Effect of Cryopreservation on the Chemical Quality Indicators in Meat of the Mullet (*Liza aurata*, Risso, 1810) Fishing from Syrian Marine Waters

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Abstract:

The aim of this research was to study the effect of cryopreservation on (-18 °C) on the chemical quality indicators in mullet meat (Liza aurata, Risso, 1810) which is considered one of the economic Syrian marine fish species. This study was carried out during the period (5/2017) to (5/2019).

Fish samples were collected randomly from landing sites of Tartous beach, then kept at (0-4°C) immediately after fishing, waiting to be transferred to the laboratory within less than an hour, and treated by special methods. Then samples were frozen and stored similar samples at (-18°C). Only eaten muscles were analyzed, fresh and frozen at successive intervals: (0, 30, 60, 90, 120 and 180) days after frozen.

It was notable that values of theobartueric acid (TBA), peroxide number (PV), free fatty acids (FFA), (pH) increased during the freezing period due to fat exposure to oxidation and hydrolysis.

Keywords: *chemical composition, Liza aurata, Omega 3, Omega 6 and Syrian coast.*

I. INTRODUCTION

Fish is a good source of nutrients beneficial to humans. The nutritional value of fish is due to its functional properties resulting from its high content of unsaturated fatty acids (PUFA), especially (ω3), mainly its content of (EPA, DHA) which have an important functional role for human health [1].

Cryopreservation has been one of the used reserve methods for thousands of years due to the high product quality [2].

Cryopreservation concept is based on reducing the products temperature to slow down the damage, allowing fish to remain fresh after the freeze is thawed [3].

However, fish and fish products can undergo undesirable changes during storage, and spoilage may limit storage time. These undesirable changes result from protein denatioration ([4], [5]), and from fat oxidation ([6], [7]). The degradation of polyunsaturated fatty acids (PUFA) leads to production of volatile compounds associated with spoilage through fat oxidation during storage [8].

The high content of unsaturated fatty acids makes fish highly sensitive to oxidation and rapid damage. Oxidation changes are mainly related to fish texture and taste. Also it was noticed changes in color and nutritional value of fish in the later stages of fat oxidation and peroxides forming [9].

In light of the lack of information regarding changes in the freezing of fish species caught from Syrian marine waters, this study aimed to study changes in chemical quality indicators in the meat of an economically important fish species from Syrian marine waters during the freezing process.

The mullet *Liza aurata* belongs to the Mugilidae family. This family is spread all over the world in temperate and tropical coastal waters. Some of its species live in fresh water. It is widely spread in the Mediterranean, Black Sea, South of Caspian Sea, as well as along the Atlantic coast [10]. It lives in coastal lakes and estuaries [11].

Mullet has been an important source of food in Mediterranean countries since ancient times [12]. It feeds on residues, silt and mollusks [13].

Fish is a staple material in diets in many countries. It is useful to know some of the biochemical aspects of fish (fish content of fat, protein and minerals) to consumers, researchers and industrialists for many different reasons, where there is interest in the beneficial health effects of body health associated with consumption of fish fat. The identification of some biochemical characteristics of the studied

fish species may also provide important information on the nutritional value of this species to consumers who wish to know detailed information about the consumed fish product, and to researchers with statistics and tables of value of food processing and processing of fish.

The food industry has a great interest in maintaining the quality and freshness of fish products, where fish species caught from Syrian marine waters lack the study of chemical composition, and therefore knowledge and evaluation of their nutritional value and subsequent manufacturing trends, as well as lack of knowledge of changes in their nutritional value and the extent of maintaining quality and its suitability for human consumption when stored by freezing.

Due to all above this study was conducted to detect the chemical composition of the studied fish species by estimating its content of moisture, fat, protein and ash, and to determine the appropriate freezing period for preserving the studied fish species, in addition to studying the effect of cryopreservation on the chemical quality indicators of the oil extracted from the studied fish species.

II. MATERIALS AND METHODS

Samples Preparing:

Samples of the studied fish species *Liza aurata* were taken from the landing sites of Tartous beach, with an average weight (80-100 g), and a total length (30-40 cm) beach, then transferred to the laboratory within (30) minutes. The head and viscera were removed and divided to parts of eaten muscles. Samples were divided into two groups. The first group was used directly to analyze the chemical composition and chemical quality indicators of the studied fish species as fresh samples.

The remaining group was retained, reserved and stored by freezing at (-18 ° C) for analysis of chemical quality indicators on frozen fish species slices monthly during the storage period. Then dissolved by cooling at (4 ± 2 ° C) for (7-10) hour. Samples were homogenized well with the normal mixer before analyzing with 3 replicates during the freezing period (0, 15, 30, 60, 90, 120, 150, 180) days.

Chemical composition:

According to re. [14], the moisture content of the studied fish species was determined by drying to a constant weight at 105 ° C using a drying oven. Protein was evaluated using Kjeldahl (N*6.25). Ash was evaluated at (550 ° C) until the appearance of gray white glowing color. Fat was extracted using Soxhlet device for 8-6 hours.

Fat oxidation indicators:

PH value was determined by a homogeneous mixture of fish meat with distilled water (w: v) (5: 15) using a pH meter device. Free fatty acids (FFA) were expressed in percent (g/100 g) as oleic acid by acid titration of the oil using known concentration alkaline (sodium hydroxide) by the addition of modified ethanol and the presence of phenolphthalein as a guide to the end of titration.

The peroxide value was expressed in meq oxygen per kg / fat, by iodine titration with the addition of ice Acetic acid [14]. TBA acid was determined and calculated as (mg malon Aldehyde / kg Fish meat) (according to re. [15].

Statistical analysis:

Statistical analysis was carried out using SPSS. ANOVA analysis, and the least significant difference (L.S.D) was calculated ($p<0.05$).

III. RESULTS AND DISCUSION

The chemical composition of the studied mullet fish species *L. aurata* is shown in Table (1).

Table (1): The chemical composition of the mullet fish *L. aurata*

The chemical composition (g/ 100g) as a raw material			
ash	fat	protein	humidity
1.41	7.35	18.0	73.19

Re. [16] showed the chemical composition of fish species *L. aurata* from the South of Caspian Sea, which was for the content of moisture, protein, fat, ash, respectively, (77.39, 22.85, 3.94, 1.48 %,). Also the species *L. aurata* recorded a content of moisture and fat attained (72.1 and 8.9%), respectively, in a study of re. [17], and attained (79.50, 17.02, 1.34 and 1.13 %), respectively, in a study of re. [18].

The biochemical composition of fish muscles varies significantly according to the species, gender, nutrition, sexual maturity, age, environmental conditions, hunting season, and location and muscle position within the body ([19], [20]).

According to Table (1), the studied fish species (*L. aurata*) is classified as medium-fat fish species, because its fat content was within the range described by re. [21] (5- 15%), and also within the range described by re. [22].

Whereas the fish were classified according to their fat content to four levels according to the researcher [22] / Lean fish /: Fish with very low fat content (<2%); / Low fish /: Includes fish

with low fat content (2-4%); /Medium fish /: Includes fish with an average fat content (4-8%); / High fish /: Includes fish with high fat content (> 8%).

The fat content of the studied fish species (*L. aurata*) was within the range described by re. [23], for the general fat content of fish (0.2-25%).

Variation in pH value:

Figure (1) shows the pH variations during the freezing period of the studied fish species (*L. aurata*) at (-18 ° C).

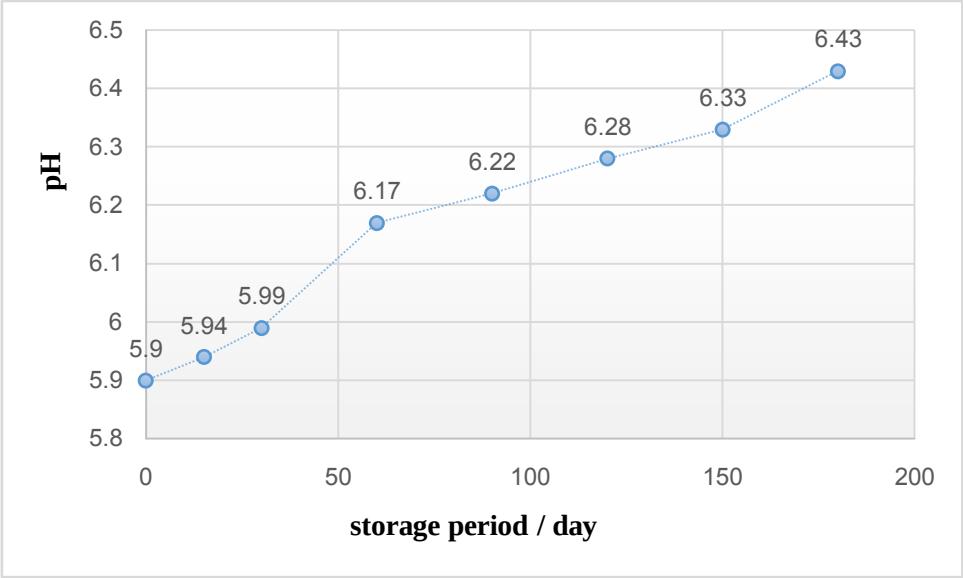

Figure (1): Variation of pH values of mullet meat frozen at -18 ° C

Samples of raw fresh fish of the studied fish species *L.aurata* recorded pH value of (5.90). pH values were close to the recommended range at rigor morits (6.0–6.8) [24].

According to re. [25], pH for fresh fish ranges from (6- 6.5). Similar results obtained in a study conducted by [17], where fresh samples of the species *L. aurata* from South of the Caspian Sea were recorded a pH value of (5.9). Differences in pH value may be due to the species, season, other factors, as a result of this reason pH value is not always a good indicator to judge on the quality and quality of Fish [26].

Figure (1) showed a gradual increase in acidity (pH) of muscles of the studied species (*L. aurata*) during the freezing period at (-18 ° C). Where pH value at the end of the freeze storage period attained (6.43) for (180 days). Similar results were also obtained for other fish species ([27], [28]). Results of our study coincided with another research which showed a constant increase in pH of the species *Sardina pilchardus* during freezing storage. The increase in Ph value during storage period could be explained by producing of each of TMA and NH3,resulting of a specific bacterial activity, especially for damage [29].

The extent of acceptability of fish for human consumption according to pH value is (6.8-7), and according to re. [30], decomposition of nitrogenous compounds causes an increase in pH value of fresh fish meat with increasing storage time.

Variation of FFA (%):

Results of free fatty acids (FFA %) during the freezing of the studied species (*L. aurata*) at (-18 ° C) were presented in figure (2).

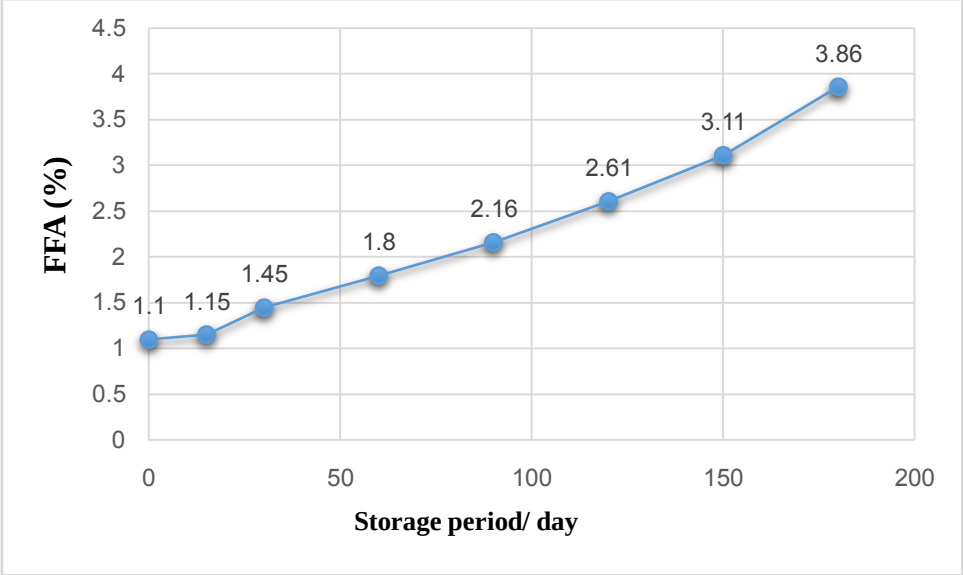

Figure (2): The free fatty acids (FFA %) of the mullet *L. aurata* frozen at (-18 ° C)

According to Figure (2), raw fresh samples of the studied species (*L. aurata*) recorded (1.10%) for free fatty acids (FFA%). Re. [31] suggested a range of fish meat content of free fatty acids (2-5%), which reflects the good quality of fresh samples of the studied fish species (*L. aurata*).

Fresh samples of *L. aurata* from the South of Caspian Sea recorded free fatty acid content (FFA%) (0.87) in a study conducted by re. [17]. Content of free fatty acids (FFA%) for the species *Scomberomorus Commerson* recorded (3.2%) in a study conducted by [32].

A gradual increase was also observed in the values of free fatty acids (FFA%) of the studied species (*L. aurata*) during the freezing period. Where FFA attained (1.15 and 3.86 %), respectively, at the 15 and 150 days post freezing, which reflecting the continued hydrolysis of fats during the freezing process. In this hand, our results agree with re. [32], where FFA increased from 3.2 to 5.66 % at (0 and 180 days), respectively under freezing for the species *Scomberomorus commerson*.

Re. [33] showed an important increase of FFA with increase the cryopreservation period. The increase in FFA (%) is caused because of the hydrolysis of the phospholipids and triglycerides through the activity of lipase and phospholipase enzymes ([34], [35]).

Peroxide value (pv) changes:

Figure (3) shows the changes in peroxide value (pv) during cryopreservation period at -18 ° C of the species *L. aurata*.

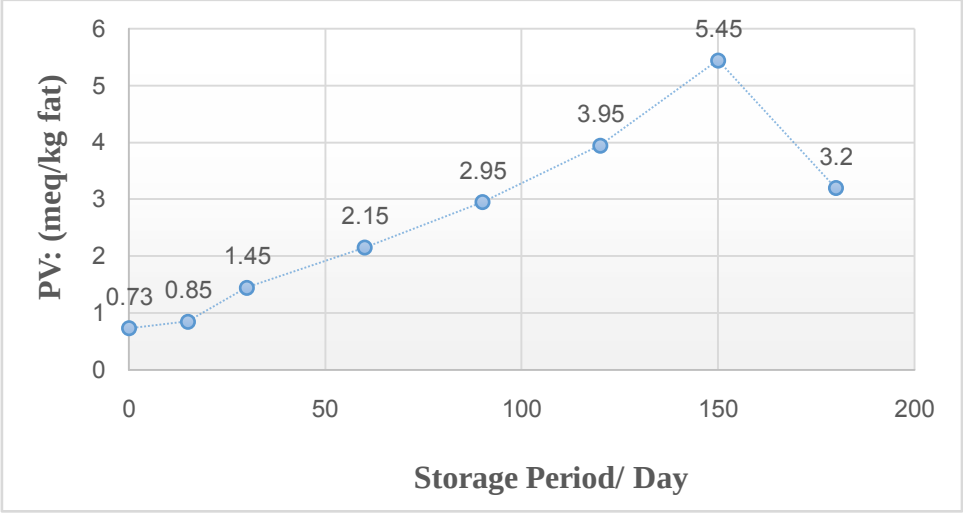

Figure (3): Peroxide value (pv) of the mullet *L. aurata* frozen at -18 ° C

The appearance of unusual smell and flavors determines the shelf life of fatty fish. The development of corruption in fish and fishy products can be monitored by measuring the increase in hydroperoxides and by determining the value of theobarbitoic acid (TBA) [36].

According to figure (3), the initial peroxide value of the oils extracted from fresh fish samples of the species *L. aurata* attained (0.73 meq oxygen / kg fat), and it represent the control.

Study of [17] recorded (0.6 meq oxygen / kg fat) as a number of pv for fresh fish samples of the species *L. aurata*. While in the study of [37], pv for fresh fish samples of the species *Oncorhynchus mykiss* recorded (0.73 meq oxygen / kg fat), when it is frozen at – 18 °C.

Figure (3) also showed a gradual increase in pv of oils extracted from muscles of the studied species *L.aurata* in the beginning of cryopreservation, where it recorded (0.85 and 5.45) in (15 and 150 days), respectively, at – 18 °C. That refer to the oxidation damage and corruption development through cryopreservation process [38].

Re. [32] recorded (2.32- 15.41) as a number of pv for the species *Scomberomorus commerson*, when it was frozen at (-18 °C) for (0 and 6 months), respectively.

While pv of the oils extracted from muscles of the species *L.aurata* showed reduction in the last period of storage, whereas it was (3.20 meq oxygen/ kg fat) at -18 °C in the day 180.

Also, re. [39] noticed the increasing of pv gradually for the species *Oreocromis mossambicus* until the 12th and 15th week of freezing, then reduction after that.

The gradual increasing in pv in the first stages of storage and reducing it in the last ones can explained by limit shelf age of the fatty fish due to fat oxidation. The initial product of fat oxidation is fatty acid hydroperoxide, which calculates as peroxide number. Peroxides are unstable compounds, decompose to aldehydes, ketones, alcohols and volatile compounds causing unwanted flavor of products ([40], [41]).

Acceptability limits for peroxide value of fish oils are (7-8 meq oxygen/ kg fat) [42].

Changes in TBA:

Figure (4) showed the changes in TBA values during cryopreservation period of the species *L. aurata* at (-18 °C).

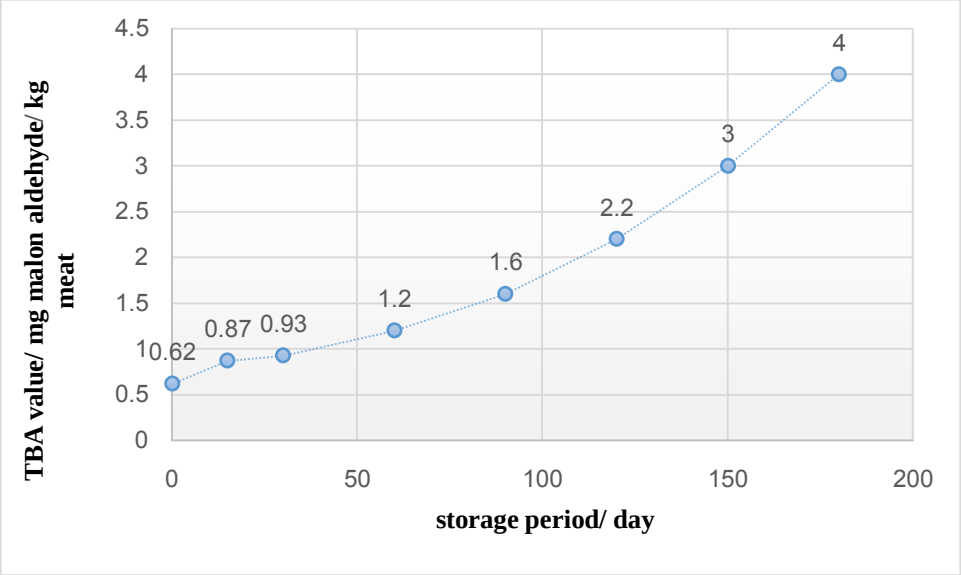

Figure (4): Value of TBA of the species *L.aurata* frozen at -18 °C

TBA is widely used as an indicator of fat oxidation degree. It is considered the product of the secondary oxidation of fat ([43], [41]). The content of TBA in fish oils refers to occurrence the oxidation in the samples [44].

According to the figure (4), the initial TBA value of fresh fish samples of the studied species *L. aurata* attained 0.62 mg malon aldehyde /kg (the control), which reflect the fresh case of samples. According to re. [45], damage limit of fish was (1- 10 mg malon aldehyde / kg: (1): which have an excellent quality, (2-3): which have a good quality, (4-5): which have a bad quality, (5-10): damaged. According to re. [46], an acceptability limit of TBA for human consumption is 7-8 mg malon aldehyde /kg.

The initial value of TBA of fresh fish samples of the studied species *L. aurata* was (0.62 mg malon aldehyde / kg. In the study of re. [17], the initial value of TBA recorded a low

value which was (0.06 mg malon aldehyde / kg). While it was 0.15 mg malon aldehyde / kg for the species *Scomber scombrus*, when samples were frozen at -18°C for a year [47].

It was observed a gradual increase in TBA value with increasing cryopreservation period to the species *L. aurata*, where TBA recorded (0.86 and 4 mg malon aldehyde / kg at -18°C in the days (15 and 180 days), respectively (figure 4). That maybe is due to peroxides decomposition to secondary products of oxidation, especially aldehyde in the later stages of fat oxidation [48].

Results of the present study agree with research of [49], which performed on the Indian species *Rastrelliger kanagurta* at – 20 °C, where TBA value attained (2.50 mg malon aldehyde / kg fat) when samples were frozen for a month. Also [47] demonstrated a gradual increase in TBA value (0.15 and 7.22 mg malon aldehyde / kg fat for the species *Scomber scombrus* at -18°C in the days (0 and 360), respectively.

The increase in TBA value indicates the formation and production of secondary oxidation compounds such as aldehydes and certain volatile compounds [50] responsible for the appearance of undesirable odors and flavors and for changes in color [51].

IV. CONCLUSION

The studied fish species *L. aurata* is one of the high nutritional value species through its high content of proteins, fats and mineral salts, which recorded (18, 7.35, 1.41%), respectively.

The studied fish species *L.aurata* is classified as a medium-fat content according to its fat content (7.35%).

According to the numbers of oxidation and hydrolyzed indices of lipids (PV peroxide number, thiobarbituric acid TBA, free fatty acids (FFA), the fish species *L. aurata* can be frozen at (-18°C) for 5 months.

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