INFLUENCE OF STORAGE AT LOW TEMPERATURES ON THE OIL STABILITY OF BOLTI AND MULLET FISH.

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Abstract: Bolti fish (*Oreochrom niloticus*) were caught from two different sources (farm water and river water), whereas Mullet fish *(Mugil cephalus*) were caught from farm water and marine water. Upon caughting fish, pH value and fish oil stability parameters were determined, then fish were subjected to storage at low temperatures (4^{o}C, 0^{o}C and -18^{o}C) for different periods (24 hours, 40 hours and 3 months, respectively). Changes in pH values and oil stability parameters were recorded during storage periods. The obtained results revealed that:

pH values of Bolti fish were 6.82 and 6.93 for farm and river water respectively, where the values of Mullet fish were 6.14 and 6.73 for farm and marine water, respectively. Upon subjecting fish to storage at low temperatures, slight and gradual decreases in pH values, were recorded, then the pH values were slightly increased thereafter, specially in case of refrigerating temperature (4^{o}C). Fish oil oxidation parameters (peroxide value, anisidine value, totox value ,diene and thiobarbituric acid) as well as oil hydrolytic rancidity parameter (free fatty acids) increased with prolonging storage period even at low temperature (4^{o}C, 0^{o}C and -18^{o}C). The lowest changes were recorded in case of storage at (-18^{o}C), where the highest ones were found at refrigerating temperature (4^{o}C).

It could be concluded that fish must be kept at low temperatures after caughting to increase the shelf life of fish , and reduce the risk of forming the unsafe compounds resulting as a function of fish oil autoxidation .

Key words: storage , bolti, mullet fish, stability parameters, oils, chilling.

Introduction

As soon as fish is caught and dies, changes of various kinds began to occur. Many of the changes can occurs simultaneously but at rate that are different and affected by processing treatment. The range of possible changes will be considered roughly in sequence, for a fish caught by trawl and kept in melting ice (Hobbs, 1982). Generally, rate of changes took place rapidly at high temperature. So lowering the temperature either by chilling or freezing is the most important single measure that can be taken to slow down deterioration of fish (Aitken *et al* ., 1982). Several studies were conducted on the postmortem changes in the farmed tilapia

(*Orechromis niloticus*) during ice storage. Fish rigor started within one hour and attained full rigor within two hours. Furthermore, the pH of the muscle was about 7 immediately after catching; then decreased generally with prolonging of storage period and the decrement at room temperature was much faster then at ice temperature (Yasmin *et al*., 2001). Further studies dealing with lipid oxidation of different fish species stored at cooling temperature were conducts by (Milo and Grosch, 1996 and Refsgaard *et al*., 1998). However, freezing treatment is usually required to preserve fish and the purpose of freezing is to obtain, a commodity that remains virtually unchanged by the process, hence, can be kept for some months with little loss of quality (Graham, 1982). The work to be described here was carried out to monitor the changes that took place in the pH values and oil stability parameters of different Bolti and Mullet fish during storage at cooling and freezing temperatures.

Materials and Methods

I-Materials:

Bolti Fish (*Oreochromis niloticus*) were caught from two different water sources (farm of Edco and river water of Rosette) where Mullet fish *(Mugil cephalus)* were caught from fresh water (farm of Edco) and Marine water of Rosette city, El-Behira Governorate, Egypt in the early morning during September 2005. Upon caughting fish, they were transferred immediately in ice boxes to the laboratory of Food Science and Technology Department, Faculty of Agriculture (Saba basha), Alexandria University, where they were remove from the ice boxes, cleaned and washed with fresh tap water. Each type of fish was divided into 4 groups.

The first one was assigned for control, the second was stored at refrigeration temperature (4^oC) for 72 hours, where the third was stored in ice box (0^oC) for 7 days and the fourth part was kept under freezing temperature (-18^oC) for 3 months.

II-Methods:

Fresh Bolti and Mullet fish were prepared by removing scales, where frozen ones were thawed in a refrigerator for 24 hours before analysis.

Crude oil was extracted from fresh, chilled and frozen fish following the method of Folsch *et al*. (1957). The extractable crude oil was kept in glass bottles at ice boxing temperature (0^oC) until performing the chemical evaluation. pH value of different fish samples were carried out following method of Pacheco-Aguilar *et al*. (1989).

Fish Oil stability parameters: peroxide value was determined using the method of AOAC (1995) and expressed as Meq/kg oil.

Anisidine value was performed colorimetery as described by Egan *et al*. (1981) using spectrophotometer (model safar Monco1900) and calculated following the next equation:

$$\text{Anisidine value} = \frac{25(1.2A_2 - A_1)}{M}$$

Where:

A_1 = the absorbance of oil solution.

A_2 = the absorbance of reaction products of oil and *p*- anisidine.

M = gram of oil present in 25 ml of tested solution.

Totox value was performed following Rossell et al (1982) procedure and calculated using the following equation:

$$\text{Totox value} = \frac{PV + An\,V}{2}$$

Where:

PV = Peroxide value.

AnV= Anisidine value.

Conjugated dienes were carried out using the method of the AOAC (1995) where absorbance were carried out at 234 nm using 1% oil solution in Octane. The free fatty acids were determined by titration with standard sodium hydroxide solution and calculated as oleic acid as given in the AOAC (1995) method. Thiobarbituric acid (TBA) was estimated using the method of Egan *et al*. (1981).

Results and discussion

Effect of storage periods on the pH values of different Bolti and Mullet fish:-

The pH values of Bolti fish were 6.82 and 6.93 at zero time for farm and river water, respectively. While the pH values of Mullet fish were 6.14 and 6.73 for farm and marine water, respectively (Table, 1). Slight decrease was recorded during cooling (4^{o}C and 0^{o}C) and frozen storage (-18^{o}C). The decrease of pH values may be attributed to the denaturation of fish proteins and the formation of lactic acid and free fatty acids (Khallaf, 1996). Slight increases on pH values were recorded especially with prolonging storage period under ice boxing temperature as given in Table (1). The increment in pH values of fish that took place thereafter could be related to the production of basic compounds caused by the enzymatic degradation of flesh muscle content (Simeonidon *et al.*, 1997).

However, no significant affect on pH value was recorded as a function of freezing at (-18C) for 3 months. These results are in agreement with those of Karacan and Boran (1996).

Table(1): Effect of storage periods on the pH values of different Bolti and Mullet Fish .

Storage periods	pH values of			
	Farm water Bolti Fish	Farm water Mullet Fish	River water Bolti Fish	Marine water Mullet Fish
Fresh fish (zero time)	6.82	6.14	6.93	6.73
Fish stored at refrigeration temperature (4^{o}C) :				
8 hours	6.59	6.00	6.72	6.20
16 hours	6.26	5.80	6.44	6.22
24 hours	6.00	5.85	6.50	6.10
Fish stored at ice boxing temperature (0 ^{o}C) :				
8 hours	6.78	6.00	6.91	6.21
16 hours	6.75	5.63	6.77	5.89
24 hours	6.52	4.74	6.43	5.65
32 hours	7.71	5.52	6.89	5.95
40 hours	7.90	6.80	7.12	6.34
Fish stored at freezing temperature (- 18^{o}C) :				
1 month	6.79	6.0	6.84	6.20
2 months	6.74	5.88	6.81	6.16
3 months	6.52	5.80	6.77	5.90

Oil stability parameters of different fresh Bolti and Mullet fish:

Autoxidation that take place in lipids, depends on oxygen that reacts with unsaturated fatty acids. Initially, peroxides are formed ,then break down to hydrocarbons, ketons, aldhydes and smaller amount of peroxides and alcohol (Washington, 1988). Furthermore, the results of oils and fats autoxidation is the development of objectionable flavors and odors known as oxidative rancidity. However oil

stability parameters of different Bolti and Mullet fish are given in Table (2). From such data it could be noted that, oil of marine water Mullet fish had the lowest values of stability parameters (peroxide value, anisidine value, totox and diene except thiobarbituric acid) among all samples . Oxidative stability parameters of oil extracted from farm water Mullet fish (peroxide value, anisidine value, totox, diene and TBA) and hydrolytic rancidity parameters (free fatty acids) were somewhere the highest between the different fish samples. The level of lipid oxidation is directly related to its fat content (Haard, 1992). Furthermore, some of these differences could be attributed to the age of fish and variation in food supply which would affect lipid decomposition and depletion (Dawson *et al.,* 1978). Similar results were found elsewhere (Rossell *et al*., 1982 and Gunstone, 1986).

Table (2): Oil stability parameters of different fresh Bolti and Mullet fish.

Samples	Peroxide value	Anisidin value	Totox	Free fatty acids	Diene	T.B.A.
Farm water Bolti fish	1.39	1.50	1.44	0.35	1.76	1.45
Farm water Mullet fish	2.12	2.07	2.39	0.56	2.29	1.11
River water Bolti fish	2.26	1.50	1.88	0.11	2.59	1.88
Marine water Mullet fish	1.30	1.36	1.33	0.14	1.83	1.39

Effect of storage at low temperatures (refrigeration (4^{o}C), ice boxing 0^{o}C) and freezing (-18^{o}C) for different periods on the oil stability parameters of different Bolti and Mullet fish:-

Chilling storage is usually involves cooling by ice or by mechanical refrigeration. It may be used for temporary preservation until some other preservative process is applied. So, most perishable foods including meat, fish and seafood may held in chilling storage for a limited time with little changes from their original condition (Frazier and Westhoff, 1978). In addition enzymatic changes in the foods are not prevented but slowed down

considerably. Oil stability parameters of different Bolti and Mullet fish stored at low temperatures: refrigeration (4^{o}C); ice boxing (0^{o}C) and freezing (-18^{o}C) for 24, 40 hours and 3 months, respectively are given in Tables (3,4 and 5).

Table(3): Effect of storage periods on the oil stability parameters of different Bolti and Mullet fish stored at refrigeration temperature (4^{o}C) for 24 hours.

Samples	Storage period (hours)	Peroxide value	Anisidine value	Totox	Free fatty acids	Diene	T.B.A.
Farm water Bolti fish	4	1.50	3.30	2.40	0.66	2.28	1.60
	8	2.24	3.50	2.87	0.82	2.34	2.20
	12	3.03	3.42	3.22	1.25	2.46	2.36
	16	4.42	4.03	4.21	1.44	2.76	4.54
	20	6.50	4.56	5.53	2.23	3.35	6.55
	24	10.55	4.90	7.72	2.76	3.56	7.78
Farm water Mullet fish	4	2.17	2.80	2.08	0.60	1.98	1.32
	8	2.26	3.00	2.63	0.65	2.29	1.55
	12	3.40	3.50	3.45	0.69	2.62	2.01
	16	4.20	3.90	4.05	0.88	2.99	2.35
	20	5.79	4.50	5.14	1.21	3.31	3.69
	24	7.99	5.33	6.41	1.56	3.46	4.90
River water Bolti fish	4	2.60	2.25	2.42	0.18	2.23	2.22
	8	2.99	2.63	2.81	0.32	2.44	5.37
	12	3.60	3.20	3.40	0.44	1.84	5.66
	16	3.89	4.44	4.14	0.73	2.52	6.20
	20	4.55	4.89	4.72	1.22	1.41	6.90
	24	5.68	5.94	5.81	1.36	1.43	7.40
Marine water Mullet fish	4	2.0	1.70	1.88	0.46	0.69	1.65
	8	2.50	2.33	2.41	087	1.39	2.32
	12	2.80	2.78	2.79	1.15	1.22	3.77
	16	3.30	3.44	3.37	1.59	2.11	4.15
	20	3.80	3.96	3.88	1.66	2.36	4.80
	24	4.30	4.76	4.53	1.22	2.21	5.35

Table(4): Effect of storage periods on the oil stability parameters of different Bolti and Mullet fish stored in ice Box at (0^{o}C) for 40 hours.

Samples	Storage period (hours)	Peroxide value	Anisidine value	Totox	Free fatty acids	Diene	T.B.A.
Farm water Bolti fish	4	1.55	2.70	2.12	0.66	1.81	1.50
	8	2.05	3.10	2.57	0.68	1.83	1.56
	12	2.40	3.40	2.90	0.76	1.88	1.73
	16	2.90	3.80	3.35	0.91	2.38	2.20
	20	3.30	4.20	3.75	1.10	2.79	2.45
	24	3.55	4.70	4.12	1.55	3.24	2.89
	28	3.90	5.50	4.70	1.75	3.64	3.30
	32	4.77	6.10	5.43	2.00	3.92	3.79
	36	6.99	6.80	6.89	2.40	4.50	4.25
	40	7.25	7.55	7.40	2.64	4.90	4.66
Farm water Mullet fish	4	2.20	2.11	2.15	0.59	1.85	1.23
	8	2.70	2.23	2.46	1.22	2.15	1.66
	12	3.11	2.65	2.88	1.35	2.19	2.25
	16	3.50	3.27	3.38	1.55	2.37	2.70
	20	3.99	3.36	3.67	1.98	0.56	2.99
	24	4.42	3.99	4.20	2.44	2.28	3.44
	28	4.80	4.46	4.63	2.47	2.34	3.80
	32	5.11	4.70	4.90	2.88	2.51	4.76
	36	5.64	5.10	5.37	3.25	2.66	4.59
	40	6.00	5.40		3.50		5.22
River water Bolti fish	4	2.30	1.77	2.03	0.29	2.29	1.86
	8	3.40	2.20	2.80	0.35	2.33	1.90
	12	4.05	2.30	3.17	0.39	2.37	2.21
	16	4.55	2.64	3.59	0.42	2.56	3.13
	20	4.90	3.11	4.00	0.63	2.77	3.35
	24	5.30	3.53	4.41	0.70	2.79	3.41
	28	5.55	3.60	4.57	0.89	2.90	4.18
	32	5.59	4.41	5.00	1.18	3.26	4.24
	36	6.42	4.78	5.60	2.13	3.41	4.90
	40	6.99	5.25	6.12	2.25	3.66	5.65
Marine water Mullet fish	4	1.30	1.37	1.28	0.36	2.22	1.56
	8	1.60	1.57	1.58	0.43	2.34	1.77
	12	1.90	1.62	1.76	0.67	2.39	2.11
	16	2.40	1.77	2.08	0.99	2.45	2.35
	20	2.60	2.40	2.50	1.20	2.49	2.65
	24	3.10	2.50	2.80	1.44	3.02	2.69
	28	3.40	2.88	3.14	1.75	3.33	3.24
	32	3.80	3.11	3.45	1.98	3.90	3.33
	36	4.20	3.26	3.73	2.30	4.41	3.58
	40	4.50	3.33	3.92	2.56	4.60	3.71

Table(5): Effect of storage periods on the oil stability parameters of different Bolti and Mullet fish stored at freezing temperature (-18^{o}C) for 3 months.

Samples	Storage period (months)	Peroxide value	Anisidine value	Totox	Free fatty acids	Diene	T.B.A.
Farm water Bolti fish	1	1.76	1.36	1.55	0.51	1.17	2.15
	2	2.11	1.66	1.88	0.76	2.33	4.96
	3	3.37	2.12	2.74	0.46	2.45	5.60
Farm water Mullet fish	1	2.38	2.58	2.45	0.56	1.55	2.22
	2	3.00	2.76	2.88	0.74	1.78	2.63
	3	3.66	3.26	1.46	0.93	2.07	3.41
River water Bolti fish	1	2.40	1.16	1.78	0.38	0.66	2.00
	2	2.57	1.32	1.94	0.47	0.76	2.55
	3	3.89	2.32	3.10	0.76	0.99	2.87
Marine water Mullet fish	1	1.43	1.26	1.34	0.20	1.59	1.77
	2	2.24	1.55	1.89	0.47	2.03	2.42
	3	2.60	2.47	2.53	0.50	2.33	2.92

From the given data it could be noted that, general increasing of oil oxidation parameters as well as hydrolytic rancidity were recorded as a function of prolonging storage periods. Furthermore, the rate of oil oxidation was relatively high in case of storaging at refrigeration temperature (4^{o}C) among all of the different storage temperatures. On the other hand, storaging under frozen conditions (-18^{0}C for 3 months) helped in keeping the oil oxidation parameters as well as hydrolytic rancidity parameters as low as possible. Deng *et al*.(1977) found that, oxygen permeability as well as hydrolytic enzymes activity will be very limited under frozen temperature (-20^{o}C), hence, the oxidation rate will be reduced. The results of Bonnell (1994) and Karacan and Boran (1996) support our findings.

From the previous results, it could be concluded that keeping fish soon after coughing at low temperature play an important role for reducing the rate of fish oil oxidation and fish oil hydrolytic rancidity. In addition, in case of using refrigeration temperature (4^{o}C) or ice boxing (0^{o}C) for storage fish, these will be more useful to keep fish in good order for a period not more than 12 hours at 4^{oC} and 20 hours at 0^{o}C, where storage fish at -18^{0C} helped to keep fish oil stability parameters in the safe range even after 3 months of storage.

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تأثير التخزين على درجات حرارة منخفضة على ثبات زيوت اسماك البلطي و البوري.

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أجريت هذه الدراسة بهدف دراسة تأثير تخزين الأسماك على درجات حرارة منخفضة على ثبات زيوت اسماك البلطي و البوري حيث تم اصطياد اسماك البلطي من مزرعة ادكو ومياه نهر النيل فرع رشيد كما تم اصطياد اسماك البوري من مياه مزرعة ادكو و المياه المالحة لمدينة رشيد في فصل الخريف (سبتمبر) من عام 2005 م بمجرد اصطياد الأسماك تم نقلها مباشرة إلى معمل قسم علوم وتكنولوجيا الأغذية - كلية الزراعة – بسابا باشا- جامعة الإسكندرية حيث تم غسيل الأسماك بالماء الجاري ثم حفظت هذه الأسماك على درجات حرارة منخفضة (درجة حرارة الثلاجة 4°م ودرجة حرارة الصندوق الثلجي 0 °م و درجة حرارة التجميد -18 °م) وقد تم تقدير ال pH أثناء فترات التخزين (24 ساعة لحرارة الثلاجة – 40 ساعة للصندوق الثلجي و ثلاثة أشهر للمجمد) كما تم تقدير مقاييس أكسدة زيوت الأسماك (الرقم البيروكسيدى – قيم الانيسيدين – التوتكس – قيمة الدايين(أحماض دهنية تحتوى على رابطتين مزدوجتين)- قيمة حمض الثيوباربتيوريك وكذلك تقدير مقاييس التزنخ التحللي لزيت الأسماك (الأحماض الدهنية الحرة). أجريت هذه التقديرات على الأسماك قبل التخزين على درجات الجرارة المنخفضة وكذلك تم تتبع التغيرات في هذه المقاييس خلال فترات التخزين وقد أظهرت النتائج مايلى:-

كانت قيم ال pH لأسماك بلطي مياه المزارع ومياه نهر النيل 6.82 و6.93 بينما كانت قيم ال pH لأسماك البوري مياه المزارع و المياه المالحة 6.14 و 6.73 على الترتيب وذلك قبل التخزين على درجات الحرارة المنخفضة وأثناء التخزين حدث نقص بسبط في قيم ال pH ثم زادت زيادة طفيفة في نهاية فترة التخزين وخاصة تلك الأسماك المخزنة على درجات حرارة الثلاجة (4°م) أما بالنسبة لمقاييس حدوث الأكسدة لزيوت الأسماك وكذلك التزنخ التحللي لها فقد زادت بطول فترة التخزين وحدثت أكثر زيادة في الأسماك المخزنة على درجة حرارة الثلاجة (4°م) بينما اقل زيادة تم تسجيلها في زيوت الأسماك المخزنة على درجة حرارة التجميد. مما سبق فانه يمكن التوصية بخفض درجة حرارة الأسماك بمجرد صيدها ثم حفظها على حرارة التجميد مما يؤدي الي تقليل حدوث الأكسدة الذاتية لزيوت هذه الأسماك ومن ثم تجنب المخاطر الناتجة من ظهور المركبات الناتجة من أكسدة هذه الزيوت بحيث تكون الأسماك في صورة جيدة وصالحة للاستهلاك الأدمي.