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The Chemical Composition of Waxed Caviar and the Determination of its Shelf Life

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Abstract: Female Pacific Grey Mullets with an average weight of 1048.30±174.93 g and average length of 47.98±2.45 cm are selected to verify the result of this study. Raw caviar derived from these sample Pasific Grey Mullets has an average weight of 143.9±23 g, salted caviar weights 107.33±21.87 g and waxed caviar weights 118.00±23.83 g. As a result of the chemical analyses which have been made, the amount of raw protein was found as 10.84±0.24% in the raw egg; however it increased during the storage process in the processed egg and was observed as 30.152±0.11% on the 50th day (0th, 10th, 20th, 30th, 40th and 50th, days). Amount of raw fat in raw and processed samples, Shelf life of waxed caviar was found as 40 days according to the chemical analyses made after 50th day is spoiled.

Key words: Pacific grey mullet (*Mugil soiuy*), caviar, shelf life, wax

INTRODUCTION

Caviars are the salt-cured and preserved eggs of aquatic animals that have been singled out and screened or otherwise separated from the supporting connective tissue. Fish eggs are commonly referred to as roe, particularly when they are in skeins. Caviar is graded according to the size of the eggs and the manner of processing. The grades are named for the types of sturgeon from which the eggs are taken. The species of sturgeon (Family Acipenseridae) that produce caviar are, in order of size, beluga, osetra and sevruga. The most widely recognized and valued caviar is made from sturgeon harvested from the Caspian Sea. (Keyvanfar *et al*., 1988; Bledsoe *et al*., 2003). Fish roes are generally processed into 3 products: whole ovaries (such as sujiko from Pacific salmon), individual eggs (caviar) and pate or pastes or other products such as dried mullet roe (Bledsoe *et al*., 2003; Ang *et al*., 1999). Mullet roe is also served as a pickled food ("Botargo") in Italy and other Mediterranean countries (Lu *et al*., 1979; Body, 1989). Dried mullet roe has a unique chewy mouth feel due to the large quantity of wax esters, which can be as high as 60-70% of the extracted oil (Lu *et al*., 1979). The caviar is packed in tin, glass, or porcelain containers equipped with tight-fitting covers. It is then ready to eat or store under refrigeration (Anonymus, 2004). The definition of caviar according to Turkish standards is given as products consumed raw, by frying or grilling after the eggs (ovariums) taken from usually sturgeon (Acipenseridae family), grey mullet (Mugillidae family), trout (Salmonidae family) by fleecing when they are alive or by opening their abdomen are cleaned from intestine pieces and veins, washed, processed through various methods using ingredients, prepared in accordance with the technique and the dried ones are made durable to heat treatment (Anonymous, 1993). In granular sturgeon caviar the average amount of protein according to the type varies between 27-29%, that of fat between 10-14% and energy (Kcal/100 g) between 203 and 240 (Moradi, 2003). Roe products generally include 16-30%. Raw fat content is in average about 10% between 5 and 20% (for instance salmon caviar) (Craig and Powrie, 1988). Despite the fact that caviar is not consumed in our country for it is not very proper for the taste of our society and expensive in economic terms, it is consumed a lot in Europe and other countries and has a high nutritive value. Increase in the caviar production will both help making use of our fishery products which we cannot use sufficiently and contribute to our country's economy. Several types of caviar from different fish species are marketed as shelf-stable products.

This study has been undertaken in order to examine the caviar processing technology proper for our society's

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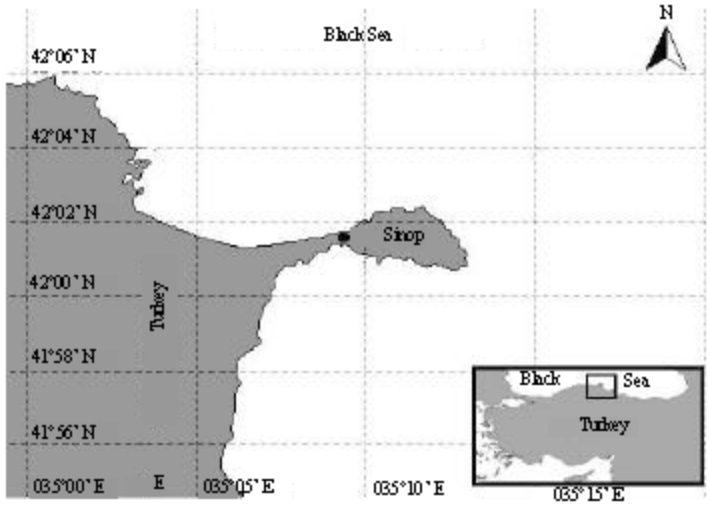

Fig. 1: Sinop Akliman from where the research material was provided

taste and determine shelf life of the caviar at the refrigerator (+4°C) conditions and it was aimed at determining the chemical composition and shelf life of waxed caviar obtained from Pacific grey mullet (*Mugil so-iuy*) in Black sea.

MATERIALS AND METHODS

Grey mullets which are the subject of this research (*Mugil so-iuy*) were caught from Sinop Akliman (Fig. 1). The study was carried out in June 2004.

The grey mullets which were caught were weighed with a sensitive scale of Precisa XB 220A series and their total lengths were measured with a ruler for measuring length. The abdomens of the fish were incised carefully in order to take out caviars and the eggs were extracted. Firstly, the wet lengths of Pacific grey mullet eggs which had been extracted were weighed. Pieces of blood and intestines on the eggs were cleared, they were salted with a dry salting method, put in a humid cloth with a pressure which will not harm the eggs and kept in salt for 3-4 h. After the caviar becomes smooth as desired, the salt on it was taken with the help of a wet brush. At the end of this procedure, the caviars were dried for 5-6 days without being directly exposed to sunlight. In order for them not to be exposed to oxidation and to be preserved for a longer time, they were plunged in melted wax and covered with wax on the surface. At the end of this procedure the caviars were wrapped up in gelatin on the surface and kept in refrigerator (4°C).

Chemical analysis: Before extraction, caviar were minced in a Warring blender and homogenised (Ultraturax T25 IKA, 7500 rpm). pH analysis were carried out according to, Curan, Nicoladies, Poulter and Pors (1980) methods with a pH meter labeled Hanna HI 221.

Total volatile bases (TVB-N), trimethylamine (TMA) and thiobarbituric acid (TBA) were analysed according to Botta *et al*. (1984), AOAC (1990), Tarladgis *et al*. (1960), respectively. Dry matter, crude ash, crude protein were determined according to AOAC (1980) and crude lipid was determined Bligh and Dyer (1959). Carbohydrate analysis and energy calculations were made according to Merrill and Watt (1973).

Statistical analysis: The significant effects of Quality changes on the shelf-life of hot-smoking vacuum-packed hot smoked Atlantic bonito, as measured by the chemical and sensory evaluations, were determined by the ANOVA method using the SPSS program at $p<0.05$.

RESULTS AND DISCUSSION

Quality control analysis and chemical composition analysis of fresh and processed eggs which were obtained from Pacific grey mullets brought to the laboratory were carried out on 10th, 20th, 30th, 40th and 50th days. The results are given in Table 1 and 2.

The average length in mature females used in the research is 47.98±2.45 cm, the average weight is 1048.30±174.93 and egg efficiency was found out as 13.84%. The average weight of the unprocessed eggs taken from the fish was calculated as 143.9±23 g, the weight of dry caviar (at the end of salting) was found as 107.33±21.87 g and the weight of waxed caviar as 118.00±23.83 g.

Table 1: Chemical composition values of pacific grey mullet caviar

Chemical Features	Raw egg	Dried caviar	10th day	20th day	30th day	40th day	50th day
Humidity (%)	77.012±0.18	26.160±0.04	26.203±0.59	24.893±1.69	25.203±1.82	23.227±0.14	23.160±0.23
Raw Protein (%)	10.840±0.24	24.577±0.2	27.360±0.42	28.077±0.59	26.06±0.26	27.620±0.10	30.152±0.11
Raw Fat (%)	11.063±0.61	39.906±0.24	34.283±1.85	36.773±1.74	38.55±0.62	40.151±0.41	38.810±0.50
Raw Ash (%)	0.993±0.21	9.073±0.08	9.783±0.13	9.026±1.07	9.825±0.47	8.803±0.11	7.370±0.180
ΣCarbohydrate (g/100g)	0.092	0.284	2.371	1.231	0.362	0.199	0.508
ΣEnergy (Kcal/100 g)	166.703	519.074	489.518	512.778	514.875	538.263	541.034
Salt (%)	2.90±0.20	35.1±0.5	29.250±0.10	26.32±0.75	22±0.13	17±0.18	13.16±0.50

Table 2: Quality control values observed during the maintenance of waxed caviar

Spoilage products	Raw egg	Processed egg	10th day	20th day	30th day	40th day	50th day
TVB-N (mg/100 g)	2.80±0.04	2.80±0.05	12.60±0.47	16.80±0.35	19.60±0.57	26.60±0.61	35.70±0.78
TMA-N (mg/100 g)	0.30±0.03	1.35±0.12	1.80±0.25	2.10±0.21	0.90±0.08	4.33±0.58	7.36±0.86
TBA (mg kg^{-1} malondialdehit)	2.08±0.05	4.80±0.17	3.58±0.59	4.83±0.52	5.66±0.71	6.86±0.97	8.58±0.83
pH	6.81±0.01	5.25±0.01	5.17±1.02	5.13±0.01	5.10±0.01	4.97±0.01	5.25±0.02

In the study the egg efficiency of the grey mullets was found as 13.84%. The egg efficiency of fish depends on type, size, genetic factors and various environmental conditions most important of which is nutrition (Yilmaz and Gül, 2002). Duyar (2000) determined the egg efficiency of grey mullet and stated that the gonad weight in females before reproduction constitutes 16-17% of the body weight. It was reported by Kara (1992) that the weight of wet caviar of the grey mullets caught in the reproduction season reaches more than 20% of the body weight. Sengör *et al*. (2000) determined caviar efficiency as 21.98% in the study they carried out in Suyo (Homa) fish trap.

Loss of weight is inevitable in a processed egg. In the present study, a loss of weight in the rate of 24±3.85% was observed in Pacific grey mullets after salting. Sengör (2000) encountered 35% loss of weight in the study they carried out on grey mullets in Sufa fish trap. Kinacigil and Alpbaz (1991) made research in the same fish trap and found an approximate value although loss of weight was not the same. When the study which is undertaken is compared to the studies in Sufa fish trap, it can be said that this difference in the loss of weight emanates from the body weight and length of the fish, maturation of the eggs, method of hunting and nutrition conditions.

The rate of humidity was found in the unprocessed eggs as 77.012±0.18%, while it was calculated as 26.16±0.04% at the end of the waxing procedure. It is thought that this has occurred due to the fact that water was cleared off from the caviar as a result of the dry salting and drying procedures. The protein value of caviar was found as 24.57%, while the protein content of the unprocessed grey mullet eggs was calculated as 10.84%. The water discharge which occurred as a result of the salting procedure increased the protein, fat, ash and carbohydrate values. Another reason why the amount of fat is high in the study is the structure of wax and the wax smeared on the samples during the analysis although not desired.

While the amount of salt in raw eggs was determined as 2.9%, this value was found as 35.14% in processed caviar. The energy value of processed caviar was found as 519.07 Kcal 100 g^{-1}. The changes which have occurred in the chemical composition during storage in cold were considered important/ unimportant in the interval ($p<0.05$).

The fact that the protein, fat and ash values obtained from the waxed caviar is more than those obtained from unprocessed and dry salted samples is in accordance with the study of Sengör (2000). Vuorela *et al*. (1979) examined the components of roes according to their maturity in their study and found out that the amount of ash in terms of dry weight in mature eggs varies between 1.8 and 4.8%. Sengör (2000) found the average amount of ash in waxed grey mullet caviar as 10.14±0.003% and amount of humidity as 23.58%±0.08 in their study. In the present study, the average amount of ash in dried caviar was found as 9.0733±0.08% and the average amount of humidity was found as 26.16±0.04% and the studies were parallel. Bledsoe *et al*. (2003) claims that the humidity rate decreased after the eggs are salted, however the protein, fat and ash content has increased. Unprocessed grey mullet egg includes 22.6% protein. 13.7% fat, 61.5% humidity and 8.1% ash (Lu *et al*., 1979). It is assumed that when unprocessed Pacific grey mullet egg is compared to literature data in the study fat value % is similar and the differences in protein %, ash %, humidity % content emanates from factors such as type pf fish, method of hunting and the maturity, age and length of fish.

While, the total amount of volatile basic nitrogen in unprocessed grey mullet egg and processed caviar was found as 2.8 mg 100 g^{-1}, it increased during the storage and was observed as 35.7 mg 100 g^{-1} on the 50th day of the storage. The quality categorization of fish and fishery products according to TVB-N values is determined as follows; a TVB-N value of 25 mg 100 g^{-1} is "very good", 30 mg 100 g^{-1} is "good", 35 mg 100 g^{-1} is "marketable" and a TVB-N value more than 35 mg 100 g^{-1} is "spoiled" (Lang, 1979; 1983). Çelik and Yanar report in a 1999 study

that TVB-N consumable value was exceeded on the 15th day of the storage in the carp hatching.

TBA is a good indicator to determine the quality of the fish whether it was frozen, chilled or stored with iced (Tarladgis *et al*., 1960; Vareltzis *et al*., 1988). It suggests that maximum level of TBA value indicating the good quality of the fish frozen, chilled or stored with ice is 5 mg malonaldehyde kg^{-1}, while the fish may consume up to the level of 8 mg malonaldehyde kg^{-1} TBA value (Schormüller, 1969). TBA value of grey mullet eggs was observed as 2.08 mg kg^{-1} Malonaldehit. With the effect of salting oxidation and TBA value increased. TBA value of processed salted caviar was found as 4.8 mg kg^{-1} Malonaldehit. The reason of this increase in TBA value is the effect of salt which increases oxidation. TBA is the secondary product of lipid oxidation. In consumable fishery products TBA value is reported as 5-8 mg kg^{-1} Malonaldehit (Schormüller, 1968; Ozden and Gökoðlu 1997). According to the TBA findings of the study, it is seen that caviar samples have a very good quality until the 30th day of storage, they are consumable between 30th and 50th days and they become spoiled as of the 50th day. Lipid oxidation varies according to time of storage, storage temperature, satiety level of fat acids and the existence of antioksidan, prooksidan in the environment (Serdaroðlu and Felekoðlu, 2005).

While, the pH value of unprocessed caviar egg was measured as 6.81, the pH value of processed caviar was observed as 5.25. The pH value of salted fishery products was reported as more than 5 (Lyhs *et al*., 2001). Despite the fact that changes are observed in the pH value in relation to enzyme activities and bacterial activities during the storage, the pH value measured on the 50th day of the storage is 5.25. There are many factors affecting quality and quality factors in fishery products. These are the body composition, size and shape of fish, the physical situation of its bacterial flora, the place it was hunted and type of feeding (Gökoðlu, 2002).

CONCLUSION

As a result of the study we have carried out, it was found out that grey mullet eggs can be processed and made use of as caviar and waxed caviar obtained from grey mullet and stored at +4°C have a good quality until the 20th day of storage, is consumable between the 30th and 40th days and is spoiled on the 50th day.

REFERENCES

Ang, C.Y.W. and K.L. Liu, Huang, Y. W. 1999. Asian Foods. Science and Technology. Technomic Pub. Co., Inc. Lancaster, PA.

A.O.A.C., 1984. Official Methods of Analysis. 14th. Edn. Association of Analytical Chemists, Washington, DC,USA.

A.O.A.C., 1990. Official Methods Of Analysis Of The Association Of Official Analytical Chemists. 15th Edn., pp: 780.

Anonymous, 1993. Processed Fish Roe, Turkish Standards 10925/4, pp: 1-11.

Anonymous, 2004. What Every Member of the Trade Community Should Know About: Caviar. U.S. Customs and border protection. (http://www.cbp.gov), pp: 20.

Bledsoe, G.E., C.D. Bledsoe and B. Rasco, 2003. Caviar and Fish Roe Products. Crit. Rev. Food Sci. Nutr., 43 (3): 317-356.

Bling, E.G. and W.J. Dyer, 1959. A rapid method of total lipid extraction and purification. Canadian J. Biochem. Physiol., 37: 911-1015.

Body, D.R., 1989. The lipid composition of the roe tissues from four common New Zealand marine fish species. J. Food Composition Anal., 2: 350-355.

Botta, J.R., J.T. Lauder and M.A. Jewer, 1984. Effect of methodology on total volatile basic nitrogen (TVB-N) determinations as an index of quality of fresh Atlantic cod (*Gadus morhua*). J. Food Sci., 49: 734-736.

Craig, C.L. and W.D. Powrie, 1988. Rheological properties of fresh and frozen chum salmon eggs with and without treatment by cryoprotectants. J. Food Sci., 53 (3): 684–687.

Duyar, H.A., 2000. An Investigation on the Chemical Composition of Muscle, Eggs and Processing of the Flesh as Croquet in Inci Kefali (*Chalcalburnus tarichi* Palas,1811). E.U. Graduate School of Natural and Applied Science. Thesis of ph.D., Izmir. pp: 118.

Gökoðlu, N., 2002. Seafood Processing Technology. ISBN:975-9703-48-3. Istanbul, pp: 157.

Kara., Ö.F., 1992. Fisheries Biology and Populasion Dinamics, E.U. Fisheries Faculty Books No 27. Bornova- Izmir, pp: 168.

Keyvanfar, A., D. Rochu and J.M. Fine, 1988. Comparative study of sturgeon oocyte soluble proteins by isoelectric focusing. Comp. Biochem. Physiol. B-Biochem. Mol. Biol., 90: 393-396.

Kinacigil. H.T. and A. Alpbaz, 1991. The caviar production of flathead Grey Mullet (*Mugil cephalus cephalus* Lin. 1758) catched in SUYO (HOMA) Lagoon. 10 year Fish. Symp., pp: 722-738.

Lang, K., 1979. Der flüchtige Basenstickstoff (TVB-N) bei Binnenland in der verkehr gebrachten frischen Seefischen. Archiv für Lebensmittelhygiene, 30: 215-217.

Lang, K., 1983. Der flüchtige Basenstickstoff (TVB-N) bei im Binnenland in der Verkehr gebrachten frischen seefischen. II. Mitteilung. Archiv für Lebensmittelhygiene, 34: 7-9.

Lu, J.Y., Y.M. Ma, C. Williams, R.A. Chung, 1979. Fatty and Amino Acid Composition of Salted Mullet Roe. J. Food Sci., 44: 676-677.

Lyhs, U., J. Lahtinen and M. Fredriksson-Ahomaa, E. Hyytiä-Tress, K. Elfing and H. Korkeala, 2001. Microbiological quality and shelf-life of vacuum-packaged 'gravad' rainbow trout stored at 3 and 8 °C. Int. J. Food Microbiol., 70: 221-230.

Merrill, A.L. and B.K. Watt, 1973. Energy value of Foods, basis and derivation. Agriculture research service. United States Department of Agriculture. Agric. Handbook, 74 (2): 3-5.

Moradi, Y., 2003. HACCP in Irain Caviar. Short Communication. Emir. J. Agric. Sci. 15 (2): 72-79.

Özden, Ö. and N. Gökoðlu, 1997. Investigation of the changes in oil of sardine, (*Sardina pilchardus*, W. 1792) stored in Cold. Food. 22 (4): 309-313.

Schormüller, J., 1968. Handbuch der Lebensmittelchemie (Band III/2). Berlin-Heidelberg-New York: Springer Verlag.

Schormüller, J., 1969. Handbuch der Lebensmittelchemie (Band IV). Berlin-Heidelberg-New York: Springer Verlag.

Serdaroðlu, M. and E. Felekoðlu, 2005. Effects of using rosemary extract and onion juice on oxidative stability of sardine (*Sardina pilchardus*) mince. J. Food Quality, 28: 109-120.

Sengör, G.F., A. Cihaner, N. Erkan, Ö. Özden and C. Varlik, 2000. Caviar Production From Flathead Grey Mullet (*Mugil cephalus*, Lin. 1758) and the Determination of it's Chemical Composition And Roe Yield.. Turkish J. Vet. Anim. Sci., 26 (1): 183-187.

Tarladgis, B.G., B.M. Watts and M. Yonathan, 1960. Distillation Method For The Determination of Malonaldehyde in Rancid Foods. J. Amer. Lipid. Chem. Soc., 37: 44-48.

Vareltzis, K., F. Zetou and I. Tsiaras, 1988. Textural Deterioration of Chub Mackerel (*Scomber japonicus* Collias) and Smooth Hound (*Mustelus mustelus* L.) in Frozen Storage in Relation to Chemical Parameter. Lebensm.-Wiss.u.-Technol., 21: 206-211.

Vuorela, R., J. Kaiteranta and R.R. Linko, 1979. Proximate Composition on Fish Roe in Relation to Maturity. J. Inst. Can. Sci. Technol. Aliment., 12 (4): 186-188.

Yilmaz, M. and A. Gül, 2002. Reproduction properties of *Cyprinus carpio* L., 1758 Living in Hirfanli Dam Lake. G.Ü. Gazi, J. Edu. Fac., 22: 25-39.