Brazilian Encapsulated Fish Oils: Oxidative Stability and Fatty Acid Composition[1]

C.M. Fantoni, A.P. Cuccio, and D. Barrera-Arellano*

Laboratório de Óleos e Gorduras, FEA/UNICAMP, Campinas, SP, Brazil

ABSTRACT: Encapsulated fish oils are extensively commercialized in Brazil. These products could have an effect in the reduction of heart diseases because of their high content of polyunsaturated fatty acids. However, information about their composition and quality are still lacking. Fatty acid composition, oxidative stability (Rancimat, 80°C, 2.5 g sample and 8.3 L/h air), peroxide value (PV), and polar compound content were determined in sixteen trademarked encapsulated fish and cod-liver oils, purchased from Brazilian markets. The highly polyunsaturated fatty acid (eicosapentaenoic acid + docosahexaenoic acid) level appear to be typical of marine oils (16.2 and 32.1%). The PV ranged from 2.1 to 20.3 meq/kg, which is considered high, whereas the Rancimat induction periods varied from 1.95 to 8.45 h. The samples analyzed contained from 0.1 to 8.3% polar components. In some cases, both composition and quality were inadequate for this kind of product. One of the samples did not contain cod-liver oil, it appears that it contained soybean oil. *JAOCS 73,* 251–253 (1996).

KEY WORDS: Brazilian encapsulated fish oils, cod liver oil, encapsulated fish oils, fatty acid composition, fish oils, marine oils, oxidative stability, polar components, Rancimat.

Encapsulated fish oils are popular and readily available in health-food stores, pharmacies, and supermarkets. They are recommended as an aid in the prevention of heart diseases (1,2). These kind of oils, rich in ω3 polyunsaturated fatty acids in the form of eicosapentaenoic acid [EPA (20:5n-3)] and docosahexaenoic acid [DHA (22:6n-3)], may reduce platelet aggregation, platelet vessel wall interactions, and blood plasma viscosity (2,3).

Recent reports, however, have expressed concern about the oxidative deterioration of fish oils and have suggested that ingestion of unstabilized fish oils entails a risk of exposure to potentially toxic products of ω3 fatty acid peroxidation. These products may play a role in carcinogenesis, inhibit prostacyclin production, and may exert other adverse biological effects (3).

It was the purpose of this work to check oxidative stability, fatty acid composition, and polar component content of commercial fish oil capsules.

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*To whom correspondence should be addressed at Laboratório de Óleos e Gorduras, FEA/UNICAMP, Caixa Postal 6091 ZC:13081-970 Campinas, S.P., Brazil.

EXPERIMENTAL PROCEDURES

The samples used in this work include all trademarks of encapsulated marine oils available in drugstores and supermarkets in São Paulo and Campinas, Brazil. In all, there were 15 commercial samples (soft gelatin capsules of fish and cod-liver oils) and one sample of shark-liver olein, still not commercial, which was fractionated in the Fats and Oils Laboratory, FEA/ UNICAMP (Campinas, Brazil) and encapsulated with soft gelatin by RP SCHERER Co. (Sorocaba, São Paulo).

All samples were stored in the freezer, and at the time of the analysis, the oil was taken out of the capsules and weighed. Peroxide value (PV) was determined by AOCS Method Cd 8-53 (4).

To determine polar components percentage, we used the IUPAC–AOAC Method (5). Oxidative stability was determined by AOCS Method Cd 12-57, and RANCIMAT equipment conditions used were temperature 80°C, air flow 8.3 L/h, and sample weight 2.5 g. The fatty acids in the oil samples were converted to methyl esters by a procedure adapted from Hartman and Lago (6). Gas chromatography was executed with a Perkin-Elmer Sigma 3B (Norwalk, CT) in a

TABLE 1
Brazilian Encapsulated Fish Oils: Oxidative Parameters and Polar Components

Sample	Oil	Peroxide value (meq/kg)	Induction period[a] (h)	Polar components (%)
1	Fish	20.3	2.0	3.2
2	Fish	6.3	10.9	7.2
3	Fish	3.4	4.2	6.7
4	Fish	4.8	5.4	6.7
5	Fish	3.8	3.6	3.1
6	Cod liver	2.1	6.3	5.7
7	Cod liver	4.5	6.6	2.6
8	Cod liver	13.8	2.4	4.3
9	Cod liver	2.6	4.3	4.0
10	Cod liver	15.5	8.5	7.0
11	Cod liver	5.0	6.7	5.8
12	Cod liver	14.1	10.4	5.4
13	Cod liver	3.5	13.6	5.9
14	Cod liver	4.4	13.0	8.3
15	Cod liver	16.0	101.2	4.4
16	Crude shark olein	3.0	4.2	0.1

[a]Rancimat 80°C; air flow 8.31 L/h; 2.5 g sample weight.

TABLE 2
Brazilian Encapsulated Fish Oils: Fatty Acid Composition

Sample[a]	$C_{14:0}$	NI[b]	$C_{14:1}$[c]	$C_{16:0}$	NI	$C_{16:1}$	NI	$C_{18:0}$	$C_{18:1}$
1	7.1	0.3	0.7	17.8	0.7	10.1	—	3.9	13.2
2	6.5	0.3	0.6	14.1	0.7	8.6	—	2.6	13.1
3A	7.4	0.3	0.7	18.0	0.6	10.1	—	3.9	12.9
3B	7.6	—	0.6	16.1	0.9	10.6	—	3.1	13.2
4	8.1	0.2	0.6	18.5	0.7	10.6	—	3.8	12.9
5	8.7	0.4	0.8	17.7	0.9	10.5	0.6	4.6	14.3
6	4.4	0.3	0.5	11.4	—	9.4	—	2.8	23.0
7	7.3	0.2	0.6	17.3	0.8	9.6	0.6	4.7	15.1
8	17.6	0.2	0.5	17.3	0.5	9.3	0.5	3.9	14.1
9	16.9	0.4	0.7	13.6	0.7	8.6	0.1	2.6	13.6
10	4.6	0.2	0.6	11.2	0.7	0.1	0.2	2.5	24.4
11	4.3	0.1	0.4	11.1	0.8	9.2	0.2	2.5	25.5
12	5.0	—	0.5	13.8	0.5	6.5	0.1	2.9	30.6
13	4.5	0.2	0.7	11.6	0.9	9.6	0.4	2.7	24.7
14	5.5	—	0.4	13.2	0.4	6.9	0.2	2.9	28.8
15A	0.5	—	—	11.9	—	0.7	—	3.5	22.8
15B	0.4	—	—	11.8	—	0.4	0.1	3.6	23.9
16	3.0	0.2	0.8	18.6	0.5	5.4	0.4	4.4	20.7

Sample	$C_{18:2}$	$C_{20:0}$	NI	$C_{18:3}$	$C_{20:1}$[c]	$C_{22:0}$	NI	$C_{22:1}$	NI
1	44.5	0.2	0.2	2.4	4.1	0.2	0.1	0.7	1.1
2	3.2	—	—	4.7	3.9	—	—	3.7	1.1
3A	3.8	0.2	0.1	2.2	4.2	0.4	0.7	1.2	—
3B	4.2	—	0.1	2.4	4.4	0.2	0.6	1.4	—
4	3.9	0.1	0.1	2.2	4.2	0.1	—	0.6	—
5	4.6	3.0	—	2.9	—	0.1	—	1.0	1.2
6	3.2	0.4	—	2.0	2.5	—	—	6.7	—
7	5.0	—	—	3.7	3.0	0.2	0.8	1.1	—
8	4.2	0.1	0.2	2.5	4.2	0.8	0.8	1.2	—
9	2.7	—	—	11.0	3.2	—	—	9.5	—
10	5.2	—	—	11.1	2.4	—	—	6.7	—
11	4.0	—	—	11.3	2.5	—	—	7.3	—
12	9.9	0.2	0.1	5.3	2.6	0.1	—	2.5	—
13	3.6	—	—	11.2	2.4	—	—	7.4	—
14	10.0	0.2	0.3	6.7	2.7	0.2	—	2.7	—
15A	51.8	0.4	0.6	5.4	0.2	0.5	—	—	—
15B	51.5	0.4	0.3	5.4	—	0.5	—	—	—
16	1.4	1.0	—	7.5	1.3	0.2	—	2.5	—

Sample	NI	$C_{20:4}$[c]	$C_{20:5}$	NI	$C_{24:0}$	$C_{22:3}$[c]	NI	$C_{22:5}$	$C_{22:6}$
1	—	1.1	16.7	—	0.4	0.7	0.3	1.8	11.2
2	—	1.0	18.9	—	0.6	0.7	0.3	2.6	13.2
3A	—	1.0	16.9	—	0.3	0.6	0.4	1.9	11.9
3B	—	1.0	17.8	0.2	—	0.5	0.3	1.9	12.7
4	—	1.2	16.4	—	—	0.5	0.4	2.1	11.4
5	—	0.8	15.2	—	0.6	0.7	0.4	2.0	8.2
6	0.6	0.7	8.6	—	0.7	0.3	0.2	1.1	8.9
7	—	0.8	14.1	0.6	0.1	0.6	0.4	2.0	9.5
8	—	0.9	16.4	—	0.6	0.3	—	1.7	10.9
9	—	0.8	12.5	—	0.4	0.4	0.2	1.7	9.8
10	—	0.6	9.5	—	0.3	0.4	0.1	1.5	7.4
11	—	0.6	9.9	0.3	—	0.4	—	1.6	7.8
12	0.8	—	10.8	0.3	—	0.4	0.1	1.3	5.5
13	0.6	—	9.5	0.5	—	0.3	0.1	1.4	7.5
14	—	0.8	11.4	—	—	0.3	—	1.3	4.8
15A	—	—	0.6	—	0.1	—	—	0.1	0.6
15B	—	—	0.5	—	0.1	—	—	—	0.7
16	2.1	0.7	4.1	1.8	0.5	0.2	1.2	2.0	1.1

[a]Samples that are divided into A and B are samples of only one trademark but from differents lots; —, not detected.
[b]NI, not identified.
[c]Not confirmed.

packed column with 10% Silar 10C. The temperature was 175°C for the column and 225°C for the injector and detector; the nitrogen flow used was 25 mL/min. All analytical results are averages of two complete analyses.

RESULTS AND DISCUSSION

Tables 1–3 show in a comparative way the oxidative state, oxidative stability, fatty acid composition, and content of highly polyunsaturated fatty acids (EPA + DHA).

A considerable range of quality is evidenced by the PV. They show that both hydroperoxides and other types of peroxide linkages, as well as their decomposition products, are present in the oils (3). The oils examined in the present study contained from 2.1 to 20.3 meq of peroxide/kg of oil. In 1994, Mounts (7) explained that the Codex Alimentarius established a maximum peroxide value of 10 meq/kg for edible vegetable oils, but recent changes in 1993 in the Codex decreased this level to 5 meq/kg for any kind of refined oil. Our data show that 7 of the 16 samples are outside of these specifications. Actually, local legislation will soon support these alterations. Anyway, all results are considered high because the PV near 0 meq/kg is typical for fresh refined vegetable oils. Oxidative stability determined with the Rancimat gives an idea of an oil's resistance against oxidation, without considering the gelatin capsule. As shown in Table 1, second column, there is a considerable difference among the samples regarding their stability; while the lowest induction period is 2.0 h for sample 1, the highest one was 13.6 h for sample 13. The Rancimat stability of 101.2 h for sample 15 was not considered further because it exceeds too much the range of expected results. The induction periods found for the samples in this work can be considered low. This result was really expected because of the susceptibility of polyunsaturated fatty acids to oxidation.

The polar components content ranged from 0.1 to 8.3%; therefore, all samples contained varying percentages of mono- and diacylglycerols and free fatty acids. However, no sample exceeded 25%, which is the maximum polar compound value for "frying oil" (8).

The fatty acid composition of encapsulated marine oils is given in Table 2. It shows some typical characteristics of marine oils, such as diversity of fatty acids and presence of some highly unsaturated fatty acids with long carbon chains. There are no large qualitative differences among the several trademarks, and the fatty acid percentages are also similar in the different trademarks. That's because of the similar origin of several different oils.

Some laboratories add vegetable oil to the marine oil to avoid fast oxidation of the polyunsaturated fatty acids (9). Others may have used this same procedure with the objective of decreasing cost because vegetable oils are cheaper. In either case, however, there is no label claim advising that food supplement benefits are reduced. Sample 15, which is completely outside of acceptable standards, can be pointed out as one of these cases. Its composition proved that there are only traces of fish oil in it (0.63% $C_{22:6}$). This sample is mainly constituted by a vegetable oil that is similar to soybean oil, whose $C_{18:3}$ percentage is normally 5 to 7%.

TABLE 3
Encapsulated Fish Oils: EPA + DHA Contents[a]

Sample	Label Claim (mg/g of EPA + DHA)	EPA + DHA (%)	EPA + DHA (mg/g sample)
1	300	27.9	279
2	300	32.14	321.4
3A/B	300	28.8/30.5	287.6/305.0
4	ND	27.8	278.3
5	ND	23.8	238.5
6	ND	17.5	174.7
7	300	23.5	235.1
8	300	31.2	312.4
9	ND	22.3	223.0
10	ND	16.9	169.0
11	ND	17.7	177.2
12	ND	16.3	163.0
13	ND	16.2	162.0
14	ND	16.9	169.4
15A/B	ND	1.3/1.1	12.5/11.3
16	—	21.2	211.8

[a]EPA, eicosapentaenoic acid; DHA, docosahexaenoic acid; ND, not declared. See Table 2 for A/B samples explanation.

Contents of EPA + DHA, the most important and critical components of marine oils, are shown in Table 3. Generally, EPA + DHA levels are less in cod-liver oils than in muscle fish oils, so that cod-liver oil consumption is oriented to the supply of A and D vitamins. Although only five samples showed EPA + DHA contents on the label, the results indicated that these label claims for almost all samples are presented with reasonable honesty. Only sample 7 presented a result that was really far from the specification.

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