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Fatty acids and cholesterol oxidation in salted and dried shrimp

Geni R. Sampaio, Deborah H.M. Bastos, Rosana A.M. Soares, Yara S. Queiroz, Elizabeth A.F.S. Torres *

Department of Nutrition, School of Public Health, University of São Paulo (USP), Master of Public Health (USP) (PRONUT-FCF/FEA/FSP), Av. Dr. Arnaldo, 715 - São Paulo, SP 01246-904, Brazil

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Abstract

The aim of this work was to evaluate the occurrence of cholesterol oxidation products and to analyze the lipidic profile in salted–dried shrimp. Fifty samples of salted–dried shrimp were evaluated, and the cholesterol oxides (7β-OH, 7α-OH, 7-Keto and 25-OH) were quantified by high-performance liquid chromatography. The cholesterol oxides: 7β-OH (34.63–72.56 μg/g), 7α-OH (5.02–12.12μg/g), 7-Keto (7.44–32.68 μg/g) and 25-OH (2.37–22.88 μg/g) were determined in all samples analyzed. Regarding to the total cholesterol content and the average thiobarbituric acid reactive substances (TBARS) content, the results ranged from 73.88 to 247.69 mg/100 g, and 0.02 to 1.30 mgMA/kg, respectively. The fatty acids profile was: 27.48% saturated, 43.90% monounsaturated and 28.61% polyunsaturated. The presence of cholesterol oxidation products and the values of TBARS indicate the degree of oxidation of this product, which was probably initiated by inadequate conditions of processing and storage.

Keywords: Shrimp; Lipidic oxidation; Cholesterol oxides; Fatty acids; COPs

1. Introduction

Cholesterol, an important biological compound widely distributed in food, readily undergoes oxidation under different conditions resulting in a large number of oxidation products (Chen & Chen, 1994). More than 80 cholesterol oxidation products (COPs) have been identified so far. The most common COPs present in foods are: 7β-hydroxycholesterol (7β-OH), 7α-hydroxycholesterol (7α-OH), 7-ketocholesterol (7-Keto), 6-ketocholesterol (6-Keto), 5,6α-epoxycholesterol (5,6α-EP), 5,6β-epoxycholesterol (5,6β-EP), 25-hydroxycholesterol (25-OH), 20-hydroxycholesterol (20-OH) and cholestanetriol (triol) (Tai, Chen, & Chen, 1999).

A revision study by Morales-Aizpuria and Tenuta-Filho (2002) reinforced the relation between cholesterol oxides in foods and its implication in cytotoxic, angiotoxic and atherogenic processes, among others (Gallina Toschi & Caboni, 1992; Guardiola, Codony, Addis, Rafecas, & Boatella, 1996; Linseisen & Wolfram, 1998; Peng, Hu, & Morin, 1991). The COPs levels found in foods should be considered potentially important, until the levels allowed are unknown. The level of plasma cholesterol is increased either by the ingestion of high cholesterol oxides containing food or by the ingestion of cholesterol oxides alone. Absorption of cholesterol oxides by the intestine is known to happen in animals (Fornas, Martinez-Salles, Camanas, & Baguena, 1984; Osada, Sasaki, & Sugano, 1994) and the relationship

* Corresponding author. Tel.: +5511 3066 7771x230; fax: +5511 3066 7771x233.
E-mail address: eatorres@usp.br (E.A.F.S. Torres).

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between the oxidation of lipoproteins and atherosclerosis has also been extensively studied (Staprans, Rapp, Pan, Hardman, & Feingold, 1996).

The occurrence of cholesterol oxides in foods is a major concern in public health along with the prevention of oxidation process that may take place during processing or storage of foods.

The profile and amount of oxides generated during processing and storage of foods are greatly dependent on their characteristics and the interactions between their components and decomposition products (Morales-Aizpuria & Tenuta-Filho, 2002).

Tai, Chen, and Chen (2000) revised the cholesterol oxides content in foods and concluded that heat is the major responsible for its generation, mainly in extensively processed food. The presence of cholesterol oxides in fish foods are seldom reported, although they are often prepared by the use of heat (Sanchez-Muniz, Viejo, & Medina, 1992; Sebedio, Ratnayake, Ackman, & Prevost, 1993).

The salted–dried shrimp is prepared from shrimps collected by the craft fishing in the northeast coast. Processing consists of shrimps cooking in brine, containing a part of salt approximately for three of shrimp, for 30 min, following by drainage in a mat of leaf of interlaced palm tree, for 4–8 h, with direct sunlight incidence. In rainy or cloudy days, the shrimp is drained and stays in covered chests. The same brine is used several times, adding new salt to each portion of cooked shrimp. The shelf-life of the product ranges from 8 to 15 days, depending on the drying degree (Kraemer, 2000; Rogers & Sanders, 1992).

Shrimps are rich in polyunsaturated fatty acids and cholesterol, therefore, possess a great potential for the cholesterol oxides formation, which is not well established. The objective of this work was to evaluate the occurrence of cholesterol oxidation products (COPs) and to analyze the fatty acid profile in salted–dried shrimp.

2. Materials and methods

2.1. Shrimp samples

Fifty samples of salted–dried shrimp acquired from different city-halls food markets of São Paulo were classified as: *shrimp 1* (collected in 2003/03/07 – summer); *shrimp 2* (collected in 2003/06/14 – autumn); *shrimp 3* (collected in 2003/06/14 – winter) and *shrimp 4* (collected in 2003/08/02 - winter).

2.2. Reagents and solvents

Cholesterol and COPs (7-K, 7α-HC, 7β-HC and 25-HC) were purchased from Steraloids Inc. – USA. High-performance liquid chromatography (HPLC) grade solvents (2-propanol and hexane) were purchased from Merck – Germany and filtered using HV-PVDF membranes with 4.7 cm × 0.45 μm from Millipore – Brazil. Samples analyzed by HPLC were filtered using Millex® HV-PVDF cartridges with 2.5 cm × 0.45 μm from Millipore — Brazil. Chloroform methanol and (sodium sulfate) Na_2SO_4 used in the extraction of cholesterol and COPs were ACS grade or equivalent. As 2-propanol is a hygroscopic solvent, it was dried over anhydrous Na_2SO_4 before use to avoid variations of HPLC retention times. Hexane was purified passing it through a column with activated alumina and silica gel before using to assure UV transparence. Sigma mixture FAME 189-19 was used as quantitative external standard.

2.3. Methods

2.3.1. Moisture

Moisture was measured as described by AOAC (1995).

2.3.2. Determination of the water activity

Water activity (Aw) was measured through the use of automatic analyzer equipment developed by Aqualab-Decagon Devices Inc., model CX-2 (Washington/USA). Aw was expressed by the ratio of the pressure of food water vapor over the pure water vapor pressure.

2.3.3. Determination of TBARS

TBARS determination was performed using the extraction method, which is recommended as ideal for analyses involving fish (Vyncke, 1975). The 1,1,3,3-tetraethoxypropane was used as standard, and the recovering content 89%. Absorbancy reading was taken at 538 nm using a Cecil Brand spectrophotometer model 1020. The values found were interpreted as mg of 2-thiobarbituric acid reactive substances (TBARS) per 1000 g of sample.

2.3.4. Lipids analysis

Lipids were extracted by the dry column methodology suggested by Marmer and Maxwell (1981), which offers a viable alternative to extraction using chloroform, methanol and water. These extracts were used in the following analyses. Ten milliliters of the dry column extract were transferred to a tared beaker and evaporated under nitrogen. Afterwards the extract was placed in a stove at 105 °C and, after 3 h, cooled in a desiccator and weighed.

2.3.5. Fatty acids

Lipid extract was submitted to cold saponification and methylation with BF_3 in methanol (Metcalfe, Schmitz, & Pelka, 1966). Fatty acids (FAs) analysis was conducted in a GC Chrompack CP9002, split injector

in a ratio 1:67, flame ionization detector and capillary column of fused silica CP-SIL 88 (50 m; 0.25 mm and 0.25 μm). The temperature of the injection port was 270 °C and detector was 300 °C. The initial oven temperature was 100 °C followed by an increase to 240 °C at a rate 5 °C/min. The carrier gas was hydrogen at 16 psi. The identification of the fatty acids was achieved by comparing of their retention times with those of the fatty acid methyl ester mixture #189-19 which was used as quantitative external standards.

2.3.6. Cholesterol and cholesterol oxides (7β-OH, 7α-OH, 7-Keto and 25-OH)

Cholesterol and cholesterol oxides were extracted using the methodology described by Csallany and Ayaz (1976) adapted from Folch, Less, and Stanley (1957). Fifteen milliliters of the dry column extract were transferred to a flask where 20 mL chloroform/methanol (2:1 v/v) was further added and homogenized for 1 min (medium speed). The homogenate was transferred to the separating funnel and washed twice with distilled water (50 mL) and mixed for 1 min. The combined water was re-extracted twice with chloroform/methanol (2:1 v/v). Non-aqueous phase was filtered with anhydrous Na_2SO_4, and then filtered with Whatman no. 1 filter paper. Filtrate was dried in vacuum rotary evaporator and freed of solvent by using a nitrogen flush.

After this procedure samples were dissolving in 3 mL of mobile phase and injected into HPLC [thermo separation products (TSP)] with: (1) Pump (SpectraSystem and Spectra Series Gradient Pumps). (2) Degasser (SCM Vacuum Membrane Degasser). (3) UV/VIS Detector (SpectraSystem UV/VIS Detectors). (4) Automatic Injector (SpectraSystem and Spectra Series Autosamplers).

Chromatography method was described by Chen and Chen (1994) adapted by Vicente (2003). The column used was CN (intermediate phase) and the mobile phase was the mixture (97:3 v/v) of hexane-isopropanol with flow rate 1.0 mL/min. The sample injection volume was 20 μL. Wavelength used in cholesterol and cholesterol oxides (7β-OH, 7α-OH, and 25-OH) were 206 nm except the 7-Keto, taken at 233 nm (Fig. 1).

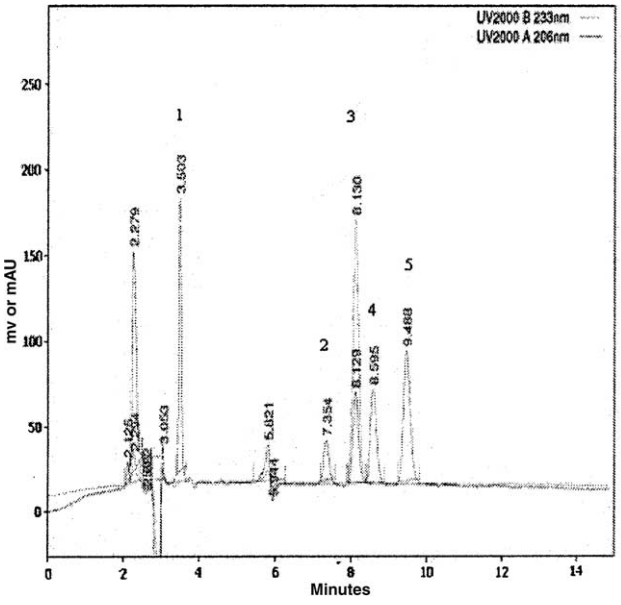

Fig. 1. HPLC of cholesterol and four COPs standards: Peak (1) cholesterol, Peak (2) 25-OH, Peak (3) 7-Keto, Peak (4) 7α-OH, Peak (5) 7β-OH.

2.3.7. Data analysis

Data are expressed as means and standard deviations. Statistical tests one-way Anova and Tukey's posteriori test were used to analyze statistical differences between samples. The software used was SPSS version 10.0.

3. Results and discussion

The salted–dried shrimp presented average moisture and water activity (Aw) level of 51.04 g/100 g and 0.74 (Table 1). The moisture level was above the allowed by Brazilian law (35%) for industrial and sanitary regulation of products by animal origin (R.I.I.S.P.O.A.) (BRASIL, 1997), suggesting that either the samples were not dried or stored properly, which agree with the study of Kraemer (2000) in salted–dried shrimp. Ashes content (less than 25%) were in accord to (R.I.I.S.P.O.A). The high level of Aw and moisture may lead to microorganisms growth, which can be harmful to this product. Labuza, Mc Nelly, Gallagher, Hawkes, and Hurtado (1972) reported that the limits for intermediate moisture food, including fisheries, are 0.60–0.85. During the drying and storage of salted fish, two types of relevant reactions occur, which implicate in losses of the nutritional

Table 1
Proximal analysis of salted–dried shrimp

	Shrimp 1	Shrimp 2	Shrimp 3	Shrimp 4
Moisture (g/100 g)	48.97 ± 0.41^{a}	50.86 ± 0.11^{a}	52.27 ± 0.21^{a}	52.05 ± 0.14^{a}
Aw	0.74 ± 0.00^{ab}	0.75 ± 0.00^{b}	0.74 ± 0.00^{ab}	0.74 ± 0.00^{a}
Fat (g/100 g)	1.22 ± 0.04^{a}	1.16 ± 0.04^{a}	1.05 ± 0.03^{a}	1.07 ± 0.03^{a}

Same letters in the column for mean values do not show statistical significant differeences ($p < 0.05$).
Shrimp 1, summer; shrimp 2, autumn; shrimp 3, winter and shrimp 4, winter.

value. In the first, the high temperature during drying leads to the partial destruction of the nutrients. In the second, the interaction of components produced during the drying and storage like non-enzymatic darkening, peroxides interaction with proteins and vitamins, diminish their bio-disposability (Labuza, 1973). The average lipid levels found in the samples of salted–dried shrimp were 1.12 g/100 g (Table 1).

Cholesterol content (mg/100 g) determined in samples were (Table 2) shrimp 1 (148.33 ± 58.44); shrimp 2

Table 2
Cholesterol (mg/100 g) and cholesterol oxides (COPs) (μg/g sample)

	Samples	Cholesterol (mg/100 g)	25-OH (μg/g)	7-Keto (μg/g)	7α-OH (μg/g)	7β-OH (μg/g)	Total COPs (μg/g)
Shrimp 1	1	198.27	22.88	26.35	6.55	–	55.78
	2	168.24	7.39	7.44	–	–	14.83
	3	247.69	–	–	5.61	–	5.61
	4	149.70	–	18.40	–	–	18.40
	5	110.51	12.49	24.94	–	–	37.43
	6	232.56	–	21.47	–	–	21.47
	7	192.41	–	32.68	6.52	35.54	74.74
	8	106.99	–	–	–	–	–
	9	83.47	–	–	–	45.54	45.54
	10	73.96	–	–	–	47.61	47.61
	11	167.28	–	–	–	52.58	52.58
	12	120.91	–	14.48	5.18	–	19.66
	13	76.24	8.82	13.94	4.36	–	27.12
Shrimp 2	14	152.21	–	–	5.02	34.63	39.65
	15	147.41	–	–	3.64	41.62	45.26
	16	175.04	–	8.50	4.88	–	13.38
	17	130.92	–	8.12	3.85	–	11.97
	18	218.30	–	–	12.12	–	12.12
	19	141.98	–	–	3.31	34.94	38.25
	20	145.62	–	–	3.07	40.27	43.34
	21	73.88	–	–	4.92	41.27	46.19
	22	146.76	–	–	4.08	39.13	43.21
	23	123.92	–	10.92	3.23	42.16	56.31
	24	106.68	–	–	5.72	41.56	47.28
Shrimp 3	25	209.64	–	–	–	44.57	44.57
	26	169.06	–	–	6.48	64.29	70.77
	27	130.93	–	–	–	–	
	28	136.98	–	–	–	–	–
	29	106.40	–	–	–	–	–
	30	125.11	9.04	15.20	–	–	24.24
	31	235.04	–	–	–	–	–
	32	176.11	–	–	–	–	–
	33	147.17	–	–	–	–	–
	34	160.88	–	–	–	–	–
	35	165.13	–	–	–	–	–
	36	164.67	–	–	–	–	–
	37	155.61	–	–	–	–	
Shrimp 4	38	230.57	–	–	2.64	50.11	52.75
	39	199.60	–	8.83	1.77	66.70	77.30
	40	166.42	–	–	–	60.81	60.81
	41	206.20	2.37	–	1.52	72.56	76.45
	42	198.08	–	13.59	–	52.28	65.87
	43	176.84	–	–	1.57	71.64	73.21
	44	192.29	–	–	9.75	–	9.75
	45	187.95	–	–	4.52	–	4.52
	46	187.34	–	–	–	–	–
	47	206.11	11.48	8.62	5.02	38.85	63.97
	48	181.40	15.08	–	1.72	41.55	58.35
	49	176.98	12.14	–	1.71	50.30	64.15
	50	176.63	8.01	–	1.48	51.14	60.63
	Range	73.88–247.69	ND–22.88	ND–32.68	ND–12.12	ND–72.56	ND–77.30

(– or ND) = Not detected. Shrimp 1, summer; shrimp 2, autumn; shrimp 3, winter; shrimp 4, winter.

(142.07 ± 36.63); shrimp 3 (160.21 ± 34.22) and shrimp 4 (191.26 ± 17.01). This variation is probably associated to several factors, which are: species, available feeding, age, sex, temperature of the water, geographical location, season, etc. (Armstrong, Leach, & Wyllie, 1991; Botta, Kennedy, & Squires, 1986), which were also observed by other studies with shrimp (Bragagnolo, Rodrigues-Amaya, & Squires, 1997; Krzynowek & Panunzio, 1989; Luzia, Sampaio, Castellucci, & Torres, 2003; Moura, Torres, Mancini-Filho, & Tenuta-Filho, 2002).

The processing and storage conditions should be the primary factors for the formation of COPs in small sun-dried fish, since these samples had been exposed to abusive conditions, i.e., in the presence of air, uncontrolled relative humidity, exposure to fluorescent light and a long storage time (Chen & Yen, 1994).

The shrimp 4 presented the highest levels of COPs (54.87 μg/g), followed by the shrimp 2 (41.33 μg/g), shrimp 1 (31.74 μg/g) and the shrimp 3 (6.74 μg/g). In this work, 7β-OH was the oxide found in largest amounts. Others researches, working with fish, (Ohshima, Li, & Koizumi, 1993; Ohshima, Shozen, Ushio, & Koizumi, 1996) also found 7β-OH as the predominant oxide A possible pathway leading to oxidized cholesterol in processed foods is the formation of fatty acid peroxy radicals. In addition, singlet oxygen produced by photo-oxidation and ultraviolet irradiation is also involved in the oxidation of cholesterol (Girotti, 1992; Herian & Lee, 1985; Luby, Hart, & Ryan, 1986). These radicals and singlet oxygen attack the 7th and 5th positions of cholesterol, and 7α and 7β-hydroperoxycholesterol and 5-hydroperoxycholesterol are produced. Since these hydroperoxy derivatives are unstable, they readily change to 7α and 7β-hydroperoxycholesterol. (Osada, Kodama, Yamada, & Sugano, 1993). Osada et al. (1993) reported that raw sardine and squid did not present COPs. However when they were submitted to air-dried processing, the COPs were formed and increased fastly (287 and 146 ppm).

Analyzing commercial samples of marine fishes Ohshima et al. (1993) found 9.6–138 ppm total COPs and 7β-OH and 7-Keto were the predominant cholesterol oxides in amounts that varied from 2–55 to 2–60 ppm, respectively.

Ohshima et al. (1996) also studied the formation of cholesterol oxides in the processing of boiled and dried anchovy. The oxides found in the boiled and dried anchovy were: 7β-OH (64.4 μg/g), α-epoxide (22.3 μg/g), β-epoxide (61.9 μg/g), 7-Keto (49.6 μg/g), 25-OH (11.8 μg/g) and triol (17.9 μg/g) all on dry weight basis. The levels of cholesterol oxides increased during the process of grilling for 6 min at 220 °C.

Kao and Hwang-Sun (1997) analyzed cholesterol oxides in dried squid and found 7α-OH, 7β-OH, α- epoxide, β- epoxide, 7-Keto, 25-OH, 20-OH and triol. When the dried squid was baked at 200 °C for 10 min, the cholesterol level decreased from 7300 to 6020 ppm, while the cholesterol oxides increased from 12.07 to 43.46 ppm, significantly lower than the reported by Osada et al. (1993).

Moura et al. (2002) evaluated the occurrence of 7-Keto free in pink-shrimp samples and found concentrations that varied from 0.185 to 0.366 μg/g, with an average value of 0.230 μg/g. These authors concluded that the reduction of free cholesterol and 7-Keto concentrations in processed pink-shrimp was related to elution of these compounds by the cooking medium, i.e., water in boiling and oil in frying (Moura & Tenuta-filho, 2002).

Echarte, Zulet, and Astiasaran (2001) evaluated the formation of COPs in different salmon preparations and found the following amounts: cholestanetriol (fried with olive oil = 1.05 μg/g fat; fried with soya oil = 1.76 μg/g fat and roasted = 1.33 μg/g fat). For the 7-Keto (raw salmon = 0.74 μg/g fat; fried in olive oil = 1.93 μg/g fat; fried with soya oil = 0.85 μg/g fat and roasted = 3.35 μg/g fat). In relation to 7β-OH (fried with soya oil = 0.74 μg/g fat and roasted = 2.7 μg/g fat). In this study, the authors were not found (7α-OH, 5,6α-epoxide and 25-OH). In general the total of oxides verified in the salmon preparations were: raw (0.74 μg/g fat); fried with olive oil (2.98 μg/g fat); fried with soya oil (3.35 μg/g fat and roasted (7.38 μg/g fat)). The authors concluded that the culinary processes used for the preparation of the salmon to the formation of COPs and that the roasted preparation presented a larger number of COPs in relation to the other types of preparations.

As previously described, the shrimp salted–dried pass through several processing stages: immersion in brine, drainage, drying under the direct incidence of the sunlight, addition of salt and also boiling. In this process, occurs an abusive condition that may collaborate to lipid oxidation.

The oxidation of cholesterol in shrimp is favored by the presence of unsaturated fatty acids, which are easily oxidized. Connor and Ling (1982) described the crustaceans as good sources of polyunsaturated fatty acids (n3), presenting low levels of saturated fatty acids and high cholesterol levels.

In this study, the major fatty acids found were (Table 3): (15:1 – 15.75%), (24:1 n9 – 14.15%), (22:6 n3 – 13.46%), (18:0 – 9.45%), (23:0 – 8.52%) and (20:5 n3 – 6.85%). The average values of the fatty acids of the samples were (Table 4): saturated (27.49%), monounsaturated (43.73%), polyunsaturated (28.79%), n3 (23.10%), n6 (4.19%) and EPA + DHA (19.96%). The ratio n3/n6 was high in our samples (11.75). In other studies, Luzia et al. (2003) found a ratio of 5.31 in the summer and 4.13 in the winter in fresh seabob shrimp.

Chanmugam, Donovan, Wheeler, and Hwang (1983) compared fatty acids profile from two shrimp species

Table 3
Fatty acids profile (%) in salted–dried shrimp

Fatty acids	Shrimp 1	Shrimp 2	Shrimp 3	Shrimp 4
6:0	0.62	0.81	–	–
14:0	0.73	0.50	0.12	–
14:1	0.16	0.30	0.12	0.21
15:0	0.86	1.32	1.30	2.06
15:1	19.80	16.36	16.16	10.68
16:0	4.14	4.30	3.94	2.48
16:1	2.45	1.54	0.62	1.04
17:0	0.13	0.67	0.29	2.17
17:1	2.51	4.26	4.50	4.43
18:0	9.11	8.51	8.98	11.19
18:1n9t	1.18	2.06	2.54	4.46
18:1n9c	7.80	2.90	1.19	1.26
18:2n6t	0.70	4.12	2.78	2.02
18:2n6c	1.42	0.67	0.20	–
18:3n6	0.25	0.68	0.28	0.67
18:3n3	0.18	–	0.05	0.06
20:0	0.06	–	–	0.04
20:1n9	0.23	0.26	0.48	0.12
20:2	0.24	0.03	0.04	–
20:3n3	1.18	3.58	4.11	8.15
20:4n6	2.75	–	–	–
20:5n3	15.01	9.92	1.93	0.53
21:0	0.05	0.11	–	0.10
22:0	0.60	0.08	–	–
22:1n9	1.60	–	–	6.81
22:6n3	14.35	15.75	12.42	11.32
23:0	2.47	11.28	9.77	10.55
24:0	8.77	0.18	0.91	0.76
24:1n9	0.65	9.82	27.26	18.85

–, Not detected; SD – standard deviations. Same letters in the column for mean values do not show statistical significant differences ($p < 0.05$). Shrimp 1, summer; shrimp 2, autumn; shrimp 3, winter; shrimp 4, winter.

Table 4
Fatty acids composition presented in salted–dried shrimp

	Shrimp 1	Shrimp 2	Shrimp 3	Shrimp 4
$\sum$ SFA (%)	27.55[a]	27.75[a]	25.29[a]	29.36[a]
$\sum$ MUFA (%)	36.38[a]	37.50[a]	53.17[b]	47.88[b]
$\sum$ PUFA (%)	36.08[b]	34.75[b]	21.54[a]	22.77[a]
PUFA/SFA	1.50[b]	1.33[ab]	0.86[a]	0.82[a]
$\sum$ n3	29.74[b]	27.44[ab]	17.44[ab]	17.79[a]
$\sum$ n6	5.12[a]	5.47[a]	3.46[a]	2.69[a]
n3/n6	9.92[a]	16.44[a]	8.81[a]	11.82[a]
EPA + DHA	29.36[c]	24.65[bc]	13.99[ab]	11.85[a]

SD, standard deviations. Same letters in the column for mean values do not show statistical significant differences ($p < 0.05$). Shrimp 1, summer; shrimp 2, autumn; shrimp 3, winter; shrimp 4, winter.

(*Macrobrachium rosenbergii* and *Penaeus aztecus*). They reported that *M. rosenbergii* presented a total of PUFA = 28.3%; n6 = 20.4% and n3 = 7.9% and *P. aztecus* presented a total of PUFA = 41.8%; n6 = 13.0% and n3 = 28.8%.

Bragagnolo et al. (1997) when analyzing the pink spotted shrimp (*Penaeus brasiliensis*), found that only 0.5% of the lipids corresponded to α-linolenic acid in this species; this acid was not detected in the seabob shrimp.

Shrimp generally presents low levels of fatty acids and conversely high levels of cholesterol. According to this, one should expect more cholesterol oxidation products than to fatty acids products. And more, this oxidation can favor the COPs formation (Tai et al., 2000).

The levels of TBARS (mgMA/kg) (Table 5) observed in the samples of salted–dried shrimp varied from 0.02 up to 1.30, most of the samples were probably oxidized at that local market. Greene and Cumuze (1981) described that values of TBARS above 0.6 sample mgMA/kg can already be detected fully in the sensory evaluation, accomplished by trained people. Kraemer (2000) evaluated malonaldehyde concentration in salted–dried shrimp, she found values that varied from 0.00 to 1.24 mgMA/kg.

Percentages of oxidation ranged between 1.31 and 3.35×10^{-8} (Table 5). The shrimp 4 presented the highest level oxidation percentages (3.35×10^{-8}) as well as total COPs. However, these data did not presented significant correlation between them. Echarte, Conchillo, Ansorena, and Astiasarán (2004), studying fish patés did not found correlated amounts of COPs with their cholesterol contents, nor with the unsaturated fatty acid contents.

4. Conclusions

This study indicated that the dried–salted shrimp samples presents high amounts of COPs and of TBARS as well, indicating that a severe oxidation process occurred probably because of inadequate conditions of processing and storage. These results reinforced the need of evaluation of the fishing handling procedures; particularly the salted–dried shrimp, including all the

Table 5
Lipid oxidation measures in shrimp salted–dried samples

Methods	Shrimp 1	Shrimp 2	Shrimp 3	Shrimp 4
Cholesterol (mg/100 g)	73.96–247.69	73.88–218.30	106.40–235.04	166.42–230.57
Total COPs (mg/100 g)	LQ[a]–7474.00	1197.00–5631.00	LQ[a]–7077.00	LQ[a]–7730.00
TBARS[b]	0.12–0.96	0.02–1.25	0.15–1.30	0.06–1.28
% Oxidation	2.96×10^{-8}–3.02	1.62×10^{-8}–2.58	2.06×10^{-8}–3.01	1.31×10^{-8}–3.35

[a] Quantification limit = 2.19×10^{-8}.
[b] mgMA/kg sample; % Oxidation = [(mg/100 g COPs)/(mg/100 g cholesterol)] × 100; shrimp 1, summer; shrimp 2, autumn; shrimp 3, winter; shrimp 4, winter.

stages – from the capture to the de shelf-life determination, in order to minimize the oxidative reactions. The high level of Aw and moisture may lead to microorganisms growth, which can be harmful to this product.

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