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EVALUATION OF NUTRITIONAL AND HYGIENIC QUALITY OF HERRING FISH AND ITS PRODUCTS

(With 5 Tables)

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تقييم الجودة الصحية والغذائية لسمك الرنجة ومنتجاتة

مرفت كمال ابراهيم رجب

لقد تم جمع ١٠٠ عينة من سمك الرنجة (المستورد) المجمدة وكذلك منتجاته وتشمل الرنجه المدخنه والمعلبة وشرائح الرنجة (٢٥ عينة من كل نوع) من السوبر ماركت المختلفة بالاسكندرية وذلك لتقييم الجودة الكيمائية لسمك الرنجة ومنتجاتة من الناحية الغذائية (مثل نسبة الدهون الكلية وتركيب الاحماض الدهنية ونسبة البروتين الكلى وكذلك نسبة المعادن وتشمل المنجنيز والنحاس والحديد والزنك) ومن الناحية الصحية وتشمل مؤشرات تحلل الدهون (مثل الرقم الحمضى ورقم الثيوباربيتيورك وغيرها) ومؤشرات تحلل البروتين (مثل متوسط النتروجين الكلى المتصاعد) ومتوسط تركيز الاس الهيدروجينى (pH). وقد أوضحت الدراسة النتائج الاتية: فى حالة المعادن كان اعلى متوسط تركيز للمنجنيز والنحاس والحديد وازنك فى الرنجة المعلبة (٢٠٣ ± ٠٩٥) والرنجة المدخنة (٧٦١ ± ٠٤) والمجمدة (٧٨٤٥ ± ٣٣٠) والمعلبة (١٤٥٣ ± ٢٨٥) على التوالى. أما بالنسبة لتركيب الاحماض الهنية فقد زاد متوسط تركيز الحمض الدهنى كربون ١: ٢٠ فى الرنجة المجمدة (١٩٨١٦ ± ٥٢٥) وفى نفس الوقت كان اعلى متوسط تركيز للحمض الدهنى كربون ١: ١٦فى الرنجة المعلبة (١٩٠٨٤ ± ٦١٢) وفى حالة الحمض الدهنى كربون ٢:٨ فكانت اعلى قيمة لة فى شرائح الرنجة (١٤٩٩٤ ± ١٠٩) كما ان اعلى تركيز للاحماض الدهنية المشبعة كان فى الرنجة المجمدة (٢٤٨ ±١٢٣) . وفى حالة مؤشرات تحلل الدهون وتشمل الرقم الحمضى والاحماض الدهنية الحرة ومؤشرات تأكسد الدهون الابتدائية (CD) والثانوية (TBA) كانت اعلى متوسطات تركيزات فى شرائح الرنجة وهى ١٦٣٤٢ ± ٥٠٩و٨١٧ ± ٢٥٥ و ٨٤٠ ± ٣٤و٤٥ ± ٠٥٢ على التوالى. كما أظهرت الدراسة ان اعلى قيمة لتركيز الاس الهيدروجينى كانت فى الرنجة المجمدة (٦٣٢٦ ±٠٨١) بينما كان اعلى متوسط تركيز للنيتروجين الكلى المتصاعد فى الرنجة المدخنة (٢٩٣٢١ ± ٠٤٩) على التوالى. وقد أوضحت الدراسة ايضا ان اعلى متوسط تركيز للكادميوم والرصاص كان فى شرائح الرنجة ١٨ ± ٣٩و٠٧ ±٠٣ وكان اعلى متوسط تركيز للزئبق فى الرنجة المعلبة ٠٨ ± ٠٤.

SUMMARY

Atotal of 100 samples of imported frozen herring fish and its products (smoked, canned and herring fillet, 25 samples of each, were collected from different retail stores in Alexandria governorate to evaluate their chemical quality. The results revealed that fat and protein contents had significantly increased in herring fillet and smoked herring with a mean value of 9.024±1.764 and 36±2.541. Concerning manganese (Mn) and zinc (Zn), canned herring showed the highest mean concentrations (0.203±0.095 and 1.453±0.285, respectively). In case of copper (Cu) and Iron (Fe), smoked and frozen herring had the highest mean values (0.761±0.04 and 7.845±0.330, respectively). Regarding fatty acids composition, frozen herring had a significant increase in concentration of Eicosenoic fatty acid with a mean value of 19.816±0.525, while canned herring showed the highest mean concentration of palmitic acid (19.084±0.612). Herring fillet showed the highest value of Linoleic acid (14.994±0.109). Regarding saturated fatty acids, canned herring had the highest value (38.074±0.218) while herring fillet showed the highest unsaturated fatty acids (74.626±2.810). The highest total unsaturated fatty acids was in frozen herring (24.8±0.123). Concerning fat changes, acid number, free fatty acids, conjugated dienes, thiobarbeturic acid, were highest in herring fillet (16.342±0.509, 8.17±0.255, 0.840±0.034 and 4.5±0.052, respectively). In case of acidity (pH) and total volatile nitrogen, the highest pH value was in frozen herring (6.3±0.081), while the highest total volatile nitrogen was in smoked herring (29.321±0.049). Regarding cadmium, lead mercury, the highest mean concentrations of cadmium and lead, were in herring fillet (0.07±0.03 and 0.39±0.18) whereas and the highest concentration of mercury was in canned herring (0.08±0.04).

Key words: *Herring, fatty acids, protein, minerals.*

INTRODUCTION

Fish products elaborated from fatty fish have lately attracted strong interest on fish processing industry and consumers due to their nutritional value, mainly associated to its high content in essential fatty acids, n-3 fatty acids (Aidos., *et al.*, 2003). Herring is a typical pelagic fatty fish with a high content of omega 3 fatty acids such as eicosapentaenoic acid (EPA, C20:5) and docosahexaenoic acid (DHA, C22:6) which have positive effect against cardiovascular disease, cancer, etc (Unde land *et al.,* 1998; El-Sharnouby, 1989; Stefánsson *et al.,* 1995; Mindieu *et al.,* 2007). Unfortunately, the development of lipid oxidation often limits the possibilities for storage and processing of this species. This is due to close contact between the highly unsaturated herring lipids and strong catalytic systems (Undeland *et al.,* 1999). The rate of lipid oxidation was monitored by the formation of different oxidised compounds resulting from lipids such as hydroperoxides, aldehydes and fluorescent interaction compounds. (Isabel Medina *et al.,* 2003).

Chemical composition of herring fish can vary widely not only from fish to fish of the same species but also, within an individual fish. Many factors influence the composition of the lipid phase in fish muscle and its deterioration: species of fish, composition of diet, nutritional status, salinity, migrations, genetic factors, season of catch in post mortem handling, time of frozen storage and the prescence of oxygen and light (Ingemanasson *et al.,* 1995).

With respect to nutritional value, it was found that smoking process have no effect on fatty acid of fresh or raw fish (Bhujyan *et al.,*1986).

It was reported that the total lipid content of fish was slightly decreased after salting and smoking processes (Abdel Nabey, 1995; Ikem and Eagiebor, 2005).

The fat content of baltic herring, mackerel and salmon from Norway has been determined .The fat content was 7%, 11.6% and 13.2%, respectively. Both fat extracted from mackerel and salmon contained much more of PUFA S in comparison to that extracted from herring. PUFA content in herring fat was 15%, whereas in mackerel and salmon were 29% and 25%, respectively. PUFA represented mostly of omega 3 family (Balass *et al.,* 2001) The lipid content of the muscle tissue of fishes sampled amounted to 8.7% in Baltic herring. The qualitative composition of the fatty acids in the fish lipids was the same but it varied quantitatively. Unsaturated fatty acids constituted 66.86% in the herring lipids, C 20 : 5 and C 22 : 5 , C 22 : 6. constituted 16.61, 28.48, and 16.49% of all fatty acids, respectively (Szczepanik and Stodolnik, 2003). There was a difference in fatty acid pattern in raw, frozen, Smoked salmon. The content of c20: 5 n3 and c22:6 n3 ranged from 4.2 to 13.3 and the n3 series of polyunsaturated fatty acids (PUFA) were 32.4% of total fatty acids in marine fish (Marta *et al.,* 2004). It was reported that smoked salmon had total lipid contents higher in c18:0, c18:2 fatty acid, Also in sigma monoenoic fatty acids, however, C16:

1polyunaturated n3 fatty acid of health benefits as c20:5, c22:5, c22:6, revealed significant decreases in smoked than frozen. Mohammed, (2004) reported that fatty acids composition of salted herring products was typical for herring, the most abundant fatty acids being oleic (c18 :1n-9), palmitic (16:0) monounsaturated fatty acids constituted the main group with a proportion of >50% of all fatty acids. EPA, 20: 5n_3) and DHA, 22: 6n _3 comprised 12% of all fatty acids (Minh Dieu, *et al.*, 2007)

Moreover several studies were carried out on hygienic quality of smoked herring. The free fatty acids contents of fish samples were very high indicating microbial spoilage activity. Fat activity begins to be noticeable to the palate when the free fatty acid values calculated as oleic acid is about 0,5 to1,5%. (Pearson, 1978). The increase in T.B.A value was related to the transformation of some unsaturated fatty acids especially those at surface to peroxides, conjugated dienes (CD) as resulted exposuer to atmosperic oxygen, appplied temperature during smoking process which may accelerate oxidation and thereby lipid breakdown, another factor is salt which can penetrates into the muscle during dry saltingor brining. (Salama and Khlafalla, 1993; Marta, 2004).

The total volatile nitrogen content (T.V.N.) of lanhouin (fermented fish product) samples were very high for both species of fish (cassava fish and king fish) ranged from 29.5 mg N /100 gm of sample to 38.98 mg N/100gm from one species to another with an average of 29.45 and 37.45 mgN/100gm for cassava fish and king fish, respectively (Anihouvi, *et al.*, 2006).

Kewaiey (2001) showed that smoked herring fish had mean pH value of 6.15 and differ significantly between salted and smoked fish, T.V.B.N. was 47.36 mgN/100gm was highly significant between salted, smoked fish at $P< 0.01$, mean F.F.A.=9.93 differ significantly at $p<0.05$ between salted and smoked fish.

Shaban, and Abo Zeed.(2004) reported that the smoking process of Lizard fish and the pH value was decreased while the amino nitrogen was increased.

Since herring fish is important to human health due to its high content of omega 3 fatty acids, on the other hand herring fish is more susceptible to deterioration during storage and processing than other types of fish, therefore the purpose of this work is to give an idea about the nutritional and hygienic quality of herring fish and its products.

MATERIALS and METHODS

A total of 100 samples of imported frozen herring fish (Clupea harengus) and its products, smoked, canned and herring fillet (25 for each) were selected randomly from Alexandria retail stores. Samples were transported in an insulated ice box to the laboratory and analyzed for chemical quality parameters.

1- Determination of chemical quality parameters

1-1- Nutritional quality parameters

1-1-1- Fat content: It was determined according to standard method obtained by AOAC (1970).

1-1-2- Fatty acids composition: The methyl esters of extracted fish lipids were prepared according to Radwan, (1978) and fatty acids composition was determined by using Gas Liquid Chromatography (GLC). (Radwan, 1978).

1-1-3- Protein content: It was determined according to standard method obtained by AOAC (1970).

1-1-4- Mineral composition (Mn, Cu, Fe, Zn,):

The principle of the minerals determination involved the production of acidic solution of the inorganic elements, after removing interferring materials by chelation solvent using ammonium pyrrolidine di-thio carbamate (APDC) and isobutyl methyl ketone (MIBK). After that minerals concentrations were determined by using flame atomic absorption spectrophotometer at wave length's specific to each element (Richard, 1986).

1-2- Hygienic quality parameters:

1-2-1-Fat quality indicators:

1-2-1-1-Acid number:

Acid number is defined as the number of milligrams of potassium hydroxide required to neutralize the free acid in 1 gm of the sample. It was determined according to Pearson (1970).

1-2-1-2- Free fatty acids: it was estimated according to Pearson (1970)

1-2-1-3- Conjugated dienes: it can be determined uşing ultraviolet (UV) – visible spectrophotometer. (Sanitago *et al.,* 1997).

1-2-1-4- Thiobarbeturic acid reactive substances (TBAR): It was determined using cold extraction method according to Li, *et al.* (2001).

1-2-2- hydrogen ion concentration (pH): The pH of fish muscle was determined according to AOAC (1980).

1-2-3- Protein quality indicator: Total volatile nitrogen (TVN) was determined by macrokejldhal Method (Malle and Pourmeyrol, 1998).

1-2-4- Contaminant levels (Cd, Pb, Hg): Cadmium and lead were determined by Hydrochloric-nitric ($HCl-HNO_3$) acid leaching method using flame atomic absorption spectrophotometer (Richard, 1986). The principle of mercury (Hg) determination method depends on the conversion of all the Hg present in the sample into the inorganic form by wet oxidation and it's reduction to the metallic state. Then, the realse of Hg from the solution as vapour using a stream of air followed by it's determination by flameless atomic absorption spectrophotometer (APHA/AWWA1992).

RESULTS

Table 1: Chemical composition (mean ± standard error) of herring fish and its products.

Herring fish and its products	Total lipids (%)	Total protein (%)	Mineral composition(p.p.m.)			
	Mean ± S.E	Mean ± S.E	Mean ± S.E			
			Mn magnesium	Cu copper	Fe iron	Zn Zinc
Frozen	7.229**±0.13 8	18**1.091*	0.051±0.003	0.746±0.058	7.845**±0.330	0.312*±0.038
Smoked	8.126**±0.768	36*±2.541	0.041±0.006	0.761±0.040	1.891**±0.472	0.609*±0.194
Canned	2.303**±0.539	23**±1.332	0.203±0.095	0.687±0.017	5.880*±0.527	1.453*±0.285
Fillet	9.024**±1.764	35*±2.160	0.151±0.049	0.698±0.022	4.899*±0.450	0.720*±0.053

* Significant at P≤ 0.,05

** Highly significant at P≤ 0.,05

Table 2: Fatty acids composition (mean ± SE) of herring fish and its products in percent. (n=25)

Fatty acids	Frozen	Smoked	Canned	Herring fillet
Capric(($C_{10:0}$)	0.963**±0.113	0.424±0.267	1.099±0.152	..,126±0.060
Lauric ($C_{12:0}$)	0.147*±0.017	0.288±0.032	0.787±0.112	0.206±0.049**
Myristic($C_{14:0}$)	8.959**±0.613	9.986**±0.264	5.733*±0.542	1.316±0.134
Pentadecanoic ($C_{15:0}$)	0.499*±0.158*	.,314±0.058	1.423**±0.080	0.321±0.012
Palmitic ($C_{16:0}$)	19.049**±.,653	19.069**±0.521	19.084**±0.612	15.130**±0.324
Palmitoleic ($C_{16:1}$)	6.155**±.,541	14.287 **±0.313	3.184*±0.418	1.152±0.154
Heptadecanoic ($C_{17:0}$)	0.733*±0.080	0.772*±0.213	0.98**7±0.198	0.502±0.039
Stearic ($C_{18:0}$)	0.998*±0.112	3.103**±0.674	5.875*±1.432	5.963±0.040***
Oleic ($C_{18:1}$)	18.099**±0.417	10.453**±0.176	14.745**±1.098	18.102**±0.650
Lenoleic ($C_{18:2}$)	1.186±0.160	2.307**±0.234	7.105*±1.134	14.994**±0.109
Lenolenic ($C_{18:3}$)	1.661±0.164	2.527**±0.146	2.003±0.132	7.317±0.504
Arachidic ($C_{20:0}$)	1.483±0.123	2.121**±0.146	3.005±0.057	0.699±0.130
Eicosenoic ($C_{20:1}$)	19.816**±0.525	18.254**±1.765	18.23*±0.769	15.872**±1.800
EPA ($C_{20:5}$) n-3	9.40**±0.660	8.60**±0.360	8.3**. ±.0568	8.800±1.543
($C_{22:5}$) n-3	0.952*±0.128	0.545±0.013	0.40±0.021	0.6±0.141
DHA ($C_{22:6}$) n-3	9.90**±0.230	6.95**±0.159	8.04 * *±0.823	8.90±0.323
Saturated fatty acids	26.831**±1.651	30.077**±0.713	38.07*.*±0.218	25.37**4±1.239
Unsaturated fatty acids	73.169**±2.872	69.921**±0.845	61.926 * *±0.714	74.626 * *±2.810
Total n-3 unsaturated fatty acids	24.8**±1.123	20.4**±0.768	20 **±0.840	23.6 **±0.304

** Highly significant at P≤0.05
* significant at P≤0.05

Table 3: Fat quality indicators (mean± SE) in herring fish and its products

Samples	Acid number [mg KOH/g of fat]	Free fatty acids (ml/gm)	Conjugated dienes (n mole/mg)	TBARS [mg alonaldehyde/ kg of sample]
Frozen	5.371**±0.315	2.686**±0.158	0.46*0±0.037	3.624*±0.151
Smoked	8.785**±0.230	4.393**±0.115	0.63*±0.022	4.378*±0.076
Canned	1.167**±0.102	0.584**±0.051	0.15*±0.037	2.391*±0.176
Fillet	16.342**±0.509	8.17**±0.255	0.84*±0.034	4.500*±0.052

* Significant at P≤ 0.05
** Highly significant P≤0.5

Table 4: Hydrogen ion concentration (pH) and total volatile nitrogen content (T.V.N.) of herring fish and its products

Herring fish and its products	Hydrogen ion conc. (PH)	Totalvolatile nitrogen (T.V.N.)
	Mean± S.D	Mean ±S.D
Frozen	6.326±0.081	26.432*±0.032
Smoked	6.157±0.035	29.32*1±0.049
Canned	6.077±0.046	28.43*±0.098
Fillet	6.253±0.041	27.8*±0.035

* Significant at P≤ 0.001

Table 5: Cadmium, lead and mercury levels (p.p.m) in herring fish and its products.

Samples	Contaminant levels(p.p.m)		
	Cadmium	Lead	mercury
	Mean ±S.D	Mean ±S.D	Mean ±S.D
Frozen	0.03±0.01	0, 16±0.05	0.074±0.04
Smoked	0.02±0.01	, 15±0.08	0.05±0.02
Canned	0. 04±0. 01*	, 18±0.04	0.08±0.04
Fillet	0.07±0..,03	,39±0.18	0.06±0.03

DISCUSSION

Chemical composition of herring fish and its products were recorded in Table (1). Results showed that the highest percent of fat was found in herring fillet (9.024%) while the lowest was in canned herring (2.303%). There was a highly significant difference in percent of fat between herring fish and its products at p≤ 0.05. The increase in fat content of herring fish products was due to the decrease in moisture content in smoke cured product. Moreover, the highest mean value of protein content (36%) was in smoked herring fish, while the lowest (18%) was in frozen herring with a highly significant difference between them at p≤ 0.05. This result was in agreement with Shaban and

Abo Zeed, (2004) who studied the effect of fish smoking process on lizard fish and Salama and Khalafalla (1993) in eels fish.

Concerning mineral composition, the mean values of manganese (Mn), ranged from 0.041 p.p.m in smoked herring to 0.203 p.p.m in canned herring. In case of copper (Cu), smoked herring showed the highest mean concentration (0.761p.p.m) while canned herring had the lowest (0.687 p.p.m). Regarding Fe and Zn, the highest levels (7.845 p.p.pm and 1.453 p.p.m, respectively) were in frozen and canned herring. While the lowest were 1.891 p.p.m and 0.312 p.p.m in smoked and frozen herring, respectively (Table 1). The obtained results lies within the Egyptian standard limits. (Egyptian Standard Regulation, 1993).

It was found that processing of herring fish does not have a major impact on the macrocontent of bony fish. Dehydration potenially can have the biggest effect, by removing water. Brining and smoking can result in a partial removal of moisture, with consequent increases in the proportions of macronutrients. Lack of care (resulting in excessive temperatures) in smoking can cause loss of lipids from herring (Holland, *et al.*,1993; Aidos, *et al.*, 2003).

Fatty acids composition of herring fish and its products were recorded in Table (2). The mean values of saturated fatty acids were 26.831%, 30.077%, 38.074% and 25.374% in frozen, smoked, canned and fillet, respectively. At the same time, the unsaturated fatty acids showed mean values of 73.169, 69.921, 61.926 and 74.626% in frozen, smoked, canned and fillet, respectively. The highest significant percent of Palmitic ($C_{16:0}$) was found in canned herring (19.084%), and the lowest was in herring fillet (15.130%), while the highest significant percent of ecicosapentaenoic (EPA) ($C_{20:5}$) n3, ($C_{22:5}$) n-3, docosahexaenoic (DHA) ($C_{22:6}$) n-3 were in frozen herring fish (9.4%, 0.952%, 9.9%), respectively. The increase in saturated fatty acids after processing may be attributed to the transforrmation (saturation) of some of the monounsaturated fatty acids and / or polyunsaturated to saturated fatty acids results from direct feeding on the phytoplankton and or feeding on fish that had already fed on phytoplankton. Nearly similar observations were reported by Gopakumar and Nair (1972), Marta., *et al.* (2004), Mohammed, (2004) and Aro. *et al.*, (1983).

The percentage of polyunsaturated fatty acids decreased as a result of salting and smoking processes (Steffens, 1997).

Table (3) illustrated the fat quality indicators in herring fish and its products. Results of lipid hydrolysis showed that the highest mean values of acid number and free fatty acids (16.342 mgkoH/gm of fat, 8.17ml/gm) were in herring fillet while the lowest were in canned herring (1.167mg/gm, 0.584ml/gm) with a high significant difference between them. Concerning, lipid oxidation changes (CD, TBA), herring fillet had the highest value (0.84nmole/mg, 4.5mg/kg), while the the lowest was in canned herring (0.15n mole/mg, 2.391mg/kg) with a highly significant difference between mean values of CD in herring fish and its products at $p \leq 0.05$.

It was reported that the TBARS of smoked fish products locally produced in Alexandria, was ranged from 2.12 to 2.95 MDA/Kgm flesh sample with a mean value of 2.51 MDA/kg flesh sample, (Saber *et al.*, 1992) and higher results were recorded by Emara (2000) after 6 monthes of storage of hot smoked fish.

Hydrogen ion concentration (pH) and total volatile nitrogen content (TVN) of herring fish and its products were recorded in Table (4). The highest level of pH was found in frozen herring (6.326) followed by herring fillet (6,253), smoked (6,157) and canned (6.077). The reduction in pH value in herring fish products in our results was due to the organic acid resulted from the smoke content. Similar results were recorded by Daoud and Abdelaziz (1996), Shaban and Abozeed (2004) and Anihouvi, *et al.* (2006).

In case of total volatile nitrogen content, the highest level (29.321mg/100gm) was in smoked herring while the lowest (26.432mg/100gm) was found in frozen herring, with a significant difference between them. According to Connel, (1990) who stated that for good quality, no greater than 100- 200mg TVN nitrogen/100gm for a variety of salted, dried fish, herring fish and its products examined in the present study are of good quality. Nearly similar observations were obtained by Stefansson *et al.*, (1995); El-kewaiey, (2001), and Shaban and Abo zeed, (2004).

Mean concentrations (p.p.m.) of cadmium (Cd), lead (Pb), mercury (Hg) in herring fish and its products were presented in Table (5). It was found that the mean values of cadmium, lead, mercury in all the examined samples were within the permissible limits obtained by Egyptian Standard Regulation (1993).

In conclusion, the present study indicated that imported frozen herring fish marketed in Alexandria are of good source of nutritional value. Moreover, the hygienic quality examination revealed that processing and smoking of frozen herring fish increase the susceptibility of lipid oxidation and hence increase the level of fat quality indicators.

At the same time, the examined herring fish products were of good keeping quality from the point of view of contaminanat levels, PH and protein quality indicators (TVN).

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