CHANGES IN PROXIMATE COMPOSITION AND LIPID QUALITY OF ATHERINA *ATHERINA* SP. DURING SUN DRYING PROCESS

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ملخص

دراسة التركيبة البيوكيميائية و جودة الدهنيات لدى سمك الأترينا إثر عملية التجفيف الشمسي: لدراسة تأثير التجفيف الشمسي على سمك الأترينا، قمنا بمتابعة بعض المؤشرات البيوكيميائية قبل و بعد عملية التحويل. أثبتت نتائج التركيبة البيوكيميائية أن كمية البروتينات و الدهنيات و المواد المعدنية سجلت إرتفاعا إثر عملية التجفيف الشمسي، على عكس المادة الجافة التي إنخفضت لتصل إلى 22.37%. كما أثبتت مؤشرات جودة الدهنيات أن نسبة الهيدروبيركسيد و الأحماض الدهنية الحرة لدى دهنيات سمك الأترينا المجفف مرتفعة مقارنة بدهنيات سمك الأترينا الطازجة، و يمكن تفسيرهذا الإرتفاع بعمليتي الأكسدة و الحلمأة إثر عملية التجفيف.

الكلمات المفاتيح: أترينا، التجفيف الشمسي، التركيبة البيوكيميائية، أكسدة، حلمأة.

RÉSUMÉ

Variations de la composition biochimique et de la qualité des lipides des athérines *Atherina* sp. au cours du séchage solaire: Dans le présent travail, l'effet du séchage solaire sur la composition biochimique et la qualité des lipides des athérines a été étudié. La teneur en lipides, protéines et en cendres dans l'athérine a augmenté significativement ($p < 0.05$) après le séchage. Cependant, celle de l'humidité a montré une forte diminution pour atteindre 22.37% dans le produit final. D'autre part, l'étude des indicateurs d'altération des lipides (Oxydation et Hydrolyse) nous a montré que la qualité des lipides des athérines est affectée par ce type de traitement. En effet, les taux des hydropéroxydes et des acides gras libres ont augmenté significativement ($p < 0.05$) après le séchage pour atteindre respectivement 2.02 meq active O_2/kg huile et 3.67%. La formation des produits d'oxydation primaire (hydropéroxydes) a été accélérée par le séchage solaire; cependant, cette oxydation était sans effet sur la flaveur du produit final.

Mots clés: *Atherina* sp. ; Séchage Solaire ; Composition biochimique ; Oxydation ; Hydrolyse.

ABSTRACT

Changes in proximate composition and lipid quality of atherina *Atherina* sp. during sun drying processing were investigated. The peroxide value PV, thiobarbituric acid reactive substances TBARS and free fatty acids FFA were determined to monitor the progressive oxidative lipid changes during processing. According to Duncan's test, significant differences ($p < 0.05$) were found in the proximate composition during the drying process. Lipid, protein and ash contents increased significantly after processing. Thus, a high decrease in moisture content was recorded in the final product to reach 22.37%. Fresh atherina oil shows an excellent quality with a low PV (0.97 meq active O_2/kg oil), FFA (1.82%) and TBARS (0.32 mg MA/kg oil) levels. After sun drying treatment, PV and FFA increased significantly ($p < 0.05$) to reach 2.02 meq active O_2/kg oil and 3.67% respectively. The primary oxidation products (lipid hydroperoxides) are produced in our processing; however, they haven't generally a flavour impact on the final dried product.

Keywords: *Atherina* sp.; Sun drying; Biochemical Composition; Oxidation; Hydrolysis.

INTRODUCTION

Many food products are characterized by their high humidity content which can be the most important cause of their deteriorations. Drying could be used for enhancing the resistance of high humid products to the degradation by decreasing their water activity. Sun-drying of fish is an old traditional practice done in many parts of the world (Sachithananthan *et al.* 1985 and N'jai, 1985), which considered an efficient technique for improving stabilisation and storage.

Lipids constitute between 10 and 40% of the total human diet. They play a pivotal role in terms of flavour and palatability of food products and, in addition, their presence affects general physical properties of foods. Furthermore, lipids are an essential source of essential fatty acids and serve as carriers of fats soluble vitamins. Like marine products, atherina are valuable sources of nutrients such as proteins and lipids. Therefore, they are characterized by their high content of polyunsaturated fatty acids (PUFAs), especially the n-3 PUFAs family including eicosapentaenoic acid (EPA or 20:5 n-3), docosapentaenoic acid (DPA or 22:5 n-3) and docosahexaenoic acid (DHA or 22:6 n-3) which may readily be oxidised to form lipid hydroperoxides (Osman *et al.* 2001, Boran *et al.* 2006). Lipid oxidation is an autocatalytic chain reaction, which takes place through four main stages: initiation, propagation, chain branching

and termination (Hultin, 1992). The primary products of lipid oxidation, lipid hydroperoxides, are generally considered not to have a flavour impact. The volatile secondary oxidation compounds, aldehydes and ketones, derived from breakdown of primary oxidation compounds are responsible for rancid flavour and odours. Lipids degradation proceeds also by enzymatic hydrolysis. Phospholipids are hydrolysed most readily, followed by triacylglycerols, to produce free fatty acids (sikorsky *et al.* 1990). Free fatty acids are not only important from the point of view of oxidation products, but they have also been reported to have a direct sensory impact (Refsgaard *et al.* 1998).

Despite the numerous cited studies on the biochemical composition and nutritional values of seafood product, few data exist on biochemical analysis of the atherinidae family especially during sun drying process. The objective of the present work was to assess the biochemical changes and lipid oxidation of *Atherina* sp. during traditional sun drying process.

MATERIALS AND METHODS

1- Samples collection and preparation

Atherina *Atherina* sp. was caught from Kerkannah's islands (Tunisia) in July 2007. The average of weight and length of sampled fish are 0.92 g and 4.74 cm respectively. Samples were separated into two lots: (i) the first one was kept in ice and transported to the laboratory where they were rapidly weighed, measured and stored at -40 °C until analysis, (ii) the second lot was traditionally sun dried by spreading fish on sand for about 4 days.

2- Biochemical analysis

Moisture

Moisture of the fish samples (5 g) was determined according to the AOAC (1990) method by drying in an oven at 105 °C (n = 6). Results were expressed as percentage of wet weight.

Ash

Ash content was determined by burning sample (5 g) for 12 h in a furnace at 525 °C (n = 6) according to the AOAC (1995) method. Results were expressed as percentage of wet weight.

Protein

Total protein content in the homogenized samples (5 g) was determined using Kjeldahl method (AOAC 1990). Results were expressed as percentage of wet weight (n = 3).

Lipids extraction and separation

Lipids were extracted by the Bligh and Dyer method (Bligh and Dyer 1959). Sample was homogenised with chloroform:methanol (1:2) for 8 min at 4 °C using a Polytron homogeniser. The homogenate was treated with chloroform with butylated hydroxytoluene BHT (50 ppm) and the mixture were homogenised for 10 min. Then, distilled water were added and homogenised again for 2mn. The homogenate was vacuum filtered with Buchner funnel and the filter was washed with chloroform. The organic layer were extracted with a separating funnel and evaporated to dryness in the rotary evaporator. After weighing, the obtained oil was solubilized in a known volume of chloroform with BHT (50 ppm) and stored at -40 °C.

Peroxide value (PV)

The peroxide value was determined according to the ferric thiocyanate method with slight modification (Chapman and McKay 1949). The method is based on the ability of lipid peroxides to oxidize ferrous ions at low pH. The resulting ferric ions react with thiocyanate and the concentration of the formed complex is spectrophotometrically determined. The results were expressed in terms of meq. of oxygen per kg of oil.

Thiobarbituric acid reactive substances (TBARS)

The TBARS was determined according to the AOCS (1998) method. This procedure allows the direct determination of TBARS in oils and fats without preliminary isolation of secondary oxidation products. Oil sample was solubilized in 1-butanol, mixed with *Thiobarbituric acid* TBA in 1-butanol, heated in water bath (95 °C) and cooled under tap water. The absorbance was measured at 532 nm against a corresponding blank. The results were expressed as mg MA/kg of oil.

Free fatty acids

Free fatty acids were determined according the method described by Bernardez *et al.* (2005). Samples (approximately 50 mg of oil) were homogenized with cyclohexane and cupric acetate-pyridine reagent, the mixture were vortexed for 2 min and centrifuged for 20 min at 7000 rpm. The upper layer was read at 710 nm. Quantification was based on a calibration curve constructed from oleic acid standards.

Statistical Analysis

Statistical analysis was performed using SPSS software, version 10.0.5. The comparison of different biochemical parameters was tested using Duncan's test (95% confidence interval) with one-way ANOVA.

RESULTS AND DISCUSSION

1- Proximate composition

Table I shows the changes of *Atherina* sp. proximate 8.13 and 15.73 g/100g respectively. The high protein contents and the moderate lipids levels in this small inshore fish are similar than those found in other species such as sardine, horse-mackerel, sarda and tuna (Bandarra *et al.* 1997, 2001, Mourente *et al.* 2002, Zaboukas *et al.* 2006).

Generally, lipid content varies within species (1.46 to 5.77 g/100g) and is affected by the catching season (1.2 to 18.4 g/100g) (Bandarra *et al.* 1997, Osman *et al.* 2001). Ash content in fresh atherina was 2.29 g/100g, such levels were higher than those found in other species (Ben-gigirey *et al.* 1999, Mazorra-Manzano *et al.* 2000). The higher ash content could be explained by the presence of the bones in the samples.

Table I. Proximate composition of *Atherina* sp. during sun drying process (mean ± standard error).

	Moisture (%)	**Protein (%)**	**Lipid (%)**	**Ash (%)**
Fresh atherina	73,79 ±0,38	15,73 ±1,92	8,13 ± 0,52	2,29 ±0,13
Sun dried atherina	22,37 ±0,62	46,24 ±1,59	21,18 ±1,16	6,38 ±0,21

According to Duncan's test, significant differences ($p < 0.05$) were found in the proximate composition during the drying process. The high increase of lipid, protein and ash levels were due to the water evaporation.

In our data, moisture content in fresh atherina (73.79%) lessen approximately four time compared with the final product (22.37%). These findings are in accordance with those reported by Hiraoka *et al.* (1998) which reported in horse mackerel fillets, final moisture of about 25% after 7 days of drying by microwave heating at 40°C.

2- Lipid degradation

Changes in peroxide value (PV), Thiobarbituric acid reactive substances (TBARS) and free fatty acids (FFA) of atherina *Atherina* sp. during sun drying process are shown in table II. The PV, TBARS and FFA values found in fresh atherina were 0.97 meq active O_2/kg oil, 0.32 mg MA/kg oil and 1.82% respectively. Such levels were lower than those found in other species such as black-skipjack (*Euthynnus lineatus),* sardine *(Sardinella gibbosa)* and mackerel (*Trachurus novaezelandie)* (Chaijan *et al*. 2006; Mazorra-Manzano *et al.* 2000; Ryder *et al.* 1984).

Result showed that drying process had a significant effect ($p < 0.05$) on the formation of primary oxidation products in the samples, with higher PV levels obtained in dried than in fresh atherina. The increase in PV levels probably was probably due to the drying temperature and the high content of unsaturated fatty acids and prooxidants in the muscle.

Table II. Changes in PV, TBARS and FFA of atherina *Atherina sp.* during sun drying process. PV: peroxide value, TBARS: Thiobarbituric acid reactive substances, FFA: free fatty acids, MA: malonaldehyde. (n = 4 ± standard error)

	PV ***(meq active O_2/kg oil)***	**TBARS** ***(mg MA/kg oil)***	***FFA*** **(%)**
Fresh atherina	0.97 ±0.09	0.32 ±0.05	*1.82 ±0.13*
Sun dried atherina	2.02 ±0.16	0.77 ±0.11	*3.67 ±0.16*

Hawrysh, (1990) reported that lipid oxidation is a process by which molecular oxygen reacts with unsaturated lipids to form lipids peroxide, and is catalysed by some factors such as temperature, water activity, pH, and chemical environment (Ashie *et al.* 1996). According to Huss (1988), the acceptability limit for PV of crude fish oil is 7–8 meq O_2/kg oil. In this study, all examined atherina oil samples didn't reach this limit after the drying process.

The initial value of TBARS was 0.32 mg MA/kg oil, suggesting that lipid oxidation didn't occur during post-mortem handling to some extent. From this result, TBARS slightly increased within drying treatment to reach 0.77 mg MA/kg oil. Generally, the increase in TBARS indicated the formation of secondary lipid oxidation products such as aldehydes and others volatiles compounds (Kolakowska 2002) responsible for rancid flavour and off-odours, as well as colour and texture deterioration (Nawar, 1996).

The percentage of FFA in fresh atherina lipids was 1.82 %. Such levels were lower than those found in herring oil (Aidos *et al.* 2001). As quality specifications for crude fish oil, Bimbo (1998) suggested that the FFA content should range between 2 and 5 %. FFA increased significantly ($p < 0.05$) after sun drying process to reach 3.67%. This suggests that atherina oil hydrolysis occur during such processing, possibly due to the high temperature of drying. Generally, the formation of FFA in fish oil during storage is related to some factors such as the initial phospholipids contents, phospholipases, lipases and temperature.

CONCLUSION

Sun drying processes are a simple method, don't require sophisticated equipment and leads to final products with lower moisture contents who are practicable for the storage life. Lipid deterioration took place during sun drying process and generated a moderate increase in the peroxide value and free fatty acids in the final product. Secondary oxidation products were not however produced in such processing.

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