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Identification of Fatty Acid in Mackerel (*Scomberomorus commersoni*) and Shark (*Carcharhinus dussumieri*) Fillets and Their Changes during Six Month of Frozen Storage at -18˚C

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ABSTRACT

Changes in the fatty acid composition and biochemical indices of mackerel (which has a substantial lipid content) and shark (which has negligible lipid content) fillets stored at -18˚C for up to six months were measured. Lipid content was measured (6.35% and 1.38%) in mackerel and shark, respectively; however it decreased during frozen storage in both fish species. In analysis of fatty acids the amount of PUFA, especially *ω*-3 ones, was more predominant in mackerel than shark, nevertheless, fatty acid composition has changed in both species during frozen storage. The amount of saturated fatty acids in contrast with unsaturated fatty acids increased due to oxidation of PUFA. The decrease in PUFA compounds (40.1% and 23.94%) was as follows: *ω*-3 (48% and 42.83%), *ω*-3/ *ω*-6 ratio (41.36% and 50%), PUFA/SFA ratio (56% and 42.23%) and EPA+DHA/C16 ratio (55.55% and 46.66%) in mackerel and shark, respectively. For both species, tiobarbituric acid (TBA), peroxide (PV), free fatty acids (FFA) and total volatile base nitrogen (TVB-N) values were significantly (P< 0.05) increased with storage time. The results showed that, among these indices, changes in the PV and TBA in mackerel were significantly (P< 0.05) larger than in shark; but changes of FFA and TVB-N in shark were significantly (P< 0.05) higher than in mackerel. It means that oxidative and hydrolytic deterioration are promoter factors of biochemical changes in mackerel and shark, respectively.

Keywords: Biochemical changes, *Carcharhinus dussumieri*, Fish fillet, Frozen storage, *Scomberomorus commersoni*.

INTRODUCTION

Marine lipids have a high content of polyunsaturated fatty acids (PUFA), in particular eicosapentaenoic (EPA, 20:5 *ω*-3) and docosahexaenoic acids (DHA, 22:6 *ω*-3) [1, 2]. There is strong evidence that consumption of fish containing high levels of these fatty acids (FAs) is favorable for human health. When fish is suggested as a means of improving health, both fat content and the PUFA composition must be considered. It is generally recognized that PUFA composition may vary among species of fish. However, little attention has been paid to the composition of different species when selecting fish for the diet [3].

Degradation of PUFA by auto oxidation during storage and processing of fish oils and fatty fish easily leads to the formation of volatiles associated with rancidity [1]. So, freezing and frozen storage have largely been employed to retain fish dietary and nutritional properties [4]. Although frozen storage of fish can inhibit microbial spoilage, the muscle proteins undergo a number of changes which modify their structural and functional properties [5].

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Autoxidation and hydrolytic degradation are the main reasons for biochemical changes.

When oxygen comes into contact with fish during frozen storage, the fats and oils turn rancid, resulting in unpleasant flavors [6]. It is the oxidation of lipids containing polyunsaturated fatty acids (PUFAs) that causes the development of off-flavors and aromas, often referred to as "rancidity". The primary products of fatty acid oxidation (lipid hydroperoxides) are generally considered not to have a flavor impact. The compounds giving rise to rancid flavors and aromas are volatile secondary oxidation products derived from the breakdown of these lipid hydroperoxides [7].

The rate and degree of the reaction are heavily dependent upon the fish species, the presence or absence of activators and inhibitors, and storage conditions [1].

In some previous studies, the effect of freezing on the lipid composition of fishes or fish fillets has been investigated. In pre- and postspawned hake, freezing and frozen storage affected polyenoics and ω-3 FAs. The decrease in the contents of ω-3 FAs in fillets from postspawned hake was lower than that observed in fillets from prespawned fish. [8]. But in Atlantic salmon muscle, it was found that ω-3 FAs are relatively stable even under adverse storage conditions. Frozen storage of salmon fillets for 3 months at -12°C showed very little loss of triglyceride and no selective change in triglyceride fatty acid composition, but an increase in lysophospholipids (LPL) and in free fatty acids [9]. The damage to the lipid fraction of whole jack mackerel (*Trachurus symmetricus murphyi*) during frozen storage showed that the lipid hydrolysis was the major damage during 75 days' frozen storage. The normal oxidative rancidity (primary and secondary products) present in fillets of different species was not observed in the whole fish. Autolytic changes were predominant, because bacterial activity was low throughtout the entire storage time [10].

Progressive lipid hydrolysis is shown as free fatty acids (FFAs). FFAs are either important from the point of view of oxidation products or have been reported to have a direct sensory impact. However, the relationship between lipolysis and lipid oxidation is a matter of some debate. It is generally accepted that FFAs oxidise more readily than esterified FFAs. Increases in FFAs during frozen storage of Atlantic salmon at -10ºC, have been shown to have a negative sensory impact that is directly related to the FFAs themselves and not the oxidation products. This "hydrolytic rancidity" was described in terms of increasing train oil taste, bitterness and a metallic taste [7]. So, the stability of ω-3 FAs during frozen storage of fish is an area of considerable uncertainty.

Narrow-barred Spanish mackerel (*S. commersoni*) and white cheek shark (*C. dussumieri*) are commercially important fishes in the Persian Gulf, commonly processed as frozen fillets [11]. This study was carried out to determine fatty acid composition and its changes in mackerel and shark as a fatty and lean fish, and to compare biochemical changes in fillets during frozen storage.

MATERIALS AND METHODS

Fish Fillet, Sampling and Processing

Narrow-barred Spanish mackerel (*S. commersoni*) and white cheek shark (*C. dussumieri*) specimens were caught by long line near the West of the Qeshm Island (Ram Chaah) in November 2005 (10 fish of each species; about 26 and 45 kg of the mentioned fish, respectively). The length of the specimens was in the 50-70 cm range and the average weight of the specimens of mackerel was 2.60 kg, while average weight in shark was 4.46 kg. The fish specimens were beheaded and gutted on board and then transported in ice within 45 minutes of landing. The fish were then filleted and frozen at -30˚C in order to minimize the effects of biochemical changes during transportation from sea to laboratory. Fillets were transported to the laboratory during the 72 hours after capture. Upon arrival in the laboratory, some of the fish fillets were

analyzed (start of storage as 0 month) and then other fillets packaged in individually celled polyethylene bags for the freezing process. All fillets were stored at under -18˚C. Analysis of frozen fish fillets was undertaken as fresh and after 1, 2, 3, 4, 5 and 6 months of storage at -18˚C. Triplicate samples (3 bags of each fish species) were drawn each month. The samples were thawed in a refrigerator (at a temperature of 4±1˚C) overnight, and analytical samples were drawn from different parts of the thawed fillet pieces. All analyses were carried out at the Department of Food Science and Technology of Tarbiat Modares University (Tehran).

Moisture and Lipid Contents

Moisture was determined by weight difference of the homogenized muscle (1-2 g) before and after 24 hours at 105˚C. Results were calculated as g water 100 g^{-1} muscle [12].

Lipids were extracted from the homogenized white muscle by the Blight and Dyer method. Results were calculated as g lipids 100 g^{-1} wet muscle [13].

Determination of Peroxide Value (PV), Thiobarbituric (TBA) and Free Fatty Acid (FFA)

The PV (meq of O_2 kg^{-1} lipid) of fillet lipid stored during frozen storage was determined periodically (on 0, 1, 2, 3, 4, 5 and 6 months) by the iodometric method according to the AOCS guidelines [14].

The thiobarbituric acid value (mg malonaldehyde (MDA) kg^{-1} of fish flesh) was determined colorimetrically by the Porkony and Dieffenbacher method [15].

Free fatty acid (%) was determined by the Kirk and Sawyer method [15].

Fatty Acid Composition

Gas liquid chromatography (Unicom model 4600) was used to determine the Fas profile of mackerel and shark oils (% of total fatty acids); this entailed using a fused-silica capillary column (BPX70; SGE, Melbourne, Australia) with 30 m×0.25 mm× 0.22 μm film thickness, a split injector (1.2 μL injections) at 240˚C and a FID at 250˚C. Helium was used as the carrier gas (pressure of 50 *psi*). The temperatures of the column and injection port were 190 and 300˚C, respectively. The peaks were identified based on their retention times using fatty acids methyl esters standards and all samples were run in triplicate. An internal standard method was used to calculate the fatty acid composition (the internal standard was C15:0).

Determination of Total Volatile Base Nitrogen (TVB-N)

The amount of TVB-N (mg 100 g^{-1} fish flesh) was determined by the direct distillation method according to Goudlas and Kontoinas [16].

Statistical Analysis

Data were presented as mean±standard division (SD) and were subjected to analysis of variance (ANOVA). Significant means were compared by one-way procedure tests and T-test (for comparison of mackerel and shark) at α= 0.05 level (n= 3).

RESULTS AND DISCUSSION

Moisture and Lipid Content

Moisture in mackerel and shark ranged between 73.32 and 75.05%, 76.33 and 74.68% in all samples, respectively (Figure1). Based on proximal analysis, water content in shark was significantly more than in mackerel. In both fishes no significant difference in moisture was obtained as a result of temperature and time of storage between fresh and stored fillets up to 6

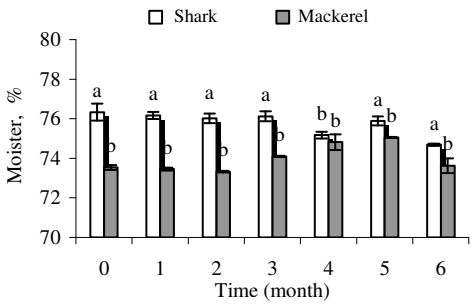

Figure 1. Comparison of moisture between mackerel and shark during frozen storage (-18˚C). Data represent means and standard deviations derived from three sampled fillets for each sampling date. Different letters (bars) indicate significant differences between mackerel and shark in each time.

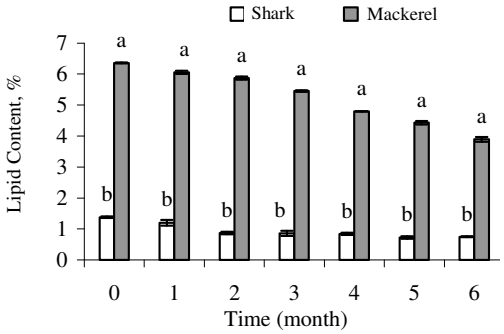

Figure 2. Comparison of lipid content between mackerel and shark during frozen storage (-18˚C). Data represent means and standard deviations derived from three sampled fillets for each sampling date. Different letters (bars) indicate significant differences between mackerel and shark in each time.

months, and some insignificant difference in moisture is due to variations in individual fish or might be as a result of permanent bags.

The levels of lipid in fish flesh vary depending on species, ranging from lean fish (< 2% total lipid) such as cod, haddock and pollack, to high lipid species (8– 20% total lipid) such as herring, mackerel and farmed salmon. A total lipid level of 5% has been suggested as a cut-off point between low and medium fat fish. In addition to species variability, lipid levels vary with sex, diet, seasonal fluctuation and tissue [7, 17]. For example the dark muscle of Mackerel was found to contain 20% lipid in comparison with 4% in the white muscle, while Atlantic herring can have a seasonal variation of 1–25% total fat. It is well established that oily fish are particularly susceptible to lipid oxidation and rancidity development because of the high content of PUFAs in their lipids, particularly the nutritionally important ω-3 Fas, EPA and DHA [7].

Lipid content ranged in mackerel and shark between 6.35 to 3.89 and 1.38 to 0.75, on wet basis, respectively (Figure 2). It has been reported that low-fat fish have a higher water content [3], as observed in this study; shark also had higher moisture than mackerel. Also the initial amount of lipids, and the amount over every period of lipid content analysis in mackerel were significantly ($P< 0.05$) more than in shark, and showed that mackerel was a fatty fish and shark a lean fish. Nevertheless, in both fish significant ($P< 0.05$) decreases were obtained on lipid content as a result of frozen storage conditions (time and temperature). Lipid deterioration is the main cause of the low shelf life of fatty fish due to progressive oxidation and enzymatic hydrolysis of unsaturated fatty acids in fish.

Fatty Acid Composition

Susceptibility to rancidity depends not only on the amount of lipid present, but also the lipid composition and its location in the fish tissue. Fish contain high levels of highly unsaturated fatty acids and uniquely high levels of ω-3 fatty acids, for example, EPA and DPA. It is for this reason that they are susceptible to oxidative rancidity.

The fatty acid profile of fish varies quite considerably between and within species and are also influenced by the factors already mentioned [7].

The fatty acid composition of mackerel and shark over 6 months is summarized in Table 1. Except for months 1, 5 and 6 no significant differences were observed among

Table1. Change of Fatty Acid Composition (Means ± SD [a] (n=5); % of Total Fatty Acids) of Mackerel (*S. commersoni*) and Shark (*C. dussumieri*) Stored 6 Months at -18°C [b].

Fatty acids, g 100 g $^{-1}$ from total lipid fraction	Time of storage													
	0		1		2		3		4		5		6	
	Mackerel	Shark	Mackerel	Shark	Mackerel	Shark	Mackerel	Shark	Mackerel	Shark	Mackerel	Shark	Mackerel	Shark
C 14:0 (Myristic acid)	6.5 ± 0.14 ^{e}	1.06 ± 0.02 ^{d}	6.72 ± 0.11 ^{de}	1.15 ± 0.04 ^{cd}	6.87 ± 0.06 ^{de}	1.24± 0.03 ^{c}	7.16 ± 0.35 ^{d}	1.51 ± 0.10 ^{b}	7.75 ± 0.25 ^{c}	1.77 ± 0.02 ^{a}	8.4 ± 0.24 ^{b}	1.80 ± 0.05 ^{a}	8.99 ± 0.08 ^{a}	1.84 ± 0.06 ^{a}
C 16:0 (Palmetic acid)	26.43 ± 0.48 ^{e}	28.3 ± 0.23 ^{c}	27.93 ± 0.28 ^{d*}	28.90 ± 0.89 ^{c*}	29.19 ± 0.86 ^{c*}	29.71 ± 0.28 ^{bc*}	30.7 ± 0.30 ^{b*}	30.66± 0.15 ^{ab*}	31.27± 0.1 6 ^{ab*}	30.63 ± 1.24 ^{ab*}	31.29 ± 0.15 ^{ab*}	31.17 ± 0.58 ^{ab*}	31.96 ± 0.35 ^{a*}	31.32± 0.41 ^{a*}
C 16:1 (Palmitoleic acid)	6.74 ± 0.05 ^{e}	2.39 ± 0.27 ^{d}	7.25 ± 0.37 ^{e}	2.75 ± 0.10 ^{d}	8.01 ± 0.13 ^{d}	3.16 ± 0.70 ^{d}	8.58 ± 0.4 ^{c}	5.41 ± 0.19 ^{c}	9.82 ± 0.12 ^{b}	7.11 ± 0.36 ^{b}	10.30 ± 0.07 ^{b}	8.02 ± 0.09 ^{ab}	10.97 ± 0.14 ^{a}	8.71 ± 0.60 ^{a}
C 17:0 (Margaric acid)	2.41 ± 0.27 ^{c}	1.03 ± 0.14 ^{e}	2.91 ± 0.01 ^{b}	1.24 ± 0.22 ^{cd}	2.97 ± 0.01 ^{b}	1.50 ± 0.08 ^{d}	3.04 ± 0.04 ^{b}	1.97 ± 0.29 ^{c}	3.18± 0.18 ^{b}	2.43 ± 0.09 ^{b}	3.56 ± 0.01 ^{a}	2.99 ± 0.08 ^{a}	3.74 ± 0.22 ^{a}	3.21 ± 0.06 ^{a}
C 17:1 (*Cis*10-heptadanoic acid)	4.60 ± 0.30 ^{a}	2.91 ± 0.28 ^{a}	3.65 ± 0.39 ^{b}	1.28 ± 0.48 ^{b}	3.30 ± 0.11 ^{b}	0.79 ± 0.05 ^{b}	2.3 ± 0.10 ^{c}	0.24 ± 0.03 ^{c}	1.77 ± 0.10 ^{d}	ND	1.33 ± 0.12 ^{de}	ND	1.02 ± 0.09 ^{e}	ND
C 18:0 (Stearic acid)	7.89 ± 0.29 ^{e}	10.84± 0.6 7 ^{e}	8.6 ± 0.18 ^{d}	11.54± 0.55 ^{de}	8.88 ± 0.08 ^{d}	12.60 ± 0.33 ^{cd}	9.49 ± 0.33 ^{c}	13.80± 0.21 ^{bc}	9.94 ± 0.23 ^{bc}	14.92 ± 0.80 ^{ab}	10.30± 0.13 ^{b}	15.43 ± 0.26 ^{a}	11.27 ± 0.19 ^{a}	15.80± 0.60 ^{a}
C 18:1 ω-9 (Oleic acid)	15.81 ± 0.18 ^{a}	22.7± 0.38 ^{a}	14.63± 0.06 ^{b}	22.53 ± 1.27 ^{a}	13.98 ± 0.07 ^{c}	21.77 ± 0.04 ^{a}	13.71 ± 0.21 ^{c}	20.19± 0.67 ^{b}	13.29± 0.04 ^{d}	18.82± 0.69 ^{b}	13.16± 0.00 ^{d}	16.85± 0.35 ^{c}	12.85 ± 0.00 ^{e}	16.87± 0.32 ^{c}
C 18:2 ω-6 *cis* (Linoleic acid)	1.67± 0.01 ^{f*}	1.42 ± 0.32 ^{c*}	1.91 ± 0.04 ^{e}	2.36 ± 0.16 ^{c}	2.19 ± 0.01 ^{d}	3.48 ± 0.15 ^{b}	2.42 ± 0.00 ^{c*}	3.52 ± 0.80 ^{b*}	2.56 ± 0.05 ^{c}	4.77± 0.38 ^{a}	2.75 ± 0.16 ^{b}	5.24 ± 0.48 ^{a}	2.96 ± 0.11 ^{a}	5.68 ± 0.16 ^{a}
C 18:2 ω-6 *trans* (Linolelaidic acid)	0.66 ± 0.10 ^{a}	ND	0.54 ± 0.08 ^{ab}	ND	0.45± 0.07 ^{bc}	ND	0.34 ± 0.03 ^{cd}	ND	0.35 ± 0.00 ^{cd}	ND	0.21 ± 0.04 ^{d}	ND	ND	ND
C 18:3 ω-3 (Linolenic acid)	1.08 ± 0.12 ^{a}	0.43± 0.07 ^{a}	0.89 ± 0.00 ^{b}	0.15 ± 0.02 ^{b}	0.81 ± 0.05 ^{bc}	0.10 ± 0.03 ^{b}	0.76 ± 0.0 1 ^{bcd}	ND	0.73± 0.00 ^{cd}	ND	0.61 ± 0.09 ^{d}	ND	0.32 ± 0.05 ^{e}	ND
C 19:0 (Nonadecanoic acid)	0.09 ± 0.00 ^{d}	ND	0.18 ± 0.02 ^{cd}	ND	0.31 ± 0.00 ^{c}	ND	0.35 ± 0.02 ^{bc}	ND	0.52 ± 0.11 ^{ab}	ND	0.52 ± 0.11 ^{ab}	ND	0.6 ± 0.10 ^{a}	ND
C 20:0 (Arachidic acid)	0.08 ± 0.00 ^{d}	ND	0.14 ± 0.01 ^{cd*}	ND*	0.19 ± 0.01 ^{c}	ND	0.32 ± 0.01 ^{b}	ND	0.40 ± 0.03 ^{b}	ND	1.22 ± 0.05 ^{a}	ND	1.17 ± 0.08 ^{a}	ND
C 20:1 (*Cis*-11-ecosenoic acid)	0.34 ± 0.03 ^{f}	0.76± 0.09 ^{a}	0.46 ± 0.01 ^{e}	0.49 ± 0.07 ^{b}	0.52 ± 0.05 ^{de}	0.39 ± 0.01 ^{b}	0.59 ± 0.00 ^{cd}	ND	0.64 ± 0.02 ^{c}	ND	0.75 ± 0.05 ^{b}	ND	0.84 ± 0.01 ^{a}	ND
C20:4 ω-6 (Arachidonic acid)	1.98 ± 0.04 ^{a}	5.14 ± 0.10 ^{a}	1.81 ± 0.03 ^{b}	5.19 ± 0.27 ^{a}	1.48 ± 0.09 ^{c}	4.01 ± 0.64 ^{b}	1.35 ± 0.09 ^{c}	2.80 ± 0.01 ^{c}	1.07 ± 0.05 ^{d}	2.46 ± 0.12 ^{cd}	1.02 ± 0.02 ^{d}	1.93 ± 0.12 ^{d}	0.86± 0.02 ^{e}	1.83 ± 0.15 ^{d}
C20:5 ω-3 (EPA)	3.85 ± 0.14 ^{a}	1.34 ± 0.15 ^{a}	3.58 ± 0.09 ^{a}	1.21 ± 0.22 ^{a}	3.21 ± 0.14 ^{b}	0.77 ± 0.03 ^{b}	3.04 ± 0.09 ^{b}	0.60± 0.05 ^{bc}	2.88 ± 0.06 ^{bc}	0.55 ± 0.04 ^{bc}	2.56 ± 0.23 ^{c}	0.40 ± 0.03 ^{c}	1.83 ± 0.18 ^{d}	ND

[a] Standard division.

[b] Means in a row with identical letters are not significantly different (P< 0.05).

ND= Not detected.

* There is no difference between mackerel and shark in each time (absence of * means that there is significant difference between mackerel and shark in each time).

Table 1 (continued).

Fatty acids, g 100 g $^{-1}$ from total lipid fraction	Time of storage													
	0		1		2		3		4		5		6	
	Mackerel	Shark	Mackerel	Shark	Mackerel	Shark	Mackerel	Shark	Mackerel	Shark	Mackerel	Shark	Mackerel	Shark
C23:0 (Tricosaenoic acid)	0.43 ± 0.08 ^{e}	1.36± 0.35 ^{d}	0.58 ± 0.04 ^{d}	1.78 ± 0.71 ^{cd}	0.66 ± 0.01 ^{d}	2.57 ± 0.21 ^{bc}	0.79 ± 0.04 ^{c}	2.97 ± 0.28 ^{ab}	0.94 ± 0.02 ^{b}	2.87 ± 0.04 ^{b}	0.99 ± 0.08 ^{ab}	3.39 ± 0.26 ^{ab}	1.08 ± 0.03 ^{a}	3.73 ± 0.22 ^{a}
C24:0 (Lignoceric acid)	0.37 ± 0.01 ^{e}	1.06± 0.06 ^{b}	0.50 ± 0.03 ^{ed}	1.02 ± 0.09 ^{b}	0.65 ± 0.00 ^{cd}	1.16 ± 0.01 ^{b}	0.76 ± 0.06 ^{bc}	1.24 ± 0.17 ^{b}	0.84 ± 0.02 ^{b}	1.20 ± 0.1 ^{b}	1.15 ± 0.15 ^{a}	1.66 ± 0.07 ^{a}	1.21 ± 0.09 ^{a}	1.70 ± 0.10 ^{a}
C 22:6 ω-3 (DHA)	12.99 ± 0.06 ^{a}	11.54a ± 0.02	12.37 ± 0.21 ^{b}	11.34 ± 0.05 ^{a}	11.53 ± 0.15 ^{c}	11.00 ± 0.01 ^{a}	10.38± 0.07 $^{d\,*}$	10.15 ± 0.21 $^{b\,*}$	9.18 ± 0.48 $^{e\,*}$	9.24 ± 0.55 $^{c\,*}$	8.01 ± 0.29 $^{f\,*}$	8.43 ± 0.35 $^{d\,*}$	7.15 ± 0.13 $^{g\,*}$	7.60 ± 0.46 $^{e\,*}$
Other	6.08 ± 0.53 ^{a}	7.64 ± 0.21 ^{a}	5.34 ± 0.2 8 ^{ab}	7.07 ± 0.29 ^{a}	4.80 ± 0.28 $^{b\,*}$	5.74 ± 0.54 $^{b\,*}$	3.91 ± 0.46 $^{c\,*}$	4.93 ± 0.52 $^{b\,*}$	2.86 ± 0.43 $^{d\,*}$	3.22 ± 0.12 $^{c\,*}$	1.87 ± 0.09 ^{e}	2.69 ± 0.31 ^{c}	1.18 ± 0.05 ^{e}	1.71 ± 0.24 ^{d}
Total, g 100 g $^{-1}$	100.01	99.99	99.99	100.00	100.00	99.99	99.99	99.99	99.99	99.99	100.00	100.00	100.00	100.00
∑ SFA	44.2 ± 0.49 $^{g\,*}$	43.71± 0.59 $^{f\,*}$	47.56 ± 0.34 ^{f}	45.63 ± 0.44 ^{e}	49.72 ± 0.71 $^{e\,*}$	48.78 ± 0.1 $^{d\,*}$	52.61 ± 0.07 $^{d\,*}$	52.15± 0.95 $^{c\,*}$	54.84 ± 0.61 $^{c\,*}$	53.82 ± 1.03 $^{b\,*}$	57.43 ± 0.01 ^{b}	56.44 ± 0.16 ^{a}	60.02 ± 0.32 ^{a}	57.6 ± 0.29 ^{a}
∑ MUFA	27.49 ± 0.55 $^{a\,*}$	28.77± 0.83 $^{a\,*}$	25.99 ± 0.09 $^{b\,*}$	27.05± 0.97 $^{ab\,*}$	25.81 ± 0.24 $^{b\,*}$	26.11 ± 0.8 $^{bc\,*}$	25.18 ± 0.63 $^{b\,*}$	25.84 ± 0.89 $^{bc\,*}$	25.52 ± 0.18 $^{b\,*}$	25.93 ± 0.81 $^{bc\,*}$	25.54 ± 0.23 $^{b\,*}$	24.87 ± 0.34 $^{c\,*}$	25.68 ± 0.1 $^{b\,*}$	25.58 ± 0.54 $^{bc\,*}$
∑ PUFA	22.23 ± 0.23 ^{a}	19.87a ± 0.31	21.1 ± 0.25 ^{b}	20.25 ± 0.46 ^{a}	19.67 ± 0.3 ^{c}	19.36± 0.57 ^{a}	18.29 ± 0.21 ^{d}	17.07 ± 0.69 ^{b}	16.77 ± 0.53 ^{e}	17.02 ± 0.78 ^{b}	15.16 ± 0.14 ^{f}	16.00 ± 0.52 ^{bc}	13.12 ± 0.26 $^{g\,*}$	15.11 ± 0.56 $^{c\,*}$
PUFA/SFA	0.50 ± 0.01 ^{a}	0.45a ± 0.00	0.44 ± 0.0 0 ^{b}	0.44 ± 0.00 ^{a}	0.39 ± 0.01 ^{c}	0.4 ± 0.01 ^{b}	0.35 ± 0.00 ^{d}	0.33 ± 0.01 ^{c}	0.31 ± 0.01 $^{e\,*}$	0.32 ± 0.01 $^{c\,*}$	0.26 ± 0.00 $^{f\,*}$	0.28 ± 0.00 $^{d\,*}$	0.22 ± 0.00 $^{g\,*}$	0.26 ± 0.00 $^{d\,*}$
∑ ω-3	17.92 ± 0.27 ^{a}	13.31 ± 0.1 ^{a}	16.84 ± 0.16 ^{b}	12.7 ± 0.26 ^{ab}	15.55 ± 0.12 ^{c}	11.87± 0.01 ^{b}	14.18 ± 0.11 ^{d}	10.75 ± 0.18 ^{c}	12.79 ± 0.53 ^{e}	9.79 ± 0.59 ^{d}	11.18 ± 0.28 ^{f}	8.83 ± 0.36 ^{e}	9.3 ± 0.13 ^{g}	7.6 ± 0.45 ^{f}
∑ ω-6	4.31 ± 0.15 ^{a}	6.56 ± 0.22 ^{bc}	4.26 ± 0.1 ^{ab}	7.55 ± 0.34 ^{a}	4.12 ± 0.18 ^{abc}	7.49± 0.58 ^{a}	4.11 ± 0.11 ^{abc}	6.32 ± 0.8 ^{c}	3.98 ± 0.07 ^{bc}	7.23± 0.45 ^{ab}	3.98 ± 0.14 ^{bc}	7.17 ± 0.41 ^{ab}	3.82 ± 0.12 ^{c}	7.51 ± 0.09 ^{a}
ω-3/ω-6	4.16 ± 0.18 ^{a}	2.03 ± 0.05 ^{a}	3.95 ± 0.06 ^{ab}	1.68 ± 0.07 ^{b}	3.77 ± 0.13 ^{b}	1.58 ± 0.12 ^{bc}	3.45 ± 0.07 ^{c}	1.70 ± 0.24 ^{b}	3.21 ± 0.15 ^{c}	1.35 ± 0.1 ^{cd}	2.81 ± 0.17 ^{d}	1.23 ± 0.09 ^{de}	2.43 ± 0.04 ^{e}	1.01 ± 0.04 ^{e}
EPA+DHA/C16	0.64 ± 0.01 ^{a}	0.45 ± 0.0 0 ^{a}	0.57 ± 0.01 ^{b}	0.43 ± 0.00 ^{a}	0.50 ± 0.01 ^{c}	0.4 ± 0.00 ^{b}	0.44 ± 0.00 ^{d}	0.35 ± 0.00 ^{c}	0.38 ± 0.01 ^{e}	0.32± 0.03 ^{cd}	0.34 ± 0.01 ^{f}	0.28 ± 0.01 ^{d}	0.28 ± 0.01 ^{g}	0.24 ± 0.01 ^{e}

[a] Standard division.

[b] Means in a row with identical letters are not significantly different (P< 0.05).

ND= Not detected.

* There is no difference between mackerel and shark in each time (absence of * means that there is significant difference between mackerel and shark in each time).

the SFA (saturated fatty acids) content between mackerel and shark. Palmitic acid (C16:0) was the major fatty acid among the SFAs and during the whole period. In the first month, the amount of palmitic acid (C16:0) in shark was significantly more than in mackerel; however, there were no differences between the other months. Also C16:0 was the major fatty acid among all other fatty acids in both fish. The same result was obtained for Channa spp. [17].

The amount of myristic (C14:0) and margaric acids (C17:0) in mackerel were more than in shark, whereas the amounts of stearic (C18:0), tricosaenoic (C23:0) and lignoceric acid (C24:0) in shark were more than in mackerel. Nonadecanoic (C19:0) and arachidic acid (C20:0) were not detected in shark.

There was no significant difference among the MUFA (monounsaturated fatty acids) content between mackerel and shark during 6 months. Oleic acid (C18:1 ω-9) was the major fatty acid among the MUFAs of each fish species. The same result was shown in Channa spp. [17], gilthead sea bream (*Sparus aurata*) and sea bass (*Dicentrarchus labrax*) [18]. The amount of palmitoleic (C16:1) and *cis*10-heptadanoic acids (C17:1) in mackerel was more than in shark, while the amount of oleic (C18:1 ω-9) and *cis*-11-ecosenoic acids (C20:1) in shark were more than in mackerel.

In both mackerel and shark, unsaturated fatty acids were more than saturated fatty acids (SFA<PUFA+MUFA) while, during frozen storage, unsaturated fatty acids decreased in contrast with saturated fatty acids. Distribution of fatty acids in mackerel and shark were seen as SFA> MUFA> PUFA. This is in agreement with findings about channel catfish [19] and seal [20] that showed MUFA to be higher than PUFA. PUFA composition may vary among species of fish [17]. The amount of PUFA in fishes is affected by diet [21]. The amounts of PUFA in mackerel were significantly more than in shark except in the last month. It is noteworthy that the highest quantity of PUFA in both fish was associated with ω-3 compounds. Eicosapentaenoic (EPA) (C20:5 ω-3) and docosahexaenoic acids (DHA) (C22:6 ω-3) were major in total ω-3 polyunsaturated fatty acids in both mackerel and shark. The same results were found for gilthead sea bream (*Sparus aurata*) and sea bass (*Dicentrarchus labrax*) [18]. The lowest amount of ω-3 compounds were found in linolenic acid (C18:3 ω-3); however, in mackerel it was significantly more than in shark. In both mackerel and shark, DHA content was more than EPA. The same results were found for seal [20] and Channa spp. [17] but, in Atlantic mackerel [22], the EPA content was more than DHA. Distribution of PUFA in mackerel is DHA> EPA> AA (arachidonic acid, C20:4 ω-6), while in shark it is DHA> AA (C20:4)> EPA.

The level of ω-6 compounds in shark was significantly more than in mackerel. Linoleic acid (C18:2 ω-6 *cis*), except in the first and third months, and also arachidonic acid (C20:4 ω-6) in shark were significantly higher than in mackerel. Linolelaidic acid (C18:2 ω-6 *trans*) was not detected in shark.

Statistical results showed that, during frozen storage, changes of PUFA were significant, decreasing by 40.1% and 23.94% especially ω-3 (48% and 42.83%) in mackerel and shark, respectively. The differences in the fatty acid composition of the fish species lipids had a decisive function in the formation of hydroperoxides. The oxidative changes in frozen fish lipids may be caused by the occurrence of radicals, indicating this process [22]. These types of radicals are easily formed in mackerel compared to shark, because mackerel contains lipids with more PUFA. During frozen storage mackerel is very susceptible to lipid peroxidation due to its high PUFA content [22].

The ω-3:ω-6 ratio has been suggested as a useful indicator for comparing relative nutritional values of fish oils. It has been suggested that a ratio of 1:1 to 1:5 would constitute a healthy human diet [3, 17]. This study has shown that marine fish are richer in ω-3 than ω-6 PUFAs. There were

significant differences in this ratio between mackerel and shark during the whole period of storage. The ω-3:ω-6 ratio in fresh fillets (4.16 and 2.02) and at the end of storage (2.43 and 1.01) were in the recommended ratio, but a decrease of 41.36% and 50%, respectively, in mackerel and shark showed that the nutritional value of these fish has been lost during frozen storage.

The PUFA/ SFA (P/S) ratio reveals that marine fish are a good source of PUFA related to saturate fatty acids. In both mackerel and shark this ratio obtained was less than 1. Any decrease of PUFA relative to SFA leads to a significant decrease of this ratio (56% and 42.23% in mackerel and shark, respectively) during frozen storage; however, in mackerel it was significantly higher than in shark during 6 months.

It has been suggested that the EPA+DHA/C16:0 ratio is a good index for determining lipid oxidation [23]. Although this ratio in mackerel was significantly more than in shark, it has decreased (55.55% and 46.66% in mackerel and shark, respectively) during frozen storage. The same result was found for oyster [23]. The negative relationship between this ratio and storage time showed that oxidation mechanisms are active during frozen storage.

Lipid Oxidation

Within edible muscle tissues there are two pools of lipids that may be involved in oxidation reactions. These are storage triacyl glycerides (TAGs), which constitute the majority of the total lipids in oily fish and the fraction that accounts for the variability in fat content, and phospholipids present in the cellular membranes. This lipid fraction represents around 1% of the total weight of the flesh. The contribution of these lipid pools to rancidity development is a matter of some debate. Although present in much smaller amounts, the physical form of phospholipids in the membrane bilayer present a large surface area for oxidation reactions to occur compared with "droplets" of storage TAG present in the muscle associated storage depots of oily fish. The amount of phospholipids substrate available for oxidation by catalysts is proportional to the surface area exposed to the aqueous phase. Potentially, phospholipids are more important in the initial onset of lipid oxidation. Phospholipids also tend to contain a higher proportion of unsaturated fatty acids than TAG. It is interesting to note that it is generally accepted that lean white fish such as cod are not prone to rancidity development on storage even though they contain highly unsaturated phospholipids. These species contain virtually no TAG or myoglobin in the muscle tissue. This implies that one or both of these components have important implications for storage stability [7].

During storage of both fish, hydroperoxide production was observed. In mackerel, the PV was more significant than in shark, however the PV was not different in first month of storage (Figure 4); an important linear increase of PV was observed up to month 6. In shark, a slower development of primary oxidation during storage was detected (Figure 3). The increase in peroxide value (PV) from an initial value of 2.32 to 15.41, and from 0.24 to 4.43 meq of O_2 kg^{-1} lipid in mackerel and shark, respectively, was significant during frozen storage and indicated oxidative deterioration. This increase of PV in frozen fish in contrast with fresh fish showed development of rancidity during frozen storage [24]. Development of an off-flavor is one of the major effects of lipid oxidation [25] and, at the further stage of lipid peroxidation, changes in color and nutritional value are observed [22]. Moreover, oxidized products of lipids formed during storage of fishery products are known to influence the soluble proteins (sarcoplasmic and myofibrillar proteins) [26]. In comparison with shark, mackerel contributed to the more accelerated oxidative degradation of lipids.

Secondary lipid oxidation was studied by the TBA. The TBA number is a measure of MDA, a byproduct of lipid oxidation. TBA

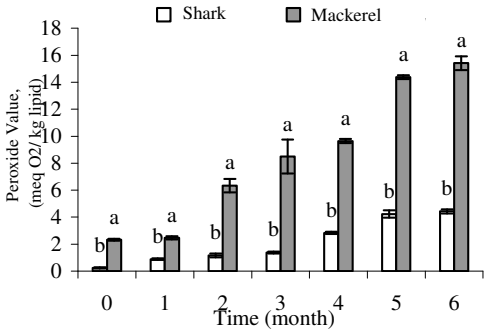

Figure 3. Comparison of peroxide value between mackerel and shark during frozen storage (-18˚C). Data represent means and standard deviations derived from three sampled fillets for each sampling date. Different letters (bars) indicate significant differences between mackerel and shark in each time.

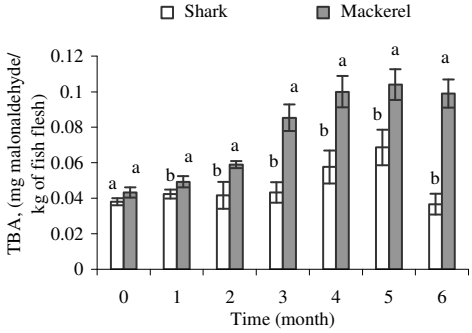

Figure 4. Comparison of TBA between mackerel and shark during frozen storage (-18˚C). Data represent means and standard deviations derived from three sampled fillets for each sampling date. Different letters (bars) indicate significant differences between mackerel and shark in each time.

records revealed an increased rate of lipid oxidation during the frozen storage of the fish species examined. The significant increase in TBA from an initial value of 0.043 to 0.104, and from 0.038 to 0.068 mg of MDA kg^{-1} of fish flesh in the mackerel and shark, respectively, was revealed during frozen storage and indicated oxidative deterioration (Figure 4). The higher increase in TBA value was obtained significantly for mackerel but in the fresh fillets, there was not any significant difference between mackerel and shark. Significant differences in the mackerel and shark indicated a high rate of lipid oxidation, and this could be due to the fact that mackerel is a fatty fish as shown by its lipid content. It is also important to note that TBA records may not reveal the actual rate of lipid oxidation, since MDA can interact with other compounds of fish body such as amines, nucleosides and nucleic acid, proteins, amino acids of phospholipids, or other aldehydes that are the end product of lipid oxidation; and this interaction may vary greatly, with species of fish [17, 26-27]. In this study, generally the TBA values recorded were extremely low (< 0.4 mg MDA kg^{-1} of fish flesh) in both stored fish. This, however, does not confirm control of lipid oxidation, since the low TBA could be a result of consumption of MDA in another reaction. As it was shown in Figure 5, at the end of the frozen storage the amount of TBA in shark decreased. It might be as a result of consumption of MDA in another reaction [28].

Lipid Hydrolysis

An increase in free fatty acid (FFA) (lipolysis) is a well established post-mortem feature in fish tissue resulting from the enzymatic hydrolysis of esterified lipids. The build up of FFA can be quite substantial [7].

The development of progressive lipid hydrolysis was observed during frozen storage of both mackerel and shark. FFA (of total lipid as oleic acid) increased significantly ($P \leq 0.05$) from 3.2 to 5.66, and from 1.06 to 8.37, in mackerel and shark, respectively, indicating extensive hydrolysis of lipids (Figure 5). There were significant differences between mackerel and shark during frozen storage. As has been shown in Figure 3, FFA in the two first months of frozen storage in mackerel was more than in shark, while it was higher in shark than mackerel for the other months. These results corroborate previous works describing notable rates of lipid hydrolysis mechanisms

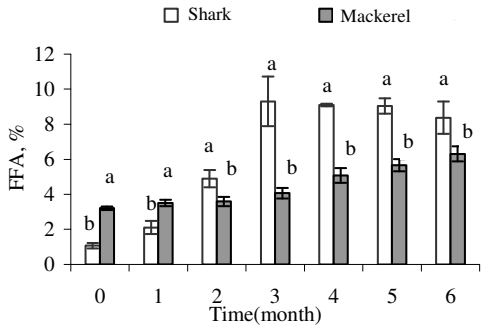

Figure 5. Comparison of FFA between mackerel and shark during frozen storage (-18˚C). Data represent means and standard deviations derived from three sampled fillets for each sampling date. Different letters (bars) indicate significant differences between mackerel and shark in each time.

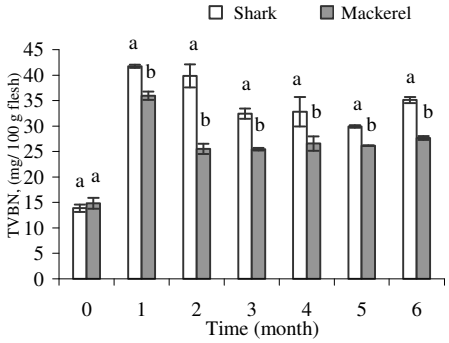

Figure 6. Comparison of TVBN between mackerel and shark during frozen storage (-18˚C). Data represent means and standard deviations derived from three sampled fillets for each sampling date. Different letters (bars) indicate significant differences between mackerel and shark in

in different types of fish during their frozen storage [4, 29-31].

The lipid origin of FFA has been debated. In the work done on hake mince during frozen storage, it has been shown that the FFA formed originated from both phospholipids and neutral lipid fractions [32]. Dekoning and Theodora carried out more detailed follow-up work with the same system in which they calculated the rates of enzymatic hydrolysis of phospholipids and neutral lipids over a range of temperatures. The decrease in the rate of FFA formation with decreasing temperature was greater for the phospholipids than for neutral lipids [33]. Tsukuda also found that FFA was derived from both phospholipids and TAG in frozen stored skipjack tuna. In the dark muscle the majority of FFA was formed from TAG but, in the light tissue, FFA was mainly due to phospholipids hydrolysis. Mackerel lipid hydrolysis on frozen storage showed an increase in FFA consistent with hydrolysis of the phospholipids fraction [34]. Similar findings were obtained when studying lipid hydrolysis in the flesh of ten species of Chinese fresh water fish. The increase in FFA in silver carp was attributed to the hydrolysis of phospholipids [35].

Much of the work on the mechanism of fish muscle lipolysis has been conducted on lean fish such as cod in which the primary lipid constituent are phospholipids and are generally accepted not to have a rancidity problem [7].

In comparison with mackerel, shark contributed to the more accelerated hydrolytical degradation of the fish lipids. Changes in mackerel were consistently lower than those observed for shark. After the third month, the FFA content in shark stabilized; this could have been due to a depletion of substrate or oxidation of the FFA [28].

While the formation of FFA itself does not lead to nutritional losses, its assessment is deemed important when an effect of FFA on lipid matter is proposed, and explained on the basis of a catalytic effect of the carboxyl group on the hydro peroxides. Moreover, being relatively small sized molecules, FFA have been shown to undergo a faster oxidation rate than bigger lipid classes of triglycerides and phospholipids; this significantly affects the dietary quality of aquatic food products [31]. It is generally accepted that FFAs phospho more readily than esterified FA, especially when enzymes such as lipoxygenase (LOX) can be involved in tissue [7].

During frozen storage a negative correlation between FFA formation and protein extractability has been observed [36]. Regardless of the source, FFA may be

directly responsible for off-flavors, the destruction of some vitamins and amino acids, changes in texture, and changes in water holding capacity. The latter two results are particularly important in frozen fish and are related to the propensity of fatty acids to bind, denature and cross-link myofibrillar proteins [7]. FFAs attach themselves hydrophobically or hydrophilically to the appropriate sites on the protein surface, creating a hydrophobic environment which results in a decrease in protein solubility [26].

There is circumstantial evidence that products of lipid hydrolysis promote protein denaturation, especially in lean fish species [36, 37]. According to the lipid content of shark, it is a lean fish species; hence, FFA might have affected protein denaturation of shark in comparison to mackerel [36].

Total Volatile Base Nitrogen (TVB-N)

TVB-N content of both mackerel and shark during frozen storage are shown in Figure 6. In fresh fillets, the TVB-N values were 14.83 and 13.86 mg 100 g^{-1} flesh for mackerel and shark, respectively. At the first month of storage, the TVB-N values showed an increasing trend up to 35.58 and 41.73 mg 100 g^{-1} of flesh for mackerel and shark, respectively, and reached their maximum level. After that they decreased, although their level was more than in fresh fillets; during the last month of storage, they showed an increasing pattern in both fish again. The amount of TVB-N did not differ significantly between mackerel and shark at the beginning of storage, however their amount in shark was significantly more than mackerel during the other months.

Although TVB-N level is a poor indicator of fish freshness [38], it has been commonly used to evaluate fish muscle spoilage [39]. For several fish species, TVB-N values were reported to increase curvilinearly or linearly with time [39]. Trimethylamine *N*-oxide (TMAO) is a natural characteristic component of muscle tissues and visceral organs of sea fish and invertebrates [38, 40], and it is believed that they use it to increase osmotic concentration and thus depress the freezing point of body fluids [40]. Freezing and frozen storage do not destroy the activity of TMAO demethylase. The rate of enzymatic cleavage of TMAO to formaldehyde (FA) and dimethylamin (DMA) depends on the substrate and FA [40]. In cod (*Gadus morhua*) and other gadoid fish, TMA constitutes most of the so-called total volatile bases until spoilage. Besides, TVB-N levels still rise due to formation of NH_3 and other volatile amines. In some fish that do not contain TMAO, or where spoilage is due to a non-TMAO reducing flora, a slow rise in TVB-N is seen during storage, probably resulting from the deamination of amino-acids [38]. The initial amount of TVB-N in both fishes showed freshness, and this is in agreement with the initial measured amount of TVB-N for chub mackerel and hake [16, 40], salmon, whiting and mackerel [36]. TVB-N levels vary from species to species and in each species it varies based on age, sex, environment and season. In frozen conditions in which the bacterial count and activity are gradually decreased, factors like texture enzymes are effective to produce TVB-N. Also, an increase in TVB-N during storage can be due to an increase of ammonia released from amination of adenosine mono phosphate or histamine.

In this study, the abrupt increase of TVB-N in the first month of storage may be due to TMAO degradation and, after it decreases, the degradation process and TVB-N amount has decreased. But, from the third month to the end of frozen storage, the increase in TVB-N level may be a result of ammonia liberation and other volatile amines from muscular damaged tissue. Shark contains a great deal of urea in its blood and muscles, which helps it in osmo-regulation in the sea water. Although bacteria are inactive under –8°C, their enzymes are active. Presence of urea in shark muscle can help increase ammonia as a result of degradation by bacterial enzymes.

CONCLUSSIONS

Frozen fish may develop a dry, stringy texture during frozen storage. The process is mainly due to the denaturation and aggregation of myofibrillar proteins and, perhaps, collagen [41]. Enzymes appear to contribute to this quality defect in several ways. Free fatty acids resulting from lipid or phospholipid hydrolysis can bind to myofibrillar proteins causing denaturation and aggregation. Products of lipid oxidation, such as malonaldehyde, can react with protein to form cross-linked proteins. TMAO demethylase forms formaldehyde (with dimethylamine) in fish and the presence of formaldehyde is related to texture deterioration by formation of the cross-linking agents during frozen storage [7].

In the present study PV, TBA, FFA and TVBN increased significantly ($P< 0.05$) during frozen storage. Comparison of results between each of the species studied has led to some marked differences in lipid oxidation and hydrolytic development. Increase in lipid oxidation which shown as PV and TBA were significantly more in mackerel than shark. Lipid deterioration is the main cause of the low shelf life of fatty fish due to progressive oxidation and enzymatic hydrolysis of unsaturated fatty acids in fish. Although the lipid content in shark was less than in mackerel, development of lipid hydrolysis described as FFA in shark was significantly more than in mackerel and promotes quality loss during frozen storage in this lean fish. On the other hand, the more TVBN is present in shark, the greater the formation of the cross-linking agent formaldehyde occurs during frozen storage. It means that oxidative and hydrolytic deterioration are promoter factors of biochemical changes in mackerel and shark, respectively.

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شناسایی اسیدهای چرب در فیله ماهیان شیر (*Scomberomorus commersoni*) و کوسه چانه سفید (*Carcharhinus dussumieri*) و تغییرات آن طی شش ماه نگهداری به حالت انجماد در ۱۸°C-

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چکیده

تغییرات ترکیب اسیدهای چرب و شاخص های بیوشیمیایی فیله در ماهیان شیر (با مقدار زیادی چربی) و کوسه چانه سفید (با مقدار اندک چربی) خلیج فارس حین نگهداری به حالت انجماد (۱۸°C-) تا مدت شش ماه اندازه گیری گردید. در آنالیز تقریبی محتوای چربی در ماهی شیر و کوسه به ترتیب (٪۶/۳۵ و ٪۱/۳۸) اندازه گیری شد، هرچند در حین نگهداری به حالت انجماد مقدار آن کاهش معنی داری (٪۴۵/۶۵ و ٪ ۳۸/۷۴ به ترتیب در شیر و کوسه) نشان داد. در بررسی اسیدهای چرب، مقدار PUFA خصوصاً انواع امگا-۳ در ماهی شیر نسبت به کوسه بیشتر بود. با این وجود، محتوای اسیدهای چرب در هر دو ماهی حین نگهداری به حالت انجماد تغییر پیدا کرد. مقدار اسیدهای چرب اشباع در برابر اسیدهای چرب غیر اشباع افزایش نشان داد. کاهش ترکیبات PUFA (٪۴۰/۱ و ٪ ۲۳/۹۴) به ترتیب در شیر و کوسه به صورت زیر می باشد: امگا-۳ (٪۴۸ و ٪۴۲/۸۳)، نسبت امگا-۳ به امگا-۶ (٪۴۱/۳۶ و ٪۵۰)، نسبت PUFA/ SFA (٪۵۶ و ٪۴۲/۲۳) و نسبت EPA+DHA/C16 (٪۵۵/۵۵ و ٪۴۶/۶۶). در هر دو ماهی شاخص های تیوباربیتوریک اسید (TBA)، پراکسید (PV)، اسیدهای چرب آزاد (FFA) و کل بازهای ازته فرار (TVBN) به طور معنی داری ($p<0.05$) در طول زمان افزایش یافت. نتایج نشان داد که در میان این شاخص ها، تغییرات پراکسید و تیوباربیتوریک اسید در ماهی شیر به طور معنی داری ($p<0.05$) بیشتر از کوسه بود اما، تغییرات اسیدهای چرب آزاد و کل بازهای ازته فرار در ماهی کوسه به طور معنی داری ($p<0.05$) بیشتر از ماهی شیر بود. این موضوع نشان دهنده آن است که تغییرات اکسیداسیونی و تغییرات هیدرولیتیکی به ترتیب در ماهیان شیر و کوسه پیش برنده تغییرات بیوشیمیایی در حین انجماد هستند.