دراسة كيمياوية لمكونات بعض الاسماك التجارية من شط العرب والخليج العربي

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درست المكونات الكيمياوية لبعض الاسماك الاقتصادية التي جمعت من الخليج العربي وشط العرب بالنسبة للفوائد والقيمة الغذائية . كما لوحظت نوعية الاسماك المدروسة عند حفظها في ثلاجة على درجة حرارة (٨° م) ان مدة بقاء الاسماك صالحة للاكل على هذه الدرجة الحرارية له علاقة بالمدة التي يمكن ان تحفظ لدى باعة الاسماك في السوق وكذلك بالنسبة للمستهلك الذي يحاول حفظ اسماكه في ثلاجة البيت .

وجدت حالات ظهر فيها تأثير طعم مركبات البترول في الاسماك وذلك راجع الى تلوث الماء في منطقة شط العرب والخليج العربي بالنفايات النفطية ان مثل هذه الظاهرة تؤثر على استهلاك الاسماك بصورة عامة وماقد تسببه من اضرار سرطانية او مرضية بصورة خاصة .

اظهرت نتائج الفحص ان اسماك البني والجفوت تحوي اعلى نسبة من الرطوبة والبروتين اما الصبور فكانت تحوى اعلى نسبة من المعادن والدهون . كانت نتيجة الفحص للاسماك ان الصبور يحوي اقل نسبة من الرطوبة والبروتين والجفوت اقل نسبة من الدهن اما ابو عوينة فيحوي اقل نسبة من المعادن .

لقد احتفظ الكطان والزبيدي بخواصه الطبيعية عند حفظه في الثلاجة لمدة اسبوعين بينما احتفظ الحف بخواصه لاسبوع واحد فقط .

من بين العشرة انواع التي اجريت الدراسة عليها وجدت آثار مكونات النفط في لحوم اسماك الكطان والصبور بصورة واضحة .

BIOCHEMICAL STUDIES ON SOME COMMERCIALLY IMPORTANT FISHES OF SHATT AL-ARAB AND THE ARAB GULF

دراسة كيميائية لمكونات بعض الأسماك التجارية من شط العرب والخليج العربي

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ABSTRACT

The paper mainly deals with the chemical composition of commercially important fishes of Shatt Al-Arab and the Arab Gulf in relation to their nutritive values. It also includes a study of their keeping quality at refrigerator's temperature (8°C). In addition, the work has further been extended to an investigation for possible contaminants from oil pollutants in the area.

From the chemical analysis, it is observed that **Pseudosciaena aneus** and **Ilisha filigera** contain highest moisture and protein respectively, whereas **Hilsa ilisha** is rich in both fat and ash. Moisture and protein are found to be lowest in **Hilsa ilisha**, fat in **Pseudosciaena aneus** and ash in **Ilisha filigera.**

The physico-chemical study on their storage quality shows that **Barbus xenthopterus** and **Pampus argentius** stand quite well for consumption even upto two weeks, while **Chirocentrus dorab** is spoiled within one week.

Possible contamination of the same fishes with petroleum or other pollutants is also investigated. **Barbus xenthopterus** and **Hilsa ilisha** amongst ten fishes are detected with oil contamination.

INTRODUCTION

A knowledge of chemical composition of fish is the most important step to evaluate its nutritive value. Some important studies on the chemical composition of fishes have been reported by Love (1970), Neuhaus and Halver (1969), and Wiechers and Dreosti (1961). No doubt, a lot of work has been done on proximate analysis of fishes as reported by Natrajan and Sreenivasan

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(1961), and Paniaotova and Bailozov (1960), but no such information are available on the fishes of this region as yet. Keeping this in mind as well as other aim in view, part of the present work was devoted for preliminary analysis of few commercially important fishes of Shatt Al-Arab and the Gulf. In industrial processing of fish, a thorough knowledge of fish with regards to its chemical composition and availability is of paramount importance. Prior information on fat or protein is necessary to study the possibilities of producing fish pickles, canned fish or other by-products.

A perusal of the literature reveals that many workers have devoted their attention to proximate analysis only (op. cit.), but few such as Khawaja and Jafri (1967), Pawar and Magar (1965), and Tomlison et al. (1961) have dealt with the biochemical changes in fish due to storage at elevated temperatures. A detailed physico-chemical study, was, therefore, undertaken to know 'keeping qualities' of some fishes at the refrigerator's temperature.

Due to crude oil pollution, there is a likely contamination of polycyclic aromatic hydrocarbons (PAH) of other products associated with the use of petroleum. Junghams (1974) and Sullivan (1974) have indicated that due to petroleum contamination, the amount of benzo (a) pyrene (BP) in sea fish is considerably higher than that in freshwater fish. During oil treatment with detergents oil particles of 0.5 micron or of smaller sizes are produced, which are easily digested and assimilated by the fish. At present, there is little information on their toxicological effects on human health, but these may cause many other serious problems as reported by Holstead (1972), such as, (i) the production of fish protein concentrate will become complicated due to contamination with hydrocarbons, because these are protein-bound and cannot be removed by normal extraction process, (ii) many fishes are killed by crude oil. The hydrocarbon of 0.5 micron, if absorbed through intestinal wall can cause damage to liver. More drastic effects like cancer with petroleum pollutants is also reported by Pearson (1970). However, keeping in view the serious effect of this type of pollutant in human system, the present study was extended to the analysis of possible oil contamination.

MATERIALS AND METHODS

Fresh fish samples, used for the study, were collected from Ashar's fish market, Basrah. Flesh for analysis was taken from the region just below the dorsal fin after removing the skin. Precautions were taken to avoid bones. Analytical balance was used for weighing the samples. Moisture, protein, fat and ash were determined by following the standard procedures used by Anonymous (1965). The results were compiled by taking the average of at least three estimations of each analysis and expressed in percentage on wet-weight basis.

The determination of quality of freshness was conducted by keeping the fish in sealed polythene bags from one to three weeks in the lower chamber of the refrigerator (8°C). Physical studies were done by organoleptic tests as outlined by Burgess et. al., (1967). Proximate composition of the same fishes was also done at different intervals. Total volatile nitrogen (TVN) was determined by following the procedure mentioned by Pearson (1970).

The procedure adopted in isolation and identification of hydrocarbons involved the preparation of samples, extraction by suitable solvents, separation by silica gel column chromatography as stated by Warner (1974). The final identification was done by fluorescence technique. In a typical experiment, the digestion was done by mixing 5 gm. of blended fish flesh with 2 gm. of 4N NaOH and heating at 90°C for 2 hr. Di-ethyl ether (25 ml.) was used for extraction. The resulting extract was then used for fractionation by column chromatography. The size of the column was 1.3 cm. X 12 cm. packed with 10 gm. of silica gel activated at 170°C. Fraction 1was the elution by ether, the other two resolutions were from chloroform and methanol using 25 ml. of each. These fractions were used for fluorescence study.

RESULTS AND DISCUSSION

Chemical Analysis :

Results of the chemical analysis of fishes are shown in Table 1. It is observed that moisture content is highest in Jewfish and lowest in Sboor and Hamam. Jewelled shad and Shabout contain highest quantity of protein which is lowest in Sboor and Pomfret. The results show that Sboor contains the highest quantity of fat in comparison with other fishes where the fat content is much lower, especially in Shanak and Jewfish which is less than 1 per cent. In all fishes, ash content ranges from 0.44 to 1.87 per cent.

From the reported results on analysis on some of the same fishes in different waters as reported in Anonymous (1962), it has been noticed that moisture, protein and ash content in most fishes are more or less the same. Only in the case of Sboor, moisture was found to be remarkably high. In the same fish, fat was found to be 9.85% as compared to 19.4% in other country. The possible reason of the relatively high moisture and low fat content of Sboor in this region may be due to the fact that the fish might have been caught after a long migration.

Sboor and Silver bar were found to be rich in major constituents. For high protein demand, Jewelled shad may be the choice whereas Shabout, Gattan and Hamam contain on an average higher constituents than in Jewelled shad. Bunni could also be equally good in its average contents as well as in its availability.

For industrial use, Jewelled shad, Shanak and Jewfish which contain low fat and high protein may be considered for canning and smoking. Similarly, with an average high nutrient content, Gattan, Shabout and Pomfret, abundantly available, can be justified for fresh consumers' market as well as for storage. Sboor having a high quantity of fat may be considered as a good source of fish oil. Fish with high protein content like Silver bar which is not much favoured for fresh consumption may be diverted to industry for manufacturing fish protein concentrate.

Keeping Quality :

Physical and biochemical changes in fishes due to storage are presented in Tables 2 and 3 respectively.

Criteria recorded for detailed study of physical condition of fish kept in the refrigerator reveal that some fishes deteriorate quite quickly, others stand an appreciable time. Almost original physical properties were observed in Gattan and Grey pomfret even after two weeks storage, which were deviated in the Silver bar. It is interesting to note that Bunni showed distinct dark patches of moulds on its ventral surface from second week onwards which resulted in simultaneous bursting of belly. The major criteria of spoilage were observed to be softness of flesh, its separation from bones, depression of the eye, ammoniacal odour and bleaching of the gills. The degree of decomposition and disintegration in relation to the above criteria were observed in decreasing order of Silver bar, Sboor, Bunni, Pomfret and Gattan respectively as the time of their storage proceeded.

Changes in chemical composition in Gattan, Bunni, Sboor, Pomfret and Silver bar were also studied. Protein, fat and ash

TABLE No. (1) — CHEMICAL ANALYSIS OF SOME COMMERCIALLY IMPORTANT FISHES

S. No.	Scientific name	Common/ Local name	Standard length (mm)	Weight (gm)	moisture	Average Values in Percentage protein N X 6.25	fat	ash
1a	**Barbus xenthopterus**	Gattan	290	480	75.96	21.68	1.82	1.50
2a	**Barbus sharpeyi**	Bunni	220	268	78.34	18.18	2.00	1.40
3a	**Barbus grypus**	Shabout	360	510	77.31	22.09	1.23	1.21
4c	**Hilsa ilisha**	Sboor	270	372	71.22	17.02	9.85	1.87
5b	**Pampus argentius**	Grey pomfret	210	490	77.93	17.91	2.00	1.16
6b	**Pseudosciaena nasus**	Jewfish	220	352	79.09	19.66	0.55	1.33
7b	**Chirocentrus dorab**	Silver bar	500	630	76.68	21.47	2.78	1.68
8b	**Ilisha filigera**	Jewelled	300	390	75.60	23.03	1.03	0.44
9b	**Caranx kalla**	Hamam	260	272	72.69	19.62	2.71	1.46
10b	**Sparus berda**	Shanak	260	388	77.59	19.95	0.66	1.34

a freshwater fish
b marine
c both

TABLE No. (2) — ASSESSMENT OF FRESHNESS BY ORGANOLEPTIC TESTS

No.	Name of fish	After one week G	O	A	T	E	C	Grade
1	Gattan	Bright red, no bacterial slime, outer slime transparent	Fresh seaweedy	Bright shining, kidney bright red, slightly slimy	Do not leave finger impressions, body firm	Fresh	Bright and shining	I
2	Bunni	Bright red, no bacterial slime, outer slime transparent	Seaweedy	Bright shining, kidney bright red, slightly slimy	Finger impressions retained, body not very firm	Fresh	Bright and shining	I
3	Sboor	Bright red, no bacterial slime	Seaweedy	Bright shining, kidney bright red, slimy skin	Firm, elastic to finger touch	Fresh, convex black pupil, translucent cornea	No discolouration	I
4	Grey Pomfret	Bright red, no bacterial slime, outer slime water transparent	Fresh seaweedy	Bright shining, kidney bright, slightly slimy	Not very firm, elastic to finger touch	Fresh	Shining	I
5	Silver bar	Dark brown	Caprylic	kidney brown in Little bright, colour, slimy skin	Retained finger indentations	Slightly sunken, translucent	Bright and shining	II

NOTE : G = Gill, O = Odour, A = Appearance, T = Texture, E = Eye, C = Colour

TABLE No. (3) — BIOCHEMICAL CHANGES OF FISH STORED IN REFRIGERATOR

S. No.	Name of fish	After weeks	Average Values in Percentage moisture	protein N X 6.25	fat	ash	TVN mg/100 g.
1	Gattan	1	77.50	20.87	1.75	1.30	20
		2	77.27	19.68	1.60	1.00	28
		3	78.54	19.52	1.25	0.80	37
2	Bunni	1	79.00	17.76	1.74	1,29	29
		2	78.92	16.28	1.06	1.14	36
		3	81.30	15.39	0.94	0.92	45
3	Sboor	1	71.33	15.79	8.80	1.36	39
		2	72.13	14.96	7.99	1.11	45
		3	73.40	12.92	6.97	0.68	50
4	Grey Pomfret	1	78.68	15.38	0.77	1.13	22
		2	81.18	15.29	0.70	0.87	34
		3	82.05	14.76	0.60	0.82	42
5	Silver bar	1	77.29	16.89	0.90	1.32	40
		2	78.59	16.30	0.80	1.10	54
		3	81.73	15.34	0.61	0.68	60

showed a declining trend as against the moisture and TVN which were on the rise in each fish as the storage period prolonged. One of the possible reasons of the decrease of protein, fat and ash is due to the event of hyperaemia which resulted in oozing out of slimy mucus-like substances from the fish during storage. It was obvious that these nutrients were partly lost through the mucus. Secondly, the decrease may be on account of microbial, enzymatic or similar decomposition. The increasing trend in moisture on the other hand is probably due to either inclusion of volatile degraded products or the absorption of vapour from the surrounding by the sample during estimation. It is observed that the value of TVN has also considerably increased in all the fishes during the three weeks period of storage. The marked increase was observed in Silver bar, which was not much significant in the case of Gattan.

Results were found to be symmetrical in both physical and chemical observations in keeping quality. Table 2 shows that the concentration of slimy mucus is very high in Sboor and Silver bar from first week onwards, both of the fishes at the same time show a high decrease in fat, protein and ash (Table 3). The quantity of slime is significantly low in Gattan which agree with higher values of fat, protein and ash in chemical estimation. This inferred that Silver bar and Sboor started spoiling very quickly compared to Bunni, Pomfret and Gattan.

Contamination :

For detection of contaminants in fish, experimental results on fluorescence studies are shown in Table 4.

TABLE No. (4) — RESULTS ON IDENTIFICATION OF HYDROCARBONS

S. No.	Name of fish	Fractions*	Fluorescence[a]
1	Gattan	1	pale blue
		2	pale blue
		3	pale blue
2	Sboor	1	pale blue
		2	pale blue
		3	palle yellow

*Fr 1 — elution by di-ethyl ether
Fr 2 — elution by chloroform
Fr 3 — elution by methanol

Bunni, Shabcut, Grey pomfret, Jewfish, Silver bar, Jewelled shad, Hamam and Shanak gave negative results.

[a]Pale yellow and pale blue are indications of crude and other oils respectively.

Results indicate that Gattan and Sboor were contaminated with hydrocarbons. Pale yellow fluorescence might be the presence of traces of crude oil. The chemical detection of contaminants in these fishes also corroborated with organoleptic tests. For this purpose, fresh fish samples were cooked and prepared for normal consumption. It was observed that kerosine like smell in these two fishes were totally intolerable and the fish was unfit for consumption.

These observations bring out certain points for further study. Attention is needed to investigate the source of these contaminants in the body of the fish, mechanism of their distribution and interaction within the body and the method by which these can be eliminated by metabolic system from the body of the fish. There are two contradictory views concerning the purging of contaminants. Blumer and Saas (1972) indicated that after contamination the petroleum hydrocarbons might persist even for the whole life of fish, whereas Vaughan (1973) found that keeping contaminated fish in clear water for a period of three to seven weeks or even shorter was sufficient to purge out all detectable level of hydrocarbons from the fish tissues. However, coordinated efforts and study are needed on this issue to establish the correct nature and the limit of tolerance of these products which may cause a great damage to biological systems.

On the basis of the preliminary study, further works need to be done on the composition of important fishes in this area to standardise techniques of keeping qualities. As a matter of fact, this knowledge is primarily important to improve the methods of utilisation, preservation, storage, marketing and formulation of new products for human consumption.

Some fish species in the region either become unfit for human consumption due to petroleum contamination or are killed by crude oil. This is a big national waste. A detailed study is necessary to find out ways and means to get rid of the pollutants. It should also include a study on the nature of tar balls disposed by merchantile vessels in the aquatic environment.

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