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Full Length Research Paper

Concentrations of metal contaminants, vitamin and mineral in waxed caviar from *Mugil cephalus* (L.,1758)

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In the research to determine the compositions of metal contaminants, vitamin, mineral and fatty acids upon the *Mugil cephalus* (L.,1758) caviar imported from Mauritania and waxed in Turkey. It has been found that the fish samples that the caviar belonged to, were caught in waters which were rich in terms of zinc (Zn) and cadmium (Cd) and their amount has been determined as 11.35 and 0.004 mg/100 g in raw caviar; 12.24 and 0.005 mg/100 g in waxed caviar respectively. It has been found that these values are close to the values that are dangerous for human health. Iron (Fe) amount, on the other hand, has been quite low, 0.87 mg/100 g. In both samples, it has been found that, it is vitamin E that is richest in it and the amount of vitamin A is above the FAO/WHO's recommendation about reliable daily consumption amount for adults. The highest value has been phosphorus (P), in terms of minerals. Furthermore, the value of protein, lipid, ash, carbohydrate, energy of waxed caviar were significantly higher ($p<0.05$) than raw caviar. Lead, mercury and copper (Pb, Hg and Cu) concentrations in raw and waxed caviar were below detection limit. Fatty acids of raw and waxed caviar oil were C16:0, C16:1, C18:1 n-9; C20:5 n3;C22:6n-3. Palmitic acid (C16:0) was determined as the dominant saturated fatty acid. Palmitoleic acid (C16:1) was also found as the major unsaturated fatty acid in raw and waxed caviar samples.

Key words: *Mugil cephalus*, waxed caviar, vitamin, mineral, metal contaminant.

INTRODUCTION

Fish roes are consumed for special dinners and invitations all over the world and caviar is a well-known example. The caviar is an expensive byproduct from fish processing industry which is considered as a high-price-flavor with a high nutritional value and which is full of vitamin A and complex vitamins B in international and domestic markets (Altug and Bayrak, 2003; Sengör et al., 2003; Shiari et al., 2006; Wang et al., 2008a; Mol and Turan, 2008). The roes of sturgeon are known as the original caviar. In the U.S. only sturgeon caviar can be labeled as "caviar." Caviar from other species must be identified with a qualifying term that includes the common name of the marine animal for use. For example, salmon caviar must be labeled "salmon caviar" (Bledsoe et al., 2003; Mol and Turan, 2008). There are over 20 species of sturgeon, mostly consumed and the most valuable of which include Acipenser *Huso huso* (Beluga sturgeon) from the Caspian and Black Seas (including the most sought-after ''beluga''), *Acipenser gueldenstaedtii* (Ossetra or Russian sturgeon), *Acipenser persicus* (Persian sturgeon), and *Acipenser stellatus* (Sevruga sturgeon) from the Black Sea. However, the caviar produced from Mullet (*Mugil cephalus*) is as popular as sturgeon caviar (Altug and Bayrak, 2003; Sengör et al., 2003; Wang et al., 2008b; Balaswamy et al., 2009). But the mullet caviar quality never reach the level of caviar quality obtained from sturgeon.

The goal of our study in this article was to investigate the metal contaminants and the fatty acid compositions of raw and waxed caviar produced from *M. cephalus* roe coming from Mauritania as raw and then waxed in Turkey. Despite the importance of these products in international commerce, there is relatively little technical

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information that has been published on trace elements, vitamin and minerals on these products. The studies have been carried out upon the mostly evaluated of the caviar microflora, their chemical composition, product quality and identification of caviar of fish species and food safety attributes (Altug and Bayrak, 2003; Sengör et al., 2003; Shiari et al., 2006; Caprino et al., 2008; Duyar et al., 2008; Wang et al., 2008a; Mol and Turan, 2008; Hedayatifard, 2009). Therefore, this study gains importance in terms of investigating the concentrations of essential and toxic elements such as Fe, Cd, Cu, Hg, Pb, and Zn.

MATERIALS AND METHODS

Materials

Materials for the study, raw and waxed caviar samples, were taken from *M. cephalus* fish's raw roes, imported from Mauritanya, supplied from commercial production establishments in Turkey. All roe samples were frozen and stored at -20°C until the analysis. A total number of 16 caviar samples (30 g each) were transported with ice to the Industrial Services Laboratories of TUBITAK–MAM (The Scientific and Technological Research Council of Turkey – at Marmara Reasearch Centre) in their original packages.

Methods

The protein analysis belonging to the samples was carried out according to the Kjeldahl Method (AOAC, 1995), the fat analysis was carried out according to the Acid Hydrolosis Soxtec System (AOAC, 1995), the moisture analysis was made by dehydrating the homogenized samples to a fixed weight with an incubator, and the crude ash was analysed by burning the samples at 550°C (AOAC, 1995). The carbohydrate and energy calculation of samples were evaluated with the method of Watt and Merril (1975), Vitamin A, B1, B2, B6, D and E were identified according to HPLC method (AOAC, 2000), Cu, Cd, Pb Zn, Hg and Fe were identified according to Atomic Absorbtion Spectrophotometric (AAS) method (AOAC, 2005).

The fatty acids that belong to the samples were prepared according to the lipids methyl esters IUPAC II. D.19. (1979) methods and analysis were carried out by using the Elmer Autosystem XL Gas Chromotography and Flame Ionization Detector (FID). Supelco 2330 Fused Silica Capillary Column (30 m x 0.25 mm x 0.20 m film width) was used for determining the fatty acid composition. The results of the research have been exposed to SPSS 13.0 packet program for Windows group comparing test (t test) and they have been given their standard deviation. Significance of differences was defined at $p<0.05$ (O uzhan et al., 2006).

RESULTS

Proximate compositons, concentrations of metal contaminants, vitamin and mineral of raw and waxed caviar produced from *M. cephalus* are shown in Table 1. In addition, the average of its fatty acid compositions are shown in Table 2.

As seen in Table 1, raw caviar and waxed gray mullet caviar have been found as including vitamin E most in terms of vitamin values and it has been found that, it includes P most, in terms of minerals. Furthermore, the values of protein, lipid, ash, carbohydrate, energy of waxed caviar were significantly higher ($p<0.05$) than raw caviar. Pb, Hg and Cu concentrations in raw and waxed caviar were below detection limit. Zn and Cd values found in raw and waxed caviar samples were respectively 11.35, 12.24 mg/100 g and 0.004, 0.005 mg/100 g.

Fe has been found in low amounts as 0.87 mg/100 g. As seen in Table 2, major fatty acids of raw and waxed caviar oil were C16:0, C16:1, C18:1n-9, C20:5n3, C22:6n-3. Palmitic acid (C16:0) was detected as the dominant saturated fatty acid. Palmitoleic acid (C16:1) was also found as the major unsaturated fatty acid in two caviar samples. Figure 1 shows saturated, mono and polyunsaturated fatty acids contents of raw and waxed caviar.

DISCUSSION

It is known that fish generally contains protein amount of about 17 to 20%, while caviar contains between 25.40 to 26.90% of roe (Mol and Turan, 2008). The study has shown that, the amount of raw protein found in raw caviar has been 25.38%, which is in accordance with the other values reported by Karaka (2008) and engör et al. (2002) for gray mullet and values given above for the roe. Similarly, the values of raw fat, moisture, ash, carbohydrade and energy (14.63%, 58.46%, 1.53%, 0. 233 Kcal/100 g) for the gray mullet, caviar is close to the amount reported by researcers such as engör et al. (2002); Karaka (2008) and Mol and Turan (2008). It has been reported that, the values can change depending on the regions that the fish are caught and the fish's time for spawning (engör et al., 2002) . The increases observed in amounts of raw protein, fat, ash, carbonhydrade and energy value and the decrease in the amount of moisture ($p<0.05$) have been reported in similar researchers by various researchers, such as engör et al. (2002); Mol and Turan (2008) and it has been concluded that the change is a result of waxing (wax-paraffin mixture).

As a result, the amounts we found by proximate analyses seem to be in accordance with the researchers'. It has been reported in terms of mineral substances, the results are as such respectively for the Indian inland water fish species' roes, Balaswamy et al. (2009)'s *Catla catla* (catla), *Cyprinus carpio* (carp), *Labeo rohita* (rohu) and *Channa striatus* (murrel) as 6.1, 8.5, 5.1 and 4.4 mg/100 g; in terms of Ca 1085, 935, 1020 and 430 mg/100 g; when compared in terms of P the gray mullet is in quite a good level with the value 11.56 mg/100 g and that it is in average level with the P value 554.6 mg/100 g. When compared in terms of Fe which is an important heavy metal, as well as a mineral substance the amounts reported by Balaswamy et al. (2009) for the species

Table 1. The proximate compositons, concentrations of metal contaminants, vitamin and mineral of raw and waxed caviar.

Compositions	Raw Caviar	Waxed Caviar
Protein (g/100g)	25.38±0.26	41.16±0.24
Fat (g/100g)	14.63±0.15	22.88±0.01
Moisture (g/100g)	58.46±0.13	25.38±1.12
Ash (g/100g)	1.53±0.02	7.17±0.01
Carbohydrate (g/100g)	nd	3.47±0.01
Energy (Kcal/100g)	233	384
Cadmium (Cd) (mg/100g)	0.004±0.00	0.005±0.00
Lead (Pb)	nd	nd
Mercury (Hg)	nd	nd
Copper (Cu)	nd	nd
Zinc (Zn) (mg/100g)	11.35±0.04	12.24±0.00
Iron (Fe) (mg/100g)	0.87±0.12	1.49±0.07
Potassiom (K) (mg/100g)	306.9±4.03	254.5±1.55
Phosphor (P) (mg/100g)	554.6±10.63	666.6±20.05
Calcium (Ca) (mg/100g)	11.56±0.00	20.36±0.00
Magnesium (Mg) (mg/100g)	17.34±0.06	22.70±0.01
Vitamin A (mg/100g)	1.54±0.00	2.95±0.02
Vitamin E (mg/100g)	4.56±0.04	9.07±0.09
Vitamin B1 (mg/100g)	0.325±0.02	0.49.0±0.00
Vitamin B2 (mg/100g)	0.81±0.01	0.905±0.03
Vitamin B6 (mg/100g)	0.71±0.01	0.17±0.00
Vitamin D (µg/100g)	3.20±0.00	13.05±0.48

Values are means ± Standard deviation n=3, $p<0.05$ nd: Not detected.

Table 2. The fatty acid compositions of raw and waxed caviar.

Fatty acids	Raw caviar (%)	Waxed caviar (%)
C14:0	2.75±0.13	2.19±0.15
C16:0	11.28±0.09	10.17±0.33
C16:1	29.80±0.36	23.21±0.09
C17:1	1.70±0.27	1.78±0.22
C18:0	1.66±0.04	1.25±0.21
C18:1n-9	7.85±0.24	10.91±0.74
C18:2 n-6	1.46±0.20	1.25±0.15
C20:5 n-3	7.29±0.36	12.22±0.84
C21:0	1.21±0.03	2.79±0.39
C 23:0	2.58±0.05	2.52±0.02
C22:6n3	5.36±0.22	8.80±1.01
C24:1	0.89±0.06	1.3±0.17
SFA	19.48	18.94
MUFA	40.25	37.20
PUFA	14.10	22.28
Unknown	26.17	21.58

Results expressed as percentage of total fatty acid methylesters. Values are means ± Standard deviation. SFA:saturated fattyacids,MUFA:monounsaturatedfattyacids,PUFA:polyunsaturated fatty acids n=3, $p<0.05$.

before mentioned (3.28 - 12.28 - 9.98 - 7.88 mg/100 g) it has been found that the amount of Fe is quite low in gray mullet (0.87 mg/100 g). It has been found sufficient to meet (306.9 to 254.5 mg/100 g) the K need, which is

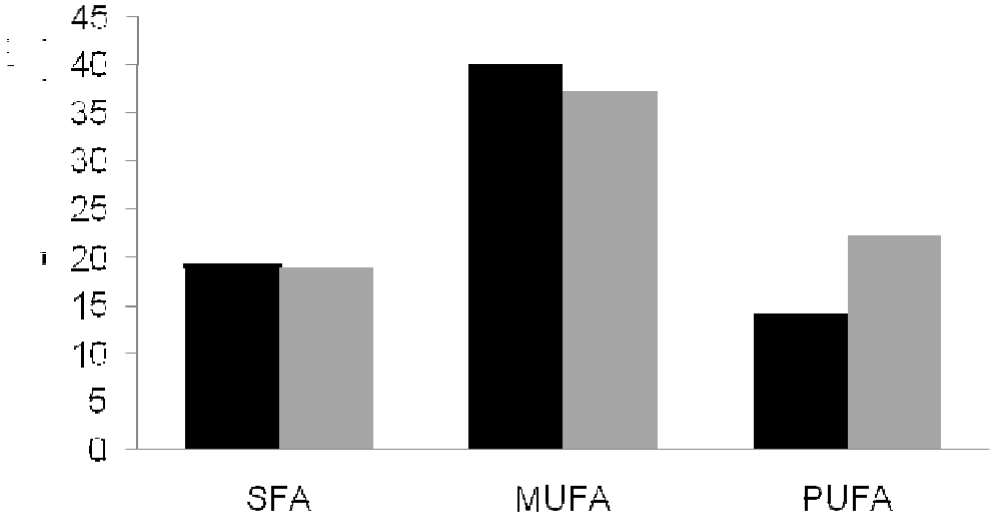

Figure 1. Fatty acids contents of raw and waxed caviar.

reported as 200 mg per day for adults (Varlik et al., 2004) on the other hand in terms of Mg, it has been found less than the amount Recommended Dietary Allowances (RDA) 300 to 350 mg per day; therefore, it is in low Mg amount (17.3 to 22.7 mg/100 g) to meet the diet (Seelig, 1982).

It has been reported in Bekhit et al. (2008) research upon New Zealand's six commercial fish species (Chinook salmon (*Oncorhynchus tshawytscha*), hoki (*Macruronus novaezelandiae*), southern blue whiting (SBW) (*Micromesistius australis*), hake (*Merlucciusaustralis*), blue warehou (*Seriolella brama*), and barracouta (*Thyrsites atun*) that Cd values of these species' roes have been such respectively 0.0002, 0.0002, 0.0002, 0.0005, 0.0012 and 0.0021 mg/100 g. Their Zn values have been such respectively 3.78, 3.22, 2.50, 4.12, 5.55, 10.8 mg/100 g and we have found from the data we received from this study that Cd (0.004 mg/100 g) and Zn (11.35 mg/100 g) values are higher than the amount reported by the researchers. While there is no maximum level specified for Zn in the Turkish Food Standards Code for fish and seafood, generally accepted level is 0.5 mg/100 g of fish or 2.5 mg/100 g of certain seafood (e.g. lobtster) (Bekhit et al., 2008) it can be said that 11.35 mg/100 g Zn is quite a high amount. Regarding the toxic level of Zn, a 45 mg/day limit recommended by the World Health Organization (WHO) in 1996 as the maximum tolerable limit for the adult population, which corresponds to 350 to 360 g of roes, Zn amount is unlikely to be the serving size for normal meals. On the other hand, Cd amount found whether in waxed or in raw caviar, has been found as quite close to the maximum amount 0.005 mg/100 g that is acceptible according to the report by Turkish Food Codex and Official Journal of the European Union.

Furthermore, it has been found that this value is within the hazard limit in the waxed caviar. Regarding the values that depend on the metal contamination of the region that the fish are caught, it has been concluded that the caviar imported from Mouritania is from the waters which are rich in terms of Cd and Zn. It has been reported in a research that the Zn concentration in roe from the Northwest Atlantic cod was 2 to 4 times higher than from Northern Norway cod, and oysters from the Atlantic had 8 to 9 times the concentration of Zn in oysters from the Pacific (Bekhit et al., 2008). As a consequence environmental factors seem to influence the amount of Zn and Cd in fish and fish roes. The amounts of Pb(<0.003 ppb), Hg(<0.001 ppb) and Cu (<0.1ppm) in gray mullet are below the level that is determinable. Major fatty acids of raw and waxed caviar oil were C16:0, C16:1, C18:1n-9; C20:5n3; C22:6n-3. These results agree with the results reported by engör et.al. (2003); Hedayatifard (2009). Mol and Turan (2008) have found those values in their study upon waxed gray mullet palmitoleic acid (C16:1), oleic acid (C18:1n9c) and docosahexaenoic acid (C22:6n3) and they have reported the acid values respectively as 24.25, 8.41 and 9.36%.

In our study, we have found the amounts of fatty acids respectively as 23.21, 10.91 and 8.80%; and these results are close to the amounts found by the researches' results stated. On the other hand, the similar increase

changes in fatty acids in raw caviar after the waxing, which is thought to be a cause of waxing, seems to be in accordance with researches of engör et al. (2003) and the other researches in literature. It has been found as insufficient in terms of the vitamin values such as B6, B1, B2, according to FAO/WHO's Recommended Nutrient Intake (RNI) of thiamin (B1) for adults that is 1.3 mg/day B6 vitamin, 1.2 mg/day for men and 1.1 mg/day for women while it has been found as close to being sufficient in terms of riboflavin (B2) reported as 1.3 mg/day for men and 1.0 mg/day for women.

The amount of vitamin A, whose intake in high amounts can be toxic, found as 1.54 mg/100 g in raw caviar and 2.95 mg/100 g in waxed caviar has been found out to be of high values when compared to the recommended amount by FAO/WHO for the adults (a maximum of 0.6 mg/day for men and a maximum of 0.5 mg/day for women). Vitamin A is fat soluble and can be stored, primarily in the liver. Routine consumption of large amounts of vitamin A over a period of time can result in toxic symptoms, including liver damage, bone abnormalities and joint pain, alopecia, headaches and vomiting, and skin desquamation (FAO/WHO, 2001). On the other hand in terms of vitamin D, whose intake over 50 µg/day is toxic and whose recommended intake by FAO/WHO is 5 µg/day, raw caviar is of quite good a level with its value of 3.20 µg/100 g. But it is thought that the increase in this amount after waxing process is a result of the waxing process. The other major lipid-soluble antioxidant in the cell antioxidant defence system and exclusively obtained from the diet is vitamin E. The major biologic role of vitamin E is to protect PUFAs and other components of cell membranes and low-density lipoprotein (LDL) from oxidation by free radicals (FAO/WHO, 2001) . Considering that Recommended Dietary Allowances (RDAs) for vitamin E is 15 mg/day (http://ods.od.nih.gov/factsheets/vitamin/), its amount in raw caviar which is 4.56 mg/100 g and in waxed caviar that is 9.07 mg/100 g can be regarded as quite good levels.

Conclusion

As a result, it has been concluded that one should be careful in consumption of the gray mullet caviar imported from Mauritania and waxed in Turkey because the amounts of metal levels of Zn and Cd are as high as to be dangerous for human health and it is of high levels in terms of vitamin A, whose excess amount of intake can be toxic. It can be important to overcome the deficiencies because of that, there are not certain limits for the import and sale of zinc in various countries, as well.

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