
<td>18:3 (n-3)</td>
<td>2–11</td>
<td>3–11</td>
</tr>
<tr>
<td>18:4 (n-3)</td>
<td>11–25</td>
<td>5–17</td>
</tr>
<tr>
<td>20:4 (n-6)</td>
<td>2–5</td>
<td>5–28</td>
</tr>
<tr>
<td>20:5 (n-3)</td>
<td>39–88</td>
<td>59–151</td>
</tr>
<tr>
<td>22:5 (n-6+n-3)</td>
<td>6–17</td>
<td>9–35</td>
</tr>
<tr>
<td>22:6 (n-3)</td>
<td>20–62</td>
<td>76–192</td>
</tr>
</tbody>
</table>

* Range of eighteen samples each of male and female cod collected over 18 months. Each sample constitutes four livers.

The EPA content of fish oils may range from 20 to 100 mg/g fatty acids for Atlantic herring oil (Ackman, 1980; McGill & Moffat, 1992), through 60–120 mg/g fatty acids for capelin oil (Ackman, 1982), to 170–250 mg/g fatty acids for anchovy oil (Ackman, 1982, Moffat et al. 1993). Again, major interspecies variation is evident but, at the same time, it is obvious that intraspecies variation is also extensive, this being associated with season (Hardy & Keay, 1972; Ackman, 1980, 1982; Opstvedt, 1985; Young, 1986), sex (Hardy & Keay, 1972) and catching area (Joseph, 1985; Urdahl, 1992). All the fatty acids are subject to this variation as illustrated for Atlantic herring oil (Table 3). Seasonal variations can result in as much as a 90% decrease in the EPA content of a fish oil (Ackman, 1982), but a 75% decrease over a season is more common. Similar changes are observed for DHA. Seasonal variations have been demonstrated in male mackerel where the concentration of 20:1 and 22:1 increased seasonally from approximately 30 to 90 and 130 mg/g fatty acids respectively (Hardy & Keay, 1972). Such variations were not observed for female mackerel, the concentration of 20:1 remaining at 63–64 mg/g fatty acids, while that of 22:1 increased from 83 to 87 mg/g fatty acids between December and June.

Extensive seasonal and geographical variations in fatty acid composition have been demonstrated for menhaden oils produced from fish obtained from two discrete catching areas, the Gulf of Mexico (B. patronus) and the Atlantic coast of Virginia (B. tyrannus). Gulf coast fish contained, on average, lower amounts of 22:6 and 20:5. Furthermore, in addition to geographical variations there were statistically significant differences in the mean levels for many of the fatty acids from oils obtained from 1982 fish relative to 1983 fish (Joseph, 1985).
The critical point is that although the range of major fatty acids remains constant, the concentration of each acid shows extensive inter- and intraspecies variation.

**SILVER-ION HPLC OF FISH OIL TRIACYLGLYCEROLS**

Ag\(^+\)-HPLC of fish body oils (Laakso et al. 1990; Laakso & Christie, 1991; McGill & Moffat, 1992) produces a triacylglycerol profile for the oils. Mackerel, herring and capelin oils, those containing high concentrations of 20:1 and 22:1, give similar overall patterns. Trisaturated triacylglycerols and those composed of one or two monoenoic acids with the appropriate number of saturated acids are present in the three types of oil. The trimonounsaturated triacylglycerols are especially evident in capelin oil (McGill & Moffat, 1992). As the triacylglycerols become more highly unsaturated so baseline resolution is lost in the Ag\(^+\)-HPLC profiles, but fractionation of these oils by Ag\(^+\)-HPLC reveals a progressive introduction of tri-, tetra-, penta- and hexaenoic acids into the triacylglycerols. Very highly unsaturated triacylglycerols (greater than twelve double bonds) are present at low concentrations in these oils.

The oils from menhaden, South African anchovy and Indian oil sardine contain lesser amounts of monoenoic acids. These fish oils still contain trisaturated triacylglycerols but do not show significant quantities of triacylglycerols substituted by two or three monoenoic acids (McGill & Moffat, 1992). The PUFA-containing triacylglycerols show an increased range of molecular composition with the presence of some very highly unsaturated triacylglycerols composed of a mixture of tetra-, penta- and hexaenoic acids. Triacylglycerols containing 520 mg EPA and 270 mg DHA/g fatty acids have been isolated. Thus, triacylglycerols with at least sixteen double bonds are present in fish body oils (McGill & Moffat, 1992).

**COD LIVER OIL**

The livers of demersal species can comprise up to 750 g lipid/kg, triacylglycerols being the major constituent. Cod liver oil contains a range of fatty acids similar to that of the pelagic body oils, but specific concentrations are different and vary (Table 3). The concentration of 20:1 and 22:1 is generally intermediate between that for typical herring and mackerel oils and the likes of menhaden and anchovy oils. Furthermore, the concentration of 22:6 is often greater than for 20:5 and can be as high as 230 mg/g fatty acids (C. F. Moffat, unpublished results).

**ENCAPSULATED FISH OILS**

Direct consumption of fish and other oils is restricted because many people find ‘oiliness’ unacceptable and have difficulty in swallowing the oil. The introduction of oils encapsulated in a soft gelatin shell has overcome this problem, leading to UK sales in 1991 worth £133 million, fish oils capturing 55-5% of this market (Market Research GB, 1992). A variety of products are readily available from supermarkets, pharmacies and healthfood shops. Cod liver oil is a major product. Not surprisingly, the fatty acid composition of encapsulated cod liver oils (Table 4) is not constant. The triacylglycerol composition of encapsulated cod liver oils shows the same broad spectrum of molecular structures as the pelagic body oils (Fig. 4). Trisaturated triacylglycerols and those with
Table 4. *Fatty acid composition (mg/g nominated fatty acids*) for various encapsulated fish oil products

<table>
<thead>
<tr>
<th>Fatty acid</th>
<th>Cod liver oil</th>
<th>Salmon oil</th>
<th>Fish oil concentrates</th>
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<tbody>
<tr>
<td>14:0</td>
<td>40-50</td>
<td>67</td>
<td>2-117</td>
</tr>
<tr>
<td>15:0</td>
<td>3-5</td>
<td>4</td>
<td>Tr</td>
</tr>
<tr>
<td>16:0</td>
<td>112-122</td>
<td>156</td>
<td>22-132</td>
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<tr>
<td>16:1</td>
<td>74-91</td>
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<td>5-113</td>
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<td>16:2</td>
<td>2-8</td>
<td>8</td>
<td>Tr-12</td>
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<td>16:3</td>
<td>2-3</td>
<td>7</td>
<td>Tr-9</td>
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<td>16:4</td>
<td>4-9</td>
<td>19</td>
<td>Tr-37</td>
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<td>18:1</td>
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<td>140</td>
<td>118-119</td>
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<td>18:2 (n-6)</td>
<td>23-42</td>
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<td>9-11</td>
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<tr>
<td>18:3 (n-6)</td>
<td>Tr-2</td>
<td>3</td>
<td>Tr-1</td>
</tr>
<tr>
<td>18:3 (n-3)</td>
<td>12-20</td>
<td>8</td>
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<tr>
<td>18:4</td>
<td>24-28</td>
<td>28</td>
<td>16-23</td>
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<tr>
<td>20:0</td>
<td>Tr-2</td>
<td>2</td>
<td>3-7</td>
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<tr>
<td>20:1</td>
<td>71-110</td>
<td>18</td>
<td>8-60</td>
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<td>20:4</td>
<td>14-15</td>
<td>27</td>
<td>13-42</td>
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<tr>
<td>20:5 (n-3)</td>
<td>100-104</td>
<td>194</td>
<td>289-323</td>
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<tr>
<td>22:1</td>
<td>47-66</td>
<td>26</td>
<td>6-41</td>
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<tr>
<td>21:5</td>
<td>4-6</td>
<td>7</td>
<td>8-12</td>
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<tr>
<td>22:5 (n-3)</td>
<td>14-26</td>
<td>28</td>
<td>26-45</td>
</tr>
<tr>
<td>22:6 (n-3)</td>
<td>96-114</td>
<td>140</td>
<td>54-247</td>
</tr>
</tbody>
</table>

Saturates† | 179-204 | 253 | 63-280 |
Monoenoic   | 447-492 | 266 | 224-246 |
Dienoic     | 27-50   | 23  | 11-21  |
Trienoic     | 16-23   | 18  | 9-12   |
Tetraenoic   | 43-62   | 74  | 65-66  |
Pentaenoic   | 123-132 | 229 | 323-380 |
Hexaenoic    | 96-114  | 140 | 54-247 |

Tr, trace (<1 mg/g fatty acids).
† Sums of saturated, monoenoic, dienoic, trienoic, tetraenoic, pentaenoic and hexaenoic acids to assess the overall double-bond distribution.

The range of values, where shown, are indicative but not definitive of the variation in sample composition.

greater than twelve double bonds per molecule are present. The trimonounsaturated triacylglycerols (15 min, Fig. 4) are a major component.

Increasingly, fish and plant oil mixtures are being sold as healthfoods. The major effect is that the plant oil enhances the concentration of linoleic acid by, for example, a factor of five, compared with cod liver oil. A series of sharp peaks eluting after the trimonounsaturated triacylglycerol peak, but before the typical unresolved mixture associated with the introduction of fatty acids with more than three double bonds in the Ag⁺-HPLC profile, is indicative of the plant oil components (Fig. 4C).

Salmon oils can contain EPA and DHA at concentrations similar to those of anchovy and menhaden oils, with associated low levels of 20:1 and 22:1 (Table 4). As with all fish oils, the composition will be variable; in this case the encapsulated oil contained
significant quantities of very highly unsaturated triacylglycerols (Fig. 5). Spiking the oil with appropriate triacylglycerol standards gives a clear indication of the relative unsaturation of triacylglycerols in specific areas of the Ag⁺-profile. The presence of a peak with an equivalent retention time to cholesterol (Fig. 5) illustrates the presence of compounds other than triacylglycerols in these oils although the estimated concentration is less than 1%.

By careful winterization and blending or by solvent crystallization and/or molecular distillation, it is possible to produce encapsulated products with a combined EPA and DHA concentration of 300 mg/g. Many such products are available which contain 180 mg EPA/g and 120 mg DHA/g (Ackman, 1988). A fish oil concentrate is available with an EPA concentration in excess of this figure (289 mg EPA/g fatty acids), but it contains a significantly lower concentration of DHA (54 mg DHA/g fatty acids). This oil still contains trisaturated triacylglycerols together with the predominantly monoenic acid containing molecular species, but the concentrations of the very highly unsaturated triacylglycerols are significantly greater than those of crude body oils (McGill & Moffat, 1992).

Encapsulated oils containing concentrations of EPA and DHA totalling above 300 mg/g are available (Table 4). Many of these products are either methyl or ethyl esters. Such products are highly processed and are no longer in the natural form.
Fig. 5. Silver ion HPLC of standard triacylglycerols and cholesterol (A), salmon oil (B) and salmon oil spiked with standards (C). TS, tristearin (31.2 μg); DPO, 1,2-dipalmitoyl-3-oleoyl-rac-glycerol (24.3 μg); DOP, 1,2-dioleoyl-3-palmitoyl-rac-glycerol (28.4 μg); C, cholesterol (31.5 μg); TO, triolein (35.6 μg); TLO, trilinolein (42.2 μg); TL, trilinolenin (75.7 μg); TA, triarchidonin (61.4 μg).

(1992) has recently reviewed the absorption of fish oils and concentrates, including esterified and free acids, and highlights the problem of data comparison, when different forms of material have been administered.

Some encapsulated fish oils are sold as vitamin supplements. Halibut liver oil, for example, is sold chiefly as a source of vitamin A, and as such may be diluted with soya-bean oil and other types of fish oil to achieve the designated concentration of the vitamin. Consequently, these oils can contain concentrations of EPA and DHA totalling between 40 and 90 mg/g fatty acids and concentrations of linoleic acid between 340 and 400 mg/g fatty acids (C. F. Moffat, unpublished results). Components of both liver oil and diluent plant oil are apparent in the triacylglycerol distribution (Fig. 6).

NON-TRIACYLGlycerol COMPONENTS IN FISH OILS

The beneficial influences of fish oils on health have been universally accepted but, as mentioned earlier, detailed knowledge or even a perception of what a fish oil actually contains is often very limited. The enormous variation in triacylglycerol structure and fatty acid composition has been illustrated, furthermore not all fish oils are tri-
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Fig. 6. Silver ion HPLC of halibut liver oil extracted from a single liver excised from a halibut (Hippoglossus hippoglossus) caught off Rockall in September 1992 (A) and commercial samples of encapsulated halibut liver oil (B and C). The components from the diluent used to achieve the designated concentration of vitamin A are evident from the sharp peaks in the profile with retention times (RT) of between 20 and 30 min.

acylglycerol based. Oil from orange roughy (Hoplostethus atlanticus), a deep-water species which is an important component of New Zealand's commercial fisheries and is also found in the North Atlantic, contains less than 100 mg triacylglycerol/g. The major lipid is wax ester composed of saturated and monounsaturated fatty acids and fatty alcohols (C. F. Moffat & A. S. McGill, unpublished results). Sterols are also present in most marine species and present in fish oils within the range 4.5–8.0 mg/g oil (Kinsella, 1987). During processing a proportion of the cholesterol undergoes dehydration to produce cholesta-3,5-diene. Other sterenes are also present in encapsulated fish oils together with n-alkanes including pentadecane and heptadecane which can give a combined concentration around 100 µg/g. Analysis of an encapsulated fish oil gave a substantial unresolved complex mixture on the GLC profile, composed of cyclic and branched hydrocarbons. Polyaromatic hydrocarbons and pesticides have also been found in commercial fish oil products although at very low levels (ng/g). Processing of fish oils for edible use does reduce the levels of these contaminants to make oils acceptable for human consumption, but close quality control and monitoring is required to ensure consumer safety. Pb, Hg and Cd are present in the marine environment but again processing of fish oils greatly reduces the concentrations of heavy metals to a level which meets the Food and Agricultural Organization/World Health Organization Codex standards (Elson et al. 1981).

Not all minor components are necessarily contaminants. Fish oils are good sources of
vitamins A, D and E. There is substantial inter- and intraspecies variation in vitamin A content which, for liver oils, can vary between 10 and 50,000 μg retinol equivalent/g oil (Kinsella, 1987). The intra- and interspecies variation of vitamin D content is less than observed for vitamin A. Most fish oils contain only moderate amounts of vitamin D (<125 μg/g oil), although halibut liver oil and oil from several tuna species contain higher concentrations with up to 6250 μg/g liver oil.

Fish cannot synthesize vitamin E. As a consequence, the concentration of this vitamin, mainly α-tocopherol, is related to diet (Ackman & Cormier, 1967; Watanabe et al. 1981). The concentration in liver oil is higher than that in body oil where concentrations range from less than 10 μg/g oil to 750 μg/g oil (Kinsella, 1987). Vitamin E is an important antioxidant and, thus, helps to inhibit lipid oxidation and the associated production of hydroperoxides, aldehydes, short-chain alkanes, ketones, lactones and polymeric material (Frankel, 1980, 1982, 1984; Miyashita et al. 1991; Shukla & Perkins, 1991). Lipid peroxides and their aldehydic breakdown products, which are responsible for the off flavours associated with rancid fat (Terao & Matsushita, 1986), are important cytotoxic components associated with oxidative stress and damage (Halliwell, 1993; Parke, 1993). Lipid peroxidation proceeds by a free-radical chain reaction and lipid radicals can cause cell membrane damage and could promote oxidative DNA damage, which may contribute to the aetiology of inflammatory autoimmune diseases such as rheumatoid arthritis as well as cancer. The contrasting physiological influences of PUFA pose interesting questions which have to be fully investigated so that the outcome of clinical trials are not compromised. In conclusion, therefore, although there is now considerable evidence from biological studies to support the view that fish oils can play a major role in promoting human health (British Nutrition Foundation, 1992) the reasons are not understood. Before the factors which influence the activity associated with fish oils can be determined, it is imperative that researchers are made more aware of the chemical composition of the oils they utilize for their studies.

REFERENCES


