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Marine Mammal Oils

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1. INTRODUCTION

Marine oils are obtained from the flesh of fatty fish, liver of lean white fish, and blubber of marine mammals. Although lipids from marine fish have been used as food and medicine, traditional uses of blubber lipids of marine mammals were mostly industrially oriented, except for Innus and Eskimos. Marine mammal oils were lubricants or ''train'' oils as well as fuel and used for lighting (1). However, recent research findings on the importance of long-chain polyunsaturated fatty acids (LC PUFA) in human health have opened new channels for their value-added use in food and pharmaceutical industries (2). During the last three decades, it has been established that Greenland Eskimos living on their traditional diet have a lower incidence of coronary heart disease than do Danes living on a western-style diet (3, 4). It has been recognized that polyunsaturated fatty acids could be useful in controlling serum triacylglycerols, but the fatty acids provided by the food industry were often of the ω6 family (1).

Lipids from marine mammals such as seal, whale, and walrus are primarily stored as subcutaneous fat or blubber. Seal blubber comprises 29% of the carcass

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TABLE 1. Lipid Content (g/100 g tissue) of Selected Tissues from Four Species of Seals.[1]

Tissue	Harp	Gray	Ringed	Hooded
Blubber	93.88 ± 1.64	91.93 ± 1.07	93.55 ± 1.98	89.43 ± 1.82
Muscle	1.92 ± 0.03	1.82 ± 0.03	1.85 ± 0.53	2.36 ± 0.74
Brain	8.10 ± 0.32	10.25 ± 0.10	6.86 ± 1.01	7.40 ± 0.79
Kidney	2.97 ± 0.18	3.42 ± 0.04	3.58 ± 0.07	3.14 ± 0.05
Heart	2.19 ± 0.31	1.81 ± 0.38	2.32 ± 0.01	2.04 ± 0.01
Liver	3.83 ± 0.19	5.60 ± 0.94	3.71 ± 0.07	3.66 ± 0.03
Lung	2.24 ± 0.46	2.04 ± 0.03	2.05 ± 0.07	1.76 ± 0.01

[1]Data from Ref. (6).

weight and is considered a valuable component of it (5). Blubber lipids are mobilized in times of energy need and replenished when food is in excess (2). Although the blubber is the major site of lipid in the body of marine mammals, lipid is also found in the muscles, liver, kidney, heart, lung, brain, and other organs. Lipid content of different tissues in different species of seals varies (Table 1) (6). In addition, milk contains a high content of fat. A study carried out on hooded seals showed that females may secrete up to 10 kg of milk on a daily basis, which contains 60% fat (7). The milkfat of marine mammals resembles the composition of the depot fats of these animals (8). The mobilization of maternal fat reserves and transfer of milkfat from mother to pup occurs at very high rates (9). Lipids in marine mammals function as a source of energy, structural components of cells and tissues, and provide buoyancy (10). The blubber of marine mammals, especially harp seal, because of its economic importance, has been the subject of numerous studies on marine oils (6).

2. LIPID CLASSES

The oils from marine mammals are of very different composition. In the characterization of marine oils, many chromatographic techniques have been employed. These techniques include thin layer chromatography (TLC), gas chromatography (GC), high-performance liquid chromatography (HPLC), and supercritical fluid chromatography (SFC). These techniques have advantages and disadvantages depending on the goal of the analysis. TLC has been an excellent tool for qualitative analysis of components present in marine oils (11).

The various lipid classes of marine mammals include triacylglycerols, diacylglycerols, monoacylglycerols, free fatty acids, wax esters, cholesterol, cholesterol esters, hydrocarbons, vitamins, and ether lipids. Some marine oils are very simple, containing almost exclusively triacylglycerols (TAGs), whereas others contain a variety of lipid classes (11), as shown in Table 2. Seal blubber, the depot lipid, is mostly composed of neutral lipids (98.9%), in contrast to intramuscular lipids (78.8% neutral and 21.1% polar lipids) (13). TAGs are the predominant components of seal blubber, whereas organ lipids include both TAGs and phospholipids, and

TABLE 2. Composition of Arterial Lipid, as wt% of Total, for Three Species of Whales.[1]

Species	Tissues	Hydrocarbons	Wax and Sterol Ester	Triacylglycerol	Wax Alcohol and Sterol	Monoacylglycerol	Phosphatide	Free Fatty Acid
Sperm whale	Aortic lesions	—	16.5	6.4	13.8	—	57.8	5.5
	Aortic intima	—	13.1	4.4	13.0	0.4	66.1	2.7
	Aortic media	—	3.3	2.8	14.8	0.3	76.9	1.9
Killer whale	Fibrous aortic atheroma	—	17.3	11.4	12.6	—	58.7	—
	Aortic intima	0.3	7.4	29.5	17.0	0.2	45.5	—
	Aortic media	0.6	4.2	23.9	16.4	0.6	54.3	—
	Fatty coronary atheroma	—	56.4	20.9	4.1	—	18.6	—
	Coronary intima media	0.7	1.7	50.4	17.3	0.9	25.8	—
Pilot whale	Aortic lesions	2.8	17.1	9.2	28.6	0.4	35.9	6.0
	Aortic intima media	0.4	13.5	4.6	20.5	0.6	57.5	3.1

[1]From Ref. (12).

differences exist that originate from their varying proportions in different tissues. In marine mammals such as whales and seals that have enormous layers of fat under skin, TAGs serve as insulating material, which permits survival even in the cold waters of the Arctic and the Antarctic (14).

In addition to TAGs, wax esters (long-chain alcohols esterified to fatty acids) are another important group of neutral lipids found in marine mammals. Most species of marine mammals have C32, C34, C36, and C38 (total of alcohol plus acid) as major components (15). Whale oils are especially interesting because some contain fatty acids that are largely in the form of wax esters (16). The oils from the blubber of the Physeteridae may consist mainly of wax esters. The sperm whale blubber oil consists of a mixture of about 79% wax esters and 21% TAGs (17). The dwarf sperm whale (K. simus) blubber oils consist of 42% wax esters and 58% TAGs (18). The blubber fat of beaked whales (Berardius, Hyperoodon, and Ziphius) is composed almost entirely of wax esters (94–99%) along with low levels of TAGs (2–6%) (19). Several of possible functions for wax esters in marine mammals has been proposed; these functions include their role as a reserve energy store, buoyancy, metabolic water, thermal insulation, and biosonar (20–22).

Among unsaponifiable matters, hydrocarbons, especially long-chain hydrocarbons, are found in detectable amounts in marine mammal oils. Some marine oils contain less than 0.1% hydrocarbons, whereas others contain as much as 90% (23). In the liver of the seal, Arctocephalus (Pinnipedia), liver squalene was 0.50% of the oil (24). High squalene contents (90%, 91%, and 92.8%) occur in shark liver oils (23–25). The 16:0, 16:1, and pristine were found in the bottlenose whale (Berardius bairdi); (26) pristine is a highly unsaturated long-chain hydrocarbon (C49) occurring in the liver oil of sei whale (Balaenoptera borealis) (27) and sperm whale (Physeter catodon) (28). In the blubber of the sei whales, pristine was present at 11.3% and squalene at 13.1% of the total unsaponifiable fraction (29). Total hydrocarbons were present at 0.3% of dry matter weight of the blubber, 1.6% in liver, and 1.3% in the muscle (30). Among cetaceans, limited data for two dolphins have been published: In Delphinus longirostris liver, very long-chain hydrocarbons (C44) were detected (31), and zamene was present in Langenorynchus acutus (32).

3. FATTY ACID COMPOSITION

The fatty acid composition of marine lipids varies significantly, especially when compared with vegetable oils. The fatty acid composition of blubber oil of marine mammals is generally similar to fish oils as it contains a large proportion of long-chain highly unsaturated fatty acids. However, the proportion of fatty acids in fish and marine mammals varies considerably (2).

A marine oil typically contains some 40 different fatty acids, with carbon numbers varying from 10 to 24, which results in many different TAGs with the same carbon number, but with different levels of unsaturation (11). The fatty acids

present in marine mammal oils can be classified as saturated and unsaturated fatty acids. The fatty acids C12:0, C14:0, C16:0, and C18:0 are among the common saturated fatty acids. In addition, marine oils usually contain detectable ($\leq$0.2%) amounts of C20:0, and sometimes recognizable C24:0, but very little C22:0; the total is normally 0.5% or less for these three fatty acids (33). Even−numbered carbon fatty acids make up about 97% of the total fatty acids, with a few notable exceptions (17). Some fatty acids with odd-numbered carbon chain such as C15:0 and C17:0, along with traces of C13:0 and C19:0, have also been found in marine oils (33). Besides, monomethyl branched fatty acids have been isolated from marine oils, such as 3-methyldodecanoic acid from blubber of the sperm whale physeter catodon (34).

In contrast to relatively small amounts of saturated fatty acids, marine mammal oils have been characterized by high amounts of monounsaturated fatty acids (MUFAs) and ω3 polyunsaturated fatty acids (PUFAs) (35, 36). For instance, the content of MUFAs in neutral and polar lipids in seal blubber is more than 60% and 46%, respectively (37). Most fatty acids are long-chain with 20 to 22 carbon atoms and have ω3 configurations. Ackman et al. (38) have pointed out that the total C20 and C22 monounsaturated and polyunsaturated fatty acids in each layer of whale blubber is nearly constant, but the ratios of the monounsaturated to polyunsaturated fatty acids change significantly. The most common long-chain PUFAs in marine lipids are eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) as well as a smaller amount of docosapentaenoic acid (DPA), all of which belong to the ω3 family (10). The high content of ω3 fatty acids in marine lipids is suggested

TABLE 3. Fatty Acid Composition (g/100 g) of Blubber of Various Species of Seal.[1]

Fatty Acid	Bearded	Gray	Harbor	Harp	Hooded	Ringed
14:0	3.05	3.83 ± 0.03	4.52 ± 0.13	4.66 ± 0.49	4.40 ± 0.38	3.36 ± 0.66
16:0 DMA	ND	ND	ND	ND	ND	ND
16:0	10.14	6.61 ± 0.08	8.03 ± 0.38	6.24 ± 0.44	9.81 ± 1.57	4.82 ± 2.07
16:1 ω7	17.77	12.77 ± 0.09	19.26 ± 0.53	14.93 ± 0.46	10.09 ± 0.35	23.12 ± 0.18
18:0 DMA	ND	ND	NNND	ND	ND	ND
18:1 ω9 DMA	ND	ND	ND	ND	ND	ND
18:1 ω7 DMA	ND	0.45 ± 0.01	ND	0.46 ± 0.00	ND	ND
18:0	2.15	0.94 ± 0.02	0.85 ± 0.02	0.95 ± 0.03	1.83 ± 0.31	0.42 ± 0.19
18:1 ω9	16.76	24.50 ± 0.44	18.61 ± 0.55	18.59 ± 1.01	22.77 ± 2.66	19.72 ± 1.33
18:1 ω7	9.49	4.95 ± 0.09	5.16 ± 0.44	3.57 ± 0.36	3.75 ± 0.47	5.03 ± 0.46
18:2 ω6	2.30	1.28 ± 0.00	1.27 ± 0.04	1.36 ± 0.20	1.63 ± 0.20	2.58 ± 0.02
20:1 ω9	5.08	12.50 ± 0.43	9.06 ± 0.33	12.56 ± 2.92	13.00 ± 1.86	6.71 ± 2.17
20:4 ω6	0.94	0.51 ± 0.00	0.44 ± 0.00	0.36 ± 0.96	0.31 ± 0.03	0.30 ± 0.02
20:5 ω3	8.28	4.85 ± 0.13	9.31 ± 0.21	6.82 ± 0.69	5.21 ± 1.65	8.72 ± 1.06
22:0	0.63	<0.3	1.19 ± 0.02	<0.3	<0.3	0.75 ± 0.67
22:1 ω11	0.27	0.62 ± 0.03	0.31 ± 0.01	0.77 ± 0.61	0.86 ± 0.33	0.34 ± 0.01
22:5 ω3	4.26	5.06 ± 0.05	4.22 ± 0.14	4.78 ± 0.25	2.29 ± 0.08	5.46 ± 0.47
22:6 ω3	7.22	8.91 ± 0.29	7.76 ± 0.98	10.48 ± 1.98	9.56 ± 2.36	9.45 ± 1.74

DMA: dimethyl acetal.
ND: not detected.
[1]From Refs. (6) and (40).

TABLE 4. Fatty Acids Composition of Blubber Expressed as a Percentage by Weight of Fatty Acids Present from both Sexes of Four Species of Phocid Seals.[1]

	P. vitulina largha		*P. fasciata*		*P. hispida*		*P. barbatus*	
Fatty Acids	Male	Female	Male	Female	Male	Female	Male	Female
12:0	0.03	0.04	0.02	0.02	0.03	0.02	0.06	0.05
12:1	tr	tr	tr	tr	0.01	tr	tr	0.01
13:0	tr	0.01	0.01	0.01	0.01	0.01	0.01	0.01
13:1 ω9	tr	tr	tr	tr	tr	tr	tr	tr
14:0	1.89	2.45	2.34	3.00	3.36	1.68	1.77	2.76
14:1	0.38	0.42	0.43	0.39	0.83	0.56	0.29	0.26
15:0	0.31	0.41	0.33	0.33	0.25	0.22	0.39	0.40
15:1 ω6	0.07	0.05	0.06	tr	0.01	0.01	0.06	0.05
16:0	6.82	7.96	5.38	7.67	5.25	3.23	7.27	9.96
16:1 ω7	10.96	10.63	9.26	8.51	19.04	9.52	12.46	14.05
16:2 ω4	0.24	0.39	0.33	0.36	0.45	0.32	0.32	0.44
16:3 ω6	—	—	—	—	0.06	0.04	—	tr
16:3 ω3	0.11	tr	0.16	—	0.25	—	0.13	–
17:0	0.54	0.47	0.42	0.35	0.47	0.41	1.88	0.80
17:1 ω8	0.39	0.32	0.25	0.27	0.39	0.27	0.57	0.33
18:0	0.93	1.10	1.05	1.75	0.66	0.73	1.66	2.30
18:1 ω9	29.75	24.15	21.31	20.91	15.79	16.21	21.25	21.69
18:2 ω6	0.89	1.10	0.82	1.07	0.81	0.59	0.62	0.82
18:2 ω4	0.21	0.22	0.23	0.16	0.20	0.17	0.21	0.16
18:3 ω6	tr	0.05	tr	—	0.27	0.07	tr	0.11
18:3 ω3	0.13	0.32	0.30	0.88	0.52	0.22	0.11	0.21
18:4 ω3	0.52	0.83	0.80	0.73	1.03	0.75	0.72	0.93
19:0	tr	0.27	0.26	tr	0.73	0.35	0.35	0.52
19:1	0.02	0.07	0.15	0.11	0.10	0.08	0.41	0.32
20:0	0.06	0.09	tr	0.36	tr	0.07	tr	0.23
20:1	—	—	—	—	—	—	3.75	—
20:1 ω9	13.83	8.94	14.99	13.58	5.01	8.17	3.94	8.99
20:2 ω6	0.15	0.16	0.20	0.29	0.13	0.13	0.24	0.24
20:2 ω4	0.11	tr	tr	tr	0.04	0.10	0.08	0.12
20:3 ω6	tr	tr	tr	0.09	0.08	0.06	0.11	0.11
20:3 ω3	tr	tr	tr	tr	tr	tr	tr	tr
20:4 ω6	0.54	0.57	0.63	1.21	0.33	0.39	1.31	0.76
20:4 ω3	0.26	0.37	0.56	0.68	0.34	0.37	0.38	0.51
20:5 ω3	6.54	10.56	8.47	8.24	11.96	10.57	14.01	9.27
21:0	0.08	—	tr	tr	—	—	0.32	0.29
21:5 ω3	—	—	—	0.06	0	0.21	0.58	0.51
22:0	—	—	—	—	—	0.05	—	—
22:1 ω11	2.69	2.42	5.07	6.49	0.68	1.57	0.82	3.26
22:2 ω6	—	—	—	—	0.16	0.20	—	—
22:4 ω6	0.68	0.81	0.81	0.64	—	1.16	1.44	0.83
22:4 ω3	—	—	—	0.21	0.22	—	—	—
22:5 ω3	7.81	7.67	7.74	6.51	11.62	14.55	9.82	4.76
22:6 ω3	12.62	16.66	17.06	14.54	17.79	26.19	12.05	13.38
24:1	0.42	0.43	0.59	0.57	1.12	0.76	0.59	0.56

[1]From Ref. (44).

TABLE 5. Fatty Acid Composition of Lipids (g/100-g lipid) from Different Tissues of Harp Seal.[1]

Fatty Acid	Blubber	Muscle	Brain	Kidney	Heart	Lung	Liver
14:0	4.66 ± 0.49	2.46 ± 0.71	0.48 ± 0.07	1.15 ± 0.88	0.91 ± 0.03	2.40 ± 0.06	1.21 ± 0.20
16:0 DMA	ND	1.86 ± 0.15	1.66 ± 0.19	3.09 ± 0.67	3.74 ± 0.10	1.93 ± 0.02	0.15 ± 0.01
16:0	6.24 ± 0.44	12.29 ± 0.91	15.45 ± 0.64	12.71 ± 0.19	10.56 ± 0.81	24.45 ± 0.67	13.63 ± 0.76
16:1 ω7	14.93 ± 0.46	7.30 ± 0.79	1.33 ± 0.22	4.05 ± 0.09	4.32 ± 0.12	2.54 ± 0.08	5.34 ± 0.13
18:0 DMA	ND	0.78 ± 0.08	4.38 ± 0.43	1.65 ± 0.28	2.69 ± 0.33	1.68 ± 0.08	0.16 ± 0.04
18:1 ω9 DMA	ND	0.84 ± 0.09	1.82 ± 0.08	0.74 ± 0.06	2.58 ± 0.05	0.92 ± 0.02	0.19 ± 0.06
18:1 ω7 DMA	0.46 ± 0.00	0.97 ± 0.11	2.69 ± 0.18	0.79 ± 0.07	1.74 ± 0.03	1.01 ± 0.00	0.13 ± 0.04
18:0	0.95 ± 0.03	5.93 ± 0.19	18.08 ± 0.69	12.30 ± 0.59	11.09 ± 0.34	8.72 ± 0.26	19.55 ± 0.87
18:1 ω9	18.59 ± 1.01	18.48 ± 0.68	14.02 ± 0.89	12.52 ± 0.45	16.09 ± 0.17	13.41 ± 0.28	11.80 ± 1.45
18:1 ω7	3.57 ± 0.36	4.88 ± 1.39	4.60 ± 0.28	5.50 ± 0.35	4.56 ± 0.25	3.96 ± 0.27	6.10 ± 0.84
18:2 ω6	1.36 ± 0.20	1.54 ± 0.12	0.15 ± 0.09	3.33 ± 0.03	3.86 ± 0.08	1.14 ± 0.02	2.04 ± 0.38
20:1 ω9	12.56 ± 2.92	11.75 ± 1.58	1.83 ± 0.24	2.20 ± 0.57	4.51 ± 0.05	2.68 ± 0.62	3.40 ± 0.58
20:4 ω6	0.36 ± 0.96	3.87 ± 0.63	5.29 ± 0.22	10.11 ± 1.08	9.90 ± 0.13	5.81 ± 0.14	9.50 ± 0.57
20:5 ω3	6.82 ± 0.69	5.56 ± 0.60	0.70 ± 0.60	9.86 ± 0.53	9.74 ± 0.13	4.86 ± 0.31	8.07 ± 1.74
22:0	<0.3	1.81 ± 0.32	0.25 ± 0.09	0.99 ± 0.67	0.58 ± 0.32	0.56 ± 0.27	0.58 ± 0.04
22:1 ω11	0.77 ± 0.61	0.93 ± 0.23	0.21 ± 0.13	0.21 ± 0.04	ND	0.81 ± 0.00	0.23 ± 0.13
22:5 ω3	4.78 ± 0.25	2.21 ± 0.32	2.92 ± 0.26	2.13 ± 0.05	1.17 ± 0.06	2.35 ± 0.04	2.16 ± 0.05
22:6 ω3	10.48 ± 1.98	6.73 ± 1.30	15.56 ± 0.64	3.29 ± 0.83	4.11 ± 0.59	5.80 ± 1.07	8.17 ± 1.83

DMA: dimethyl acetal.
ND: not detected.
[1]From Refs. (6) and (40).

as a consequence of cold temperature adaptation, because at lower habitat temperatures, ω3 PUFA remain liquid and oppose any tendency to crystallize (33). Most long-chain PUFAs are formed in unicellular phytoplankton and multicellular sea algae and eventually pass through the food web and become incorporated into the body of fish and other higher marine species, including marine mammals, which often eat fish (39). The fatty acid composition of oils from most species of marine mammals has been summarized (1). Seal oils, because of the increasing interest in seal fishery and product development, have been in focus and frequently studied by researchers. The fatty acid composition of oils from different species of seal has been reviewed (2). Table 3 shows the fatty acids and their contents in blubber lipid from six species of seals.

The fatty acid composition of blubber of marine mammals such as seals is regulated by the diet (41), location (42), season, as well as physiological conditions such as age (43) and sex (44) of the animal. Table 4 presents the fatty acid compositions of seals of different species and sexes. In some marine mammals, the depot fats are largely dietary fatty acids laid down with a minimum change, but the fatty acids of the lipids of the essential organs have terrestrial characteristics (1). Fatty acid composition also depends on tissue and species of the animal. However, differences are most apparent among tissues (Table 5). Seal blubber, for example, had a high content of monounsaturated fatty acids, but it was low in arachidonic acid, dimethyl acetals, and DHA. Lung tissue lipids were high in palmitic acid, and heart tissue lipids had a higher content of linoleic acid. The proportions and fatty acid constituents in defferent tissues are different, most probably because of their varying functional requirements (6). The lipids of vital organs of seals and whales contain high proportions of fatty acids of the ω6 family, similar to those of terrestrial animals. The distinction between the fatty acids of functional organs such as liver, heart, and other organs with depot fat has been discussed (6, 45).

The fatty acid distribution in the TAG molecules in blubber oil of marine mammals is different from that of fish oils. The ω3 fatty acids (EPA, DPA, DHA) in blubber oil of marine mammals tend to be located primarily in the *sn*-1 and *sn*-3

TABLE 6. Positional Distribution of Fatty Acids in Triacylglycerols from Blubber Fat of Marine Mammals.[1]

		Fatty Acids (mol %)											
	Position	14:0	16:0	16:1	18:0	18:1	18:2	20:1	22:1	20:5	22:5	22:6	18:4	20:4
Harbor seal	1	4	11	15	1	29	1	18	8	3	2	3	—	—
	2	11	13	30	1	30	3	3	1	1	1	1	—	—
	3	1	4	14	1	26	1	16	7	8	6	10	—	—
Harp seal	1	1	7	9	1	27	1	17	4	6	4	15	—	—
	2	6	9	27	2	36	5	4	1	2	1	3	—	—
	3	1	5	11	1	20	2	7	1	12	11	26	—	—
Sei whale	1	3	13	3	4	14	1	33	10	3	1	6	1	5
	2	12	6	12	1	29	5	10	2	5	1	3	4	6
	3	4	6	2	2	7	1	28	16	6	3	16	1	3

[1]From Ref. (14).

TABLE 7. Fatty Acid Distribution in Different Positions of Triacylglycerols of Harp Seal Blubber Oil.[1]

Fatty Acid	*sn*-1	*sn*-2	*sn*-3
Total saturates	6.34	25.56	4.32
Total unsaturates	90.51	73.25	94.32
Total monounsaturates	62.91	65.98	51.09
Total polyunsaturates	27.60	7.27	43.23
Eicosapentaenoic acid (EPA)	8.36	1.60	11.21
Docosapentaenoic acid (DPA)	3.99	0.79	8.21
Docosahexaenoic acid (DHA)	10.52	2.27	17.91
Total omega–3	25.65	5.56	38.87
Total omega–6	0.75	1.58	3.34

[1]From Ref. (2).

positions of TAGs (Tables 6 and 7), whereas in fish oils, they are located abundantly in the *sn*-2 position of TAGs (46). In harp seal oil, as measured by ^{13}C NMR, only 3.2% of DHA and 4.6% of EPA were esterified to the *sn*-2 position of the TAG (47). During digestion, the fatty acids are liberated from *sn*-1 and *sn*-3 positions of the TAG by a position-specific enzyme such as pancreatic lipase, whereas the fatty acids attached to the *sn*-2 position are distributed in the body in the form of chylomicron (2).

4. OXIDATIVE STABILITY

Marine oils, like other highly unsaturated oils, are susceptible to oxidation and are more sensitive to oxidative deterioration than vegetable oils. Furthermore, they contain only insignificant amounts of natural antioxidants, such as tocophorols (48). The long-chain PUFAs (EPA, DPA, DHA) contain five or six double bonds that render them prone to atmospheric oxidation accompanied by the development of a fishy taste and smell (49). The secondary products of oxidation may give rise to unacceptable flavors and odors in the oil, impair digestibility of the oil, and can damage or destroy the body's cells, as a result of free radical attack (48). Although antioxidants are generally available for prevention of lipid oxidation in foods, natural antioxidants, such as tocopherols, unfortunately are not effective in inhibiting oxidation of marine oils (50). The autoxidation rate of PUFA depends on the type and structures of fatty acids in lipids (51). For instance, seal oil is more stable than fish oil and less vulnerable to the natural process of oxidation because of its fatty acid composition and distribution and location of fatty acids in the triacylglycerol molecules as well as because of its minor components (48). Removal of minor components from oil may result in lower oxidative stability of oils (52–55). Interesterification may change the oxidative stability of marine oils. Oxidative stability of minke whale blubber oil was reduced after redistribution of fatty acids with lipase or $NaOCH_3$ (50). The lower oxidative stability of interesterified whale oil seemed to

TABLE 8. Changes of Tocopherol and Acid Value of Seal Blubber Oil during Processing.[1]

Sample	α-Tocopherol (mg/100g)	Acid Value (mg KOH/g oil) (as % Oleic Acid)
Crude	2.8 ± 0.18	2.72 ± 0.10 (1.367%)
Alkali–refined	3.20 ± 0.11	0.08 ± 0.00 (0.040%)
Refined–bleached (RB)	3.1 ± 0.12	0.03 ± 0.01 (0.015%)
Refined–bleached and deodorized (RBD)	2.4 ± 0.09	0.04 ± 0.01 (0.020%)

[1]From Ref. (56).

be caused by displacement of PUFAs located at the *sn*-1 and *sn*-3 positions in TAG to the *sn*-2 position. PUFAs located at the *sn*-1 and *sn*-3 positions in whale oil might become more susceptible to free radical oxidation when they are transferred to 1,2- or 2,3-positions (50). Furthermore, overprocessing of marine oils may adversely affect their keeping quality by the removal of their endogenous natural antioxidants (Table 8), and it is recommended that processing be minimized or that important minor components with antioxidant activity be returned to the oil to improve their quality (56).

Control of autoxidation of unsaturated fatty acids is vital to preserve integrity, nutritional value, and functionalities of marine oils. Several reports in the literature have reviewed these matters in detail. Controlling of the availability of essential reactants in the oxidation process, such as oxygen, light, and other factors, may provide a means of retarding autoxidation. The level of available oxygen for reactions can be controlled by reducing the partial pressure of oxygen (57, 58) or replacing the headspace of the container with a nonreactive gas such as nitrogen. Proper packaging of lipid is also necessary to prevent contact of oxygen with unsaturated fatty acids. Microencapsulation that has been practiced as a packaging technique for oils can coat oil droplets and prevent their contact with atmospheric oxygen (59). In addition, hydrogenation controls autoxidation by reducing the reactivity of lipid molecule, but at the cost of reducing or eliminating PUFA and compromising the nutritive value of the oil. Moreover, antioxidants may be added at very low concentrations to control oxidation without changing the color and flavor to preserve the nutritive value of oils (2).

5. PROCESSING

The basic processing steps for the manufacturing of marine oils for human consumption involve cooking or rendering to release the oil followed by possible degumming, alkali refining, bleaching, and finally deodorization as well as possible

addition of antioxidants (2). During these processing steps, free fatty acids, mono- and diacylglycerols, phospholipids, sterols, vitamins, hydrocarbons, pigments, proteins and their degradation products, suspended mucilaginous and colloid-like matter, and oxidation products of fatty acids are removed from the oil (60). Processing steps of marine oils are similar to those for vegetable oils; however, the quality of crude marine oils is less uniform than that for crude vegetable oils. To obtain high-quality crude marine oils, proper handling and chilling of raw material to minimize oxidative damage after landing is vital (2).

The rendered, crude oil from blubber of marine mammals can also be treated with silica at low temperature under vacuum followed by bleaching and deodorization, as described by Mag (48). The resulting oil, which is completely bland, is essentially free of proteinaceous materials, phosphatides and mucilage, and prooxidant metals and very low in colored compounds, peroxides, and secondary oxidation products. This method avoids the use of acids and bases that are required in conventional degumming and alkali refining of marine oils, thus eliminating the risk of contamination as well as reducing the number of processing steps. The method is also environmentally friendly because it does not require soapstock and waste water processing (48). Another approach for preparing and stabilizing food-grade marine oil has been proposed by Kendrick and Macfarlane (49). This method includes treating the oil with silica, optionally in the presence of carbon, and with vacuum steam deodorization at 140–210°C in the presence of antioxidants (49). Regardless of the processing method employed, the resultant product must be stabilized by addition of food-grade antioxidants, particularly mixed tocopherols.

6. PRODUCTION OF ω3 FATTY ACID CONCENTRATES

Supplementaion of ω3 fatty acids has been recommended in addition to making attempts to substitute saturated fatty acids with PUFA in dietary lipids. Marine oils serve as a rich source of ω3 fatty acids and may be used as the raw material for preparation of ω3 fatty acid concentrates. It has been suggested that PUFA concentrates devoid of more saturated fatty acids are much better than marine oils because they allow keeping the daily intake of total lipids as low as possible (61). Enriched fatty acids or esters can be produced by fractional vacuum distillation (62), low-temperature crystallization (63), chromatographic separation, including HPLC (64–66), silver resin chromatography (67), supercritical fluid extraction (68), urea complexation (69, 70), and enzyme hydrolysis (71), among others.

Fractional vacuum distillation takes advantage of differences in the boiling points of fatty acids under vacuum. This method is a an old one and requires high temperature. The fractionation of marine oil esters is difficult because separation of such components becomes less effective with increasing molecular weight (72).

Low-temperature crystallization is based on the fact that the melting point of fatty acids changes considerably with the type and degree of unsaturation (73). At low temperatures, long-chain saturated fatty acids that have higher melting

points crystallize out and PUFAs remain in the liquid form. Briefly, the process consists of cooling the oil or fatty acids in a solvent, which holds for a specified period of time, and of removing the crystallized fraction by filtration. This method requires the least amount of equipment and the simplest apparatus and has been an indispensable method for preparing pure fatty acids (74, 75).

Fatty acids could also be separated according to their carbon number or degree of unsaturation with appropriate adsorbents (63). Chromatographic techniques such as HPLC and silver resin chromatography have been successfully employed to prepare ω3 fatty acid concentrates. However, these methods have certain shortcomings, including use of organic solvents, loss of resolution of the column upon repeated use, and difficulties in scaling up the process for commercial production (76).

Supercritical fluid extraction (SFE) is a method that circumvents some problems associated with conventional separation techniques. Carbon dioxide, as an inert, inexpensive, nonflammable, and environmentally acceptable gas is the solvent of choice because of its moderate critical temperature and pressure (76). SFE has been used effectively to refine marine oils and remove cholesterol, polychlorinated biphenyls (PCB), Vitamin E, and other components (77). The disadvantages of this process include the use of extremely high pressures and the high capital cost.

The simplest and most efficient technique for obtaining ω3 PUFA concentrates in the form of free fatty acids is urea complexation. This technique is well established for elimination of saturated and monounsaturated fatty acids (70). In this method, the saturated and monounsaturated fatty acids can easily complex with urea after hydrolysis of TAG with alkaline, and crystallize out on cooling and may subsequently be removed by filtration (70). This method is favored by many researchers because complexation depends on the configuration of the fatty acid moieties because of the presence of multiple double bonds, rather than of pure physical properties such as melting point or solubility (10).

It is generally considered that PUFA in the acylglycerol form is nutritionally more favorable than the corresponding methyl or ethyl esters as impaired intestinal absorption of alkyl esters of ω3 fatty acids has been observed in laboratory animals (78–81). Although most methods produce PUFA concentrates in the form of free fatty acids or their corresponding alkyl esters, enzyme hydrolysis is a technique proposed to produce ω3 fatty acids concentrates in the form of acyglycerols by hydrolyzing the TAG with lipase. Saturated and monounsaturated fatty acids can be easily hydrolyzed because they do not present any barriers to lipases such as the commercial microbial lipases (71).

Commercial marine mammal oils, such as seal blubber oil products, are available in form of soft gel capsules as nutritional supplements (82). The quality parameters of three commercial seal oil capsules are listed in Table 9.

Marine mammal oils or their ω3 concentrates can also be modified for different applications. Modifications include the changing of the fatty acid composition and/or their location in the glycerol backbone. Structured lipids containing both ω3 long-chain PUFAs, possibly from seal blubber oil, or their ω3 concentrates, and medium-chain fatty acids (MCFAs), which are saturated fatty acids with 6–12

TABLE 9. Quality Comparison of ω3 Seal Oil Capsules (Laboratory Analysis).[1]

Quality Indicators	Brand A	Brand B
EPA w/w %	6.89 ± 0.07	6.43 ± 0.07
DPA w/w %	4.11 ± 0.02	3.76 ± 0.00
DHA w/w %	8.16 ± 0.01	8.50 ± 0.10
18:3 ω3 w/w %	0.48 ± 0.01	0.48 ± 0.00
18:4 ω3 w/w %	1.10 ± 0.04	1.35 ± 0.06
Tocopherols mg/100 g	Up to 400	Up to 1400
Acid value mg KOH/g oil	3.21 ± 0.05	1.69 ± 0.03
Conjugated dienes	5.80 ± 0.25	7.63 ± 0.13
TBARS value μmol/g oil	4.20 ± 0.05	4.50 ± 0.15

[1]From Ref. (56).

carbon atoms, have been produced. Enzyme-catalyzed synthesis of structured lipids has been proposed, with commercial lipase preparations (83). The final products, with reduced calorie, exhibit the combined health benefits of long-chain PUFAs and MCFAs, which are believed to possess many unique nutritional and metabolic characteristics (83).

7. APPLICATIONS

Marine oils have been widely used in food and pharmaceutical industries as well as in nonedible applications. The nonedible uses of marine oils primarily exploit their highly unsaturated nature. In leather manufacturing, sulfated marine oils are used to treat leather to prevent its brittleness and dryness. Oleochemicals (fatty acids, fatty alcohols, esters of methyl and other alcohols, nitrogen derivatives) derived from marine oils find a wide range of industrial applications, including use in lubricants, corrosion inhibitors, plastic and rubber compounding, floatation agents, personal care products, cleaners, textile and paper additives, asphalt additives, and tableting, among others. In addition, marine oils have long been used as an alternative fuel to petroleum-based products (2). Other industrial uses of marine oils are in the manufacturing of polyurethane resins, cutting oils, caulks and sealants, printing ink formulations, insecticides, and buffing compounds (84). Refined marine oils have also been used in skin and hair care products. Marine oils may be used in the manufacturing of animal and poultry feed. Traditionally, marine oils have been used as an economic source of calories to stimulate growth of farmed animals. However, current knowledge about successful inclusion of EPA and DHA to mitochondria, microsomes, and lipoprotein membranes of chicken by feeding marine oil supplemented diets has provided novel uses for marine oils in the animal feed industry (2). It has been demonstrated that chicken has a natural predisposition to accumulate EPA and DHA from the precursor C18:3 (ω3) (85). Thus, inclusion of fish meal in chicken diet enhanced the accumulation of EPA and DHA in chicken flesh

(85). Feeding seal blubber oil at 1.25% to hens was found to increase long-chain ω3 PUFA and decrease arachidonic acid in the egg yolk lipids without any detriment to their sensory properties (82). This result is not surprising because deodorized oil was used in this study and the level of inclusion of seal oil was modest. In the food industry, the major global use of marine oils has been in the manufacturing of margarine and other edible oil products. In this, hydrogenated marine oils were a low-priced alternative to vegetable oils. However, hydrogenation reduces the unsaturation of fatty acids and negates the potential health benefits of PUFA; if not fully hydrogenated, introduction of trans-fats to product formulation is also of concern. Therefore, incorporation of long-chain fatty acids into the diet continues to be a topic of interest for food manufacturers, scientists, and consumers (2).

8. HEALTH BENEFITS AND DISEASE PREVENTION

Recognition of the health benefits associated with consumption of seafoods (ω3 fatty acids) is one of the most promising developments in human nutrition and disease prevention research in the past three decades. According to our current knowledge, long-chain ω3 PUFAs play an important role in the prevention and treatment of coronary artery disease (86), hypertension (87), diabetes (88), arthritis and other inflammatory (89), autoimmune disorders (90), as well as cancer (91, 92) and are essential for normal growth and development, especially for brain and retina (93). The most direct and complete source of ω3 oils is found in the blubber of certain marine mammals, especially in the harp seal. Among its advantages is that the body's absorption of ω3 fatty acids from marine mammal blubber may be faster and more thorough than is the case with flaxseed and fish oils (48). As marine mammal oils contain a high concentration of MUFAs, it is possible that some of their beneficial effects may be ascribed to their MUFAs or to the combined effect of MUFA and ω3 PUFA (94). A pilot study indicated that a low dose of seal oil supplementation can reduce atherogenic risk indices in young healthy persons, and the effects are strongly dependent on the integrated ω3 fatty acids dose (95,96). The essential fatty acids found in seal oil include a high level of DPA (up to ten times that of fish oils). There is growing evidence that DPA is the most important fatty acid that keeps artery walls soft and plaque free (48). Marine oils are also attractive from a nutritional point of view because they are thought to provide specific physiological functions against thrombsis, cholesterol buildup, and allergies (50). Oils from the blubbers of seal and whale have beneficial effects on selected parameters that play a role in cardiovascular disease; it has been hypothesized that the effect of whale oil is not mediated by its ω3 fatty acids alone (97). The difference in the beneficial effects of whale and seal oils on cardiovascular disease may argue against the distribution of ω3 fatty acids in TAG as being relevant to the superiority of whale oil, because the ω3 fatty acids are mainly in the *sn*-1 and *sn*-3 positions of both oils. The effect of whale oil is probably not mediated by ω3 fatty acids alone as the content of these fatty acids is relatively low in whale oil. Thus, in addition to

ω3 fatty acids, other dietary factors may play a role in the protective effects against atherosclerosis and thrombosis in Greenland Eskimos (97).

The beneficial effects of PUFA have also been ascribed to their ability to lower serum TAG, to increase membrane fluidity, and to reduce thrombosis by conversion to eicosanoids (98). Both EPA and DHA induced increases in the serum concentrations of the corresponding fatty acids as well as in their relative contents in platelets (99). However, distribution of ω3 PUFA in TAG molecules influences glycerolipid metabolism and arachidonic acid contents of serum and liver phospholipids as well as thromboxane (TX) A_2 production. In rats that were fed marine oils, for instance, plasma and liver TAG concentrations were more effectively reduced by dietary seal oil than by fish oil. Furthermore, dietary seal oil reduced arachidonic acid content in liver phosphatidylcholine and phosphatidylethanolamine and serum phosphatidylcholine more effectively than fish oil. Activities of fatty acid synthase (FAS), glucose-6-phosphate dehydrogenase (G6PDH), and the malic enzyme were significantly lowered when hamsters were fed seal oil (100). The predominant effect of seal oil was caused by the suppression of fatty acid synthesis in the liver (101). In addition, reduction of TX A_2 production of platelets and whole blood platelet aggregation by seal oil has been observed (102, 103).

9. HEALTH EFFECTS OF DPA

Docosapentaenoic acid (DPA) is an elongation product of EPA. Unlike other ω3 fatty acids, DPA has not been studied in any detail. Because of its availability, DPA is present in a much lower concentration compared with that of EPA and DHA in marine oils, and because of the difficulty in purifying it from mixtures containing EPA and DHA with similar physicochemical properties (104). Although only less than 1% DPA can be found in most fish oils, it is relatively more abundant in seal oil. Harp seal oil contains 4–6% of DPA. DPA is almost as important as either EPA or DHA. About one-third of the long-chain ω3 fatty acids circulating in human blood are attributed to DPA as the effective agent (105). DPA may have pharmacological effects different from those of EPAs and DHAs, and it has recently appeared as a focus topic (104).

It has been demonstrated that angiogenic activity in endothelial cells induced by vascular endothelial growth factor (VEGF) can be suppressed by ω3 PUFA treatment. Among LC PUFA, DPA was the most potent inhibitor of angiogenesis; the inhibitory activity by DPA pretreatment was approximately six-fold in comparison with that of EPA and DHA, which indicates that DPA could be developed as a novel drug or supplement against angiogenesis-related diseases (106). Angiogenesis plays a major role in tumor growth and metastasis, and blocking angiogenesis can restrict tumor growth. In addition, the stimulative effect of EPA on endothelial cells migration may be caused by DPA. In vitro studies have revealed that the activity of DPA to stimulate endothelial cell migration is ten times higher than EPA (107). Therefore, it is possible that the antiarteriosclerotic function of seal oil is mainly caused by DPA rather than by EPA and DHA (104). Evidence suggests that DPA is the

most important fatty acid in keeping artery walls soft and plaque-free (105). A recent study published by Tokyo Medical and Dental University indicates that DPA can be more than ten times as effective as EPA in helping to heal damaged blood vessels (105). Moreover, arachidonic acid-stimulated blood platelet aggregation was inhibited by ω3 fatty acids in a dose-dependent manner, among which DPA was the most potent inhibitor (105). DPA exhibits considerable activity for interfering with the cyclooxygenase pathways, thus inhibiting platelet aggregation most effectively (108). In addition, it has been suggested that the DPA concentration in platelet is inversely associated with coronary artery disease in women (109), and a high proportion of DPA in serum is associated with a decreased risk of acute coronary events in middle-aged men (110).

10. COMPARISON OF FISH OIL AND MARINE MAMMAL OIL

Fish oils and marine mammal oils are generally characterized by a large group of saturated and unsaturated fatty acids, which are commonly associated with their mix of TAGs (16). However, differences exist between the oils from fish and marine mammal sources.

Fish oils may generally be described as flesh oil, liver oil, or oil of the whole fish (111). The livers of white lean fish are known to be high in oil content. The fish livers of cod, halibut, and shark contain approximately 50% oil and serve as an important source of Vitamin A and Vitamin D (112). TAG is the major component of depot fats of fish. Ether lipids, however, are restricted to the liver oils of deep sea sharks (113). Like marine mammal oils, fish oils are rich in MUFA and PUFA, and they are good sources of ω3 PUFA such as EPA and DHA. However, DPA, which is abundant in blubber of marine mammals, especially seals, is found in much lower level or is absent in fish oils. Furthermore, the molecular configurations of EPA and DHA in fish oil vary slightly from that found in marine mammal oils (48). Research has shown that seal oil may be more beneficial than fish oil in reducing the risk of heart disease and diabetes, Which is likely because of the relative absence of DPA in fish oil and possibly the slower rate at which the body can use EPA and DHA from fish oil (105). Fish oils vary considerably in the type and level of their fatty acids depending on the particular species and their diets. For example, fish species raised by aquaculture often have a lower level of ω3 fatty acids than those in the wild (48), and freshwater fish contain higher levels of the ω6 fatty acids than do marine fish (112). The fatty acid distribution in TAG of fish oil is also different from that of marine mammal oil. In fish oil, PUFAs occupy the *sn*-2 position of TAG, saturated and MUFAs the *sn*-1 position, and MUFAs the *sn*-3 position. In marine mammals, however, the *sn*-1 and *sn*-3 positions are occupied by LC PUFA such as EPA and DHA, and especially the *sn*-3 position, as noted earlier. The *sn*-2 position is esterified to saturated fatty acids and especially to C16 and C18 MUFAs (14, 112). The different distribution of fatty acids might be a factor for lower oxidative stability of fish oils compared with seal oil (48).

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