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The Iranian (*Acipenser persicus*) and Russian (*Acipenser gueldenstaedtii*) Sturgeon's Fatty Acids Changes During Cold Storage

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Abstract: The Iranian (*A. persicus*) and Russian (*A. guldenstaedti*) sturgeon are major species of acipenseridae caught in Caspian Sea and have the most desirable caviar. This study was conducted to investigate the caviar fatty acids (FAs) profile in spring and autumn of Iranian (*A. persicus*) and Russian (*A. guldenstaedti*) sturgeon and its changes during frozen storage (-18°C). The identified Iranian spring sturgeon caviar FAs were saturated fatty acids (SFAs) Lauric (C12:0), Myristic (C14:0), Palmitic (C16:0), Stearic (C18:0), Arachidic (C20:0), mono unsaturated fatty acids (MUFAs), Palmitoleic (C16:1), Oleic (C18:1), Erucic (C 22:1 (n-9)), PUFAs Linoleic C18:2 (n-6), Linolenic (C18:3 (n-3)) acids and C16 isomers. But, only C16:0, C18:0, C18:1, C18:2 (n-6), C 22:1 (n-9) and C14:0 was found in autumn Iranian sturgeon's caviar. Also, FAs in Russian Iranian sturgeon's caviar were C12:0, C14:0, C16:0, C18:0, C20:0, C16:1, C18:1, C 22:1 (n-9), C18:2 (n-6), C18:3 (n-3) and C16 isomers. Except C16:0 and C18:2 all mentioned FAs were observed in autumn Russian sturgeon's caviar. The shelf life of FAs and quality of caviar was decrease during preservation period and it recommended that caviar can maintains up to 2 months.

Key words: Fatty Acids · Shelf Life · Caviar · Sturgeon · Cold Storage

INTRODUCTION

Lipids play an important role in human healthy body [1, 2]. The place of fish meats and its products have discussed due to its contents of ω-3 and ω-6 FAs, which could be used to prevent diseases (malnutrition and heart disease) and recover more quickly from disease [3]. Fatty acids of fish meats and its products are most the effective to improve cardiovascular diseases [1, 2].

The researches on marine fats and oils have begun from several decades [4, 5]. The fatty acids of rainbow trout (*Onchorhyncus mykiss*), Atlantic salmon (*Salmo salar*) and Herrings (*Clupeidae harengus*) fish tissue have been identified in this regards [6]. But little attention paid to the fatty acids profile of their products such as caviar at sturgeon.

Caspian Sea is the biggest lake in the world and have a lot of important resources included meat and caviar of Acipenseridae. Iranian sturgeon (*A. persicus*) and Russian sturgeon (*A. guldenstaedti*) have high commercial value in universal trades. Iranian caviar is popular as golden caviar that is the most desirable caviar in the world. The caviar is one of the valuable products and maintenance of shelf life of them is very critical.

The freezing and frozen storage have largely been used to retain fish dietary and nutritional properties [7]. But, a number of changes were happen during frozen storage which can modify their structural and functional properties [8] and lead to unpleasant flavors [9].

The effect of frozen storage on the lipid composition of fishes has been investigated in some studies [10, 11]. There are little study on quantity and quality of FAs and shelf life of Iranian (*A. persicus*) and Russian sturgeon (*A. guldenstaedti*) caviar. Therefore, this study was carried out to identify the quantity and quality of the fatty acids profile of Iranian (*A. persicus*) and Russian sturgeon (*A. guldenstaedti*) caviar and their stability in cold storage at -18°C in spring and autumn seasons.

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MATERIALS AND METHODS

Twenty fishes were caught from Caspian Sea in spring and autumn from each Iranian (*A. persicus*) and Russian sturgeon (*A. guldenstaedti*) in this research. The samples were immediately transported under ice powder in foamed polystyrene self-draining boxes within 45 minutes to laboratory and then their caviar was removed and frozen by plate freezer at -30°C in order to minimize the effects of biochemical changes. They kept in freezer at -18°C after freezing.

Timetable of Sampling: The caviar samples were used for determination of fatty acids and stability of its fatty acids profile at -18°C. Analysis of frozen caviar samples was undertaken as fresh (0) and after, 30, 60, 90 and 120 days under cold storage at -18°C.

The samples were thawed in a refrigerator (at a temperature of 4±1°C) overnight and blend with each other by laboratory mixer to obtain a homogeneous mixture. The obtained mixture was used for fatty acids identification.

Fatty acid Analysis: According to given time table the samples were prepared and the total lipids were extracted by chloroform-methanol (1:1, v/v) and estimated gravimetrically [12]. The fatty acids in the total lipids were esterifies into methyl esters by saponification with 0.5 N-methanolic NaOH and transesterified with 14% BF3 (Trifluoride Bore) (w/v) in methanol [13]. The fatty acids methyl esters were analyzed on a Hewlett Packard 6890 Gas Chromatograph (GC) equipped with a Flame Ionization Detector (FID). The esters were separated on a BPX-70 column (120 m ×0.25 mm i.d.). Column injector and detector temperatures were 285 and 320°C, respectively. The carrier gas was nitrogen (flow 0.6 ml min^{-1}). Identification of UFAs was performed by comparison to retention time of authentic standards. All the experiments were carried out in triplicate.

Statistical Analysis: All the data were subjected to analyses of variance (one-way ANOVA), at the $P<0.05$ confidence level using Duncan's multiple range test [14].

RESULTS AND DISCUSSION

The identified fatty acids ($mg^{-1}g$) of spring and autumn Iranian and Russian sturgeon's caviar and their changes after storage period (4 months) in -18°C are shown in Table 1 and 2. The results showed that identified FAs in spring Iranian sturgeon's caviar were including as saturated fatty acids (SFAs) Lauric (C12:0), Myristic (C14:0), Palmitic (C16:0), Stearic (C18:0), Arachidic (C20:0), mono unsaturated fatty acids (MUFAs), Palmitoleic (C16:1), Oleic (C18:1), Erucic (C 22:1 (n-9)), Linoleic C18:2 (n-6), Linolenic (C18:3 (n-3)) acids and C16 isomers. But only Palmitic (C16:0), Stearic (C18:0), Oleic (C18:1), Linoleic C18:2 (n-6), Erucic (C 22:1 (n-9)) and Myristic (C14:0) acids was found in autumn Iranian sturgeon's caviar.

The identified FAs in Russian Iranian sturgeon's caviar were C12:0, C14:0, C16:0, C18:0, C20:0, C16:1, C18:1, C 22:1 (n-9), PUFAs Linoleic C18:2 (n-6), Linolenic (C18:3 (n-3)) acids and C16 isomers. But C16:0 and C18:2 didn't observe in autumn Russian sturgeon's caviar. The highest level of FAs was related to C18:1 in spring (56.25 and 44.60 $mg^{-1}g$) and autumn (48.80 and 55.10 $mg^{-1}g$) Iranian and Russian sturgeon's caviar ($P<0.05$). The FAs of fish and fish products varies based on species, sex, diet, season and tissue lipid levels [15]. Therefore, observed FAs variations in fresh caviar probability are due to diet, season and tissue lipid levels.

Table 1: The fatty acids in spring and autumn of Iranian sturgeon's caviar after storage period (4 months) ($mg^{-1}g$).

	Spring						Autumn					
Fatty acids	Fresh	30 days	60 days	90 days	120 days	P value	Fresh	30 days	60days	90 days	120 days	P value
Palmitic (C16:0)	27.17^{a}±0.42	27.00^{a}±0.07	26.70^{b}±0.37	25.30^{c}±0.91	24.46^{d}±0.20	0.0001	24.20^{a}±0.14	23.90^{b}±0.35	23.50^{c}±0.70	23.40^{c}±0.60	23.40^{c}±0.05	0.0009
Stearic (C18:0)	2.90^{a}±0.21	1.89^{b}±0.14	1.80^{c}±0.14	1.72^{d}±0.35	1.66^{d}±0.14	0.010	2.20^{a}±0.07	2.00^{a}±0.06	1.95^{b}±0.12	1.95^{b}±0.03	1.94^{b}±0.00	0.0193
Oleic (C18:1)	56.25^{a}±0.14	55.17^{b}±0.07	53.30^{c}±0.21	52.40^{d}±0.07	51.00^{e}±0.07	<0.0001	48.80^{a}±0.34	48.50^{a}±0.14	48.00^{b}±0.84	47.80^{c}±0.17	47.00^{d}±0.41	0.0002
Linoleic (C18:2)	1.31^{a}±0.07	1.30^{a}±0.06	1.20^{b}±0.07	1.15^{c}±0.14	1.10^{d}±0.00	<0.0001	1.50^{a}±0.07	1.41^{b}±0.04	1.38^{b}±0.02	1.20^{c}±0.02	1.17^{d}±0.21	<0.0001
Erucic (C22:1)	2.34^{a}±0.07	2.02^{b}±0.07	1.80^{c}±0.14	1.64^{d}±0.06	1.45^{e}±0.21	0.0231	2.10^{a}±0.70	2.00^{a}±0.67	1.72^{b}±0.21	1.70^{b}±0.12	1.20^{c}±0.14	<0.0001
Myristic (C14:0)	0.81^{a}±0.05	0.80^{b}±0.00	0.77^{c}±0.04	0.00^{d}±0.00	0.00^{d}±0.00	0.0001	1.00^{a}±0.17	0.91^{b}±0.11	0.89b^{c}±0.12	0.80^{c}±0.13	0.70^{d}±0.19	0.0013
Palmitoleic (C16:1)	11.3^{a}±0.91	10.90^{b}±0.14	10.10^{c}±0.06	0.00^{d}±0.00	0.00^{d}±0.00	0.0001	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	-
Lauric (C12:0)	2.90^{a}±0.14	0.00^{b}±0.00	0.00^{b}±0.00	0.00^{b}±0.00	0.00^{b}±0.00	0.0221	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	-
Linoleic (C18:3)	1.00^{a}±0.41	0.00^{b}±0.00	0.00^{b}±0.00	0.00^{b}±0.00	0.00^{b}±0.00	0.0161	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	-
Arachidic (C20:0)	0.95^{a}±0.21	0.00^{b}±0.00	0.00^{b}±0.00	0.00^{b}±0.00	0.00^{b}±0.00	0.0071	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	-
C16 isomers	10.17^{a}±0.14	0.00^{b}±0.00	0.00^{b}±0.00	0.00^{b}±0.00	0.00^{b}±0.00	0.0321	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	-

Means with different superscripts in the same raw are significantly different ($P<0.05$).

Table 2: The fatty acids of Russian sturgeon's caviar (spring and autumn) after storage (4 months) ($mg^{-1}g$)

	Spring						Autumn					
Fatty acids	Fresh	30 days	60 days	90 days	120 days	P value	Fresh	30 days	60 days	90 days	120 days	P value
Palmitic (C16:0)	28.60^{a}±0.14	27.34^{b}±0.17	26.03^{c}±0.02	25.96^{c}±0.64	25.34^{d}±0.23	0.0002	26.50^{a}±0.21	25.30^{b}±0.28	24.34^{c}±0.14	23.46^{d}±0.28	22.70^{e}±0.35	<0.0001
Stearic (C18:0)	2.30^{a}±0.01	2.10^{b}±0.07	1.97^{c}±0.14	1.64^{d}±0.44	1.05^{e}±0.35	<0.0001	2.50^{a}±0.00	2.20^{b}±0.14	2.01^{c}±0.00	1.82^{d}±0.08	1.70^{e}±0.14	<0.0001
Oleic (C18:1)	44.60^{a}±0.04	44.58^{a}±0.11	44.55^{a}±0.34	44.52^{a}±0.24	40.50^{b}±0.38	<0.0001	55.10^{a}±0.00	41.70^{b}±0.91	41.50^{c}±0.00	41.42^{c}±0.14	40.10^{d}±0.12	0.0021
Linoleic (C18:2)	1.70^{a}±0.07	1.65^{b}±0.12	1.60^{b}±0.13	1.55^{c}±0.17	1.54^{c}±0.27	0.0021	1.50^{a}±0.14	1.50^{a}±0.07	1.48^{b}±0.09	1.45^{c}±0.11	1.40^{d}±0.23	0.0011
Erucic (C22:1)	2.30^{a}±0.14	2.01^{b}±0.07	1.97^{c}±0.16	1.41^{d}±0.17	1.40^{d}±0.21	<0.0001	3.30^{a}±0.35	2.30^{b}±0.14	2.10^{c}±0.71	1.99^{cd}±0.07	1.90^{d}±0.14	<.0001
Myristic (C14:0)	1.20^{a}±0.13	1.01^{b}±0.37	0.46^{c}±0.25	0.00^{d}±0.00	0.00^{d}±0.00	<0.0001	1.10^{a}±0.07	0.93^{b}±0.14	0.82^{c}±0.11	0.76^{cd}±0.09	0.70^{d}±0.04	0.0008
Palmitoleic (C16:1)	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	-	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	-
Lauric (C12:0)	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	-	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	-
Linoleic (C18:3)	1.75^{a}±0.10	0.46^{b}±0.04	0.00^{c}±0.00	0.00^{c}±0.00	0.00^{c}±0.00	0.0012	2.00^{a}±0.04	1.70^{b}±0.090	1.52^{c}±0.18	1.41^{d}±0.11	1.30^{e}±0.25	<.0001
Arachidic (C20:0)	0.95^{a}±0.14	0.81^{b}±0.27	0.32^{c}±0.21	0.00^{d}±0.00	0.00^{d}±0.00	0.0302	1.00^{a}±0.12	0.75^{b}±0.02	0.73^{b}±0.01	0.71^{b}±0.00	0.70^{b}±0.00	0.0061
C16 isomers	14.30^{a}±0.08	10.53^{b}±0.27	0.00^{c}±0.00	0.00^{c}±0.00	0.00^{c}±0.00	0.0112	13.6^{a}±0.14	11.30^{b}±0.48	8.45^{b}±0.35	3.32^{c}±0.14	0.00^{d}±0.36	0.0031

Means with different superscripts in the same raw are significantly different (P<0.05).

The fatty acid changes of Iranian and Russian sturgeon's caviar during time table of 120 days of storage at -18°C is summarized in Table 1 and 2. A clear reduction trend was established in FAs during the period of storage (fresh meat to 120 days of storage meat) (P<0.05). According to the obtained results, saturated and unsaturated fatty acids of Iranian and Russian sturgeon in most spring and autumn samples were the same. Except palmitoleic acid in (0.00 vs. 11.31 $mg^{-1}g$ in spring Russian and Iranian sturgeon in fresh samples, respectively) and lauric acid that was 2.9 $mg^{-1}g$ in fresh sample of spring Iranian sturgeon and 0.00 $mg^{-1}g$ in others. It is revealed that the species of fish is affected FAs composition [16]. The amount of palmitic, linoleic, myristic, Linoleic and C16 isomers acids in spring of Iranian sturgeon caviar was lower than in Russian ones, whereas the amounts of all FAs in autumn Iranian sturgeon caviar was lower than in Russian sturgeon caviar. The oleic acid (C18:1 ω-9) was the major FAs and during the whole period. The obtained results for caviar was similar to in *Channa* spp. [17], gilthead sea bream (*Sparus aurata*), sea bass (*Dicentrarchus labrax*) [18] and mackerel meat FAs [4].

The obtained results indicated that apparently FAs profile of spring Iranian sturgeon caviar is richer than others. Also, the autumn Iranian sturgeon caviar showed poorer FAs profile and stability. This phenomenon obviously reflected effects of season on Fas profile. It is in agreement with other [15]. Moreover, the results showed that USFAs were more than SFA (SFA<PUFA+MUFA). The differences in the fatty acid composition of the caviar lipids had a decisive function in the formation of hydroperoxides. The oxidative changes in frozen caviar may be due to the occurrence of radicals [18]. These types of radicals are easily formed. The lipid peroxidation leads to FAs reduction during frozen storage of caviar and lead to decreases caviar nutritional value. The PUFA/ SFA ratio reveals that fish and fish products are a good source of PUFA related to SFAs. This ratio obtained was less than 1 in caviar. Any decrease of PUFA leads to a significant decrease of this ratio during frozen storage. The negative relationship between this ratio and storage time showed that oxidation mechanisms are active during frozen storage. Finally, the FAs can divide into 3 groups during frozen storage as stable FAs (lauric acid, palmitic acid, palmitileic acid, C16 isomers and linoleic acid) semi-stable FAs (oleic acid) and unstable FAs (myristic acid, stearic acid, linolenic acid, erucic acid and arachidonic acid). The decrease in FAs showed that the nutritional value of caviar has been lost during frozen storage.

CONCLUSION

Determination of fatty acid composition indicated that palmitic (C16:0) and oleic (C18:1) acids are more abundant FAs in Iranian and Russian sturgeon's (spring and autumn) caviar. The season and species have important roles on FAs composition of Iranian (*A. persicus*) and Russian (*A. guldenstaedti*) caviar. The shelf life of FAs and quality of caviar was decrease due to oxidation and hydrolysis during preservation period. Therefore, it demonstrated that caviar can preserve up to 2 months.

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