111 - CHANGE IN MAILLARD REACTION AND LIPID OXIDATION IN STORED FISH

A.A. EL-SAWY
F. OSMAN
A. KAOUSAR
H. HEBASH

SUMMARY: Fish was stored at - 20°C for 135 days. Sample was taken for each 15 days. The flavour of stored fish was extracted and fractionation to its neutral-acidic and basic fractions was done. The neutralacidic fraction was further fractionated into carbonyl and noncarbonyl. The analysis of all fractions was carried out by G.L.C. Amino acids, fatty acids and lipid characteristics were done at each interval period. It was found that indol and kother nonvolatile nitrogenous constituents were indicators of incipient spoilge to some extent. Indol occurs in fish in increasing concentration as putterfaction proceeds. Enzymes enhance the carbonyl-amino reactions. Such reactions are known to result in the development of bitterness.

Key Words: Maillard Reaction, lipid oxydation.

INTRODUCTION

Deterioration in the quality of fish has frequently occurred during frozen storage due to undesirable process taking place in lipid and protein. These changes in fish are of great commercial importance since they determine the storage life of frozen sea foods. Deterioration in flavour is considered to be the most serious problem especially when the poor freezing practices are employed and the quality of fish is inferior.

The authors studied the effect of storage on Maillard reaction and lipid oxidation in fish for 90 days (1,2). This paper is a continuous work dealing with storage of fish for further period (135 days) to detect the deterioration via the flavouring components concent.

MATERIALS AND METHODS

Fresh Bolti fish (Tilapia Nilotica) was bought from the local market and stored at -20°C for 135 days. Sample was taken every fifteen days for the following analysis:

Lipid (acid value, iodine value, peroxide value and fatty acid composition), protein (amino acid composition), total aroma, its fractionation into neutral - acidic and basic fractions, and fractionation of neutral - acidic into carbonyl and noncarbonyl fractions were done as mentioned in the previous paper (1) (using G.L.C and GC MS).

RESULTS AND DISCUSSION

Effect of storage on the fat characteristics and fatty acid composition

The fatty acid composition of Bolti fish stored for 135 days is given in Table 1. There is apparent significant change in the facty acid composition. Linoleic acid reached trace amount by storage for 105, 120 and 135 days. Also oleic acid was 23. 17% by storing for 105 days, then decreased to 22% and 20% by storage for 120 and 135 days respectively. Linolenic was found in trace amount during this period of storage (from 105 to 135 days).

These results were in-accordance with those reported by El-Sawy *et al.* (3). That the rate of oxidation of methyl alerate, methyl linoleate, methyl linolenate are (1:12:25).

The chemical characteristics iodine value (I.V.), peroxide value (P.V.) and acid value (A.V) of the lipid of stored fish for interval periods (105, 120 and 135 days) are given in Table 2.

The analysis revealed that the iodiene value showed a remarkable decrease from (33.81 to 25.78). This decrease is incoincident with the remarkable decrease of linoleic and risappearance of linolenic acid.

While the peroxide value increased gradually reaching its maximum value 13.77 by storage.

Effect of storage on volatile components of roasted fish:

The gas chromatography of the volatile compents of roasted fish for different periods with their concentration are illustrated in three tables. It is clear from Table 5 that ketones do not exceed approximately 3% for 3-heptanone by storage for 105 days. Hughes found that nothing was known regarding the influence of these ketones on the flavour of cooked fish (4).

*From the Chemistry Depart. Faculty of Science, Benha University, Benha, Egypt.
** From Chemistry of Flavour Lab. National Research Centre, Dokki, Cairo, Egypt.

Concerning aldehydes, which play an important role in development of fish flavour, it is observed that nonanal was found in high concentration 20.25% by storage for 105 days. Then they decreased by increasing the storage period for 135 days. On the contrary octanal increased from nil to 3.43% and 18.74% at 105, 120 and 135 days respectively.

After 135 days the unsaturated aldehyde 2,4-undecdienal disappeared accompanied by the formation of 2,4,6 - dodectrienal.

Evidence relating to the flavours of individual carbonyls to specific attributes of fish flavour has been reported by Diemair and Schams (5). The rancid and talgigen components belong to the higher constituents of the saturated and unsaturated fatty acids (e.g. nonanal and decanal).

On the contrary to the aldehydes, the aliphatic alcohol concentration increase by increasing the period of storage. This increase was gradual and remarkable by storage for 120 days. 1-Octen-3-ol was present in its maximum concentration (24%) by storage for 105 days, then decreased, gradually by increasing the time of storage 120 and 135 days.

Table 1: Fatty acid composition of the stored fish for 135 days at 20°C (concemetration %).

Fatty acid	105 days	120 days	135 days
C_{12}	0.74	0.14	0.14
$C_{14.0}$	2.15	2.15	3.0
C_{16}	1.2	1.2	2.0
$C_{16.0}$	60.7	62.01	63.86
$C_{16.1}$	6.4	6.0	6.0
C_{18}	2.0	3.0	4.0
$C_{18.1}$	23.17	22.0	20.0
$C_{18.2}$	trace	trace	trace
$C_{18.3}$	trace	trace	trace
$C_{20.1}$	trace	trace	trace
$C_{20.4}$	trace	trace	trace

Table 2: Chemical characteristic of the lipid of the stored fish.

Time (days)	acide value	peroxide value	iodine value
105	22.8	10.0	33.81
120	26.88	12.95	32.11
135	43.7	13.77	25.78

Table 3: Voltaile Components Stored Fish for 105 days (Concentration %).

1	0.8						Ethanol
2	1.2	Trace		2.71			Propanal, methylamine
3	1.7						Butanal
4	2.2						Unidentified
5	2.8						Ethylamine
6	3.3	43.39	Trace	0.66	1.24	9.0	Propanol, isoporyl pyrazine
7	4.0						Unidentified
8	4.8	11.97		0.21			Pentanal, propyl pyrazine
9	5.6	Trace		0.48	0.48		Trimethyl amine, 1-methyl pentanal
10	6.1	1.76		0.28			Hexanal, 2,3-dimenthyl pyrazine
11	6.6						Methyl hexanoate, 2,5-dimethyl pyrazine
12	7.4	2.26		0.15	1.99		Heptanal, 2,4 imethyl pyrazine
13	8.7	2.36	Trace	0.06	2.32		1-Hexenol, 2-hexanal, 2,3-diethyl pyrazine
14	10.8	1.26	1.36	0.07			Octanal, Unidentified
15	11.9	Trace	9.26			6.0	Methyl heptanoate, 2,5-diethyl pyrazine
16	1.b6	Trace	2.91	2.8			1-Penten-3ol, 2,6-diethyl pyrazine
17	14.5	Trace	2.91	0.17	20.25	16.0	Nonanal, 1-hexe-3ol, 2,5-diethyl-3-methyl pyrazine
18	16.5	Trace		0.24	1.44		Octyl alcohol, furfural, 2,6-diethyl-3-methyl pyrazine
19	18.2	Trace	22.44		4.08		Benzaldehyde, unidentified
20	19.3	1.04					Decanol, 5-methyl furfural, dimethyl isobutyl pyrazine
21	19.8		1.13	5.08		24.0	1-Octen-3-ol, unidentified
22	20.9	9.13	2.1	.16	26.46		2, Acetyl furan, indol
23	22.4	1.51	25.59		7.92		Benzyl alcohol, dodecanal
24	24.7	1.13		1.24	13.1		Unidentified
25	25.8	2.77	14.57	0.55	Trace	4.5	2,4-UNDECADIENAL
26	28.0	17.33	Trace	0.11			2,4,6-Dodecatrienal, Unidentified
27	31.8	2.26	Trace	0.07	6.22	3.0	3, Heptanone, methyl octanoate
28	32.7	Trace		0.47	13.39		3-Octanone, unidentified
29	33.5	Trace	Trace	44.32		37.5	Methyl undeconoate, gfurfuryl acohol
30	34.9	1.76	6.76	4.18	1.05		3-Nonanone, unidentified
31	37.0						Unidentified
32	39.4						Unidentified
33	43.1	Trace	10.92	0.76	Trace		Unidentified
34	46.0			34.9			Guaicol

Wilkinson (6) has suggested that when linoleate is oxidaized 1- octen-3-ol may be formed by a secondary oxidation of the C 13- hydroxy conjugated diene resulting from the corresponding hydroperoxide.

In the previous paper (1), aliphatic amines play a significant role in the fresh fish flavour, while the aromatic pyrazine takes an important role in producing the characteristic roasted dehydrated fish.

These pyrazines arise from Maillard reaction of dehydrated fish (7,8). Among these pyrazines are iso propyl pyrazine, propyl pyrazine, 2,3 - dimethyl pyrazine, 3,6-dimethyl pyrazine, 2,5-diethyl pyrazine, 2,6-diethyl pyrazine, 2,5-diethyl-3 methyl pyrazine and 2,6-diethyl-3-methyl pyrazine.

At 105 days storage indol was detected in low amount (0.16%). This concentration increases by increasing the time of storage (13.3% and 12.5%) by 120 and 135 days respectively.

Indol and other nonvolatile nitrogenous constituent were indicators of incipient spoilage to some extent. Indol occurs in fish in increasing concentration as putterfaction proceeds (9).

From the forgoing results, it is concluded that, of the chemical reactions leading to flavour deterioration in frozen fish, the most important is often the development of oxidative rancidity in the lipid constituent.

Enzymes affecting amino acid composition can be active in frozen fish. Also they enhance the carbonyl amino reactions. Such reactions are known to result in the development of bitterness.

Change in amino acid concentrations by storage

Table 6 respesents the amino acid composition together with their concentration. Seven major amino acids were identified. They are glycine, valine, alanine, glutamic acid methionine, histidine and histamine.

Table 4: Voltaile Components Stored Fish for 120 days (Concentration %).

Peat	tR	aroma concentrate	neutral acidic	basic	carbonyl	non-carbonyl	Components
1	0.8						Ethonal
2	1.2						Propanal, methylamine
3	1.7	Trace	21.99		Trace		Butanal
4	2.2						Unidentified
5	2.8						Ethylamine
6	3.3	Trace	Trace		4.16		Propanol, isopropyl pyrazine
7	4.0	Trace	Trace		9.42		Unidentified
8	4.8	Trace	Trace		9.32		Pentanal, propyl pyrazine
9	5.6	Trace	Trace		5.93		Trimethylamine, 1-methyl pentanal
10	6.1						Mexanal, 2,3-dimethyl pyrazine
11	6.6	Trace	Trace		2.79	1.65	Methylhexanoate, 2,5-dimethyl pyrazine
12	7.4	5.53	Trace		3.38		Heptanal, 2,6 dimethyl pyrazine
13	8.7	Trace		29.46			1-Hexenol, 2-hexanal, 2,3-diethyl pyrazine
14	10.8	Trace	Trace		3.43	0.91	Octanal, Unidentified
15	11.9	9.33	3.51			0.64	Methyl heptanoate, 2,5-diethyl pyrazine
16	12.6	Trace	Trace		30.36		1-Penten-3ol, 2,6-diethyl pyrazine
17	14.5	Trace	1.24	23.8		28.89	Nonanal, 1-hexe-3-methyl pyrazine
18	16.5	Trace	11.95			50.84	Octyl alcohol, furfural, 2,6-diethyl-3-methyl pyrazine
19	18.2	5.99	Trace		2.89		Benzaldehyde, unidentified
20	19.3						Decanol, 5-methyl furfural, dimethyl isobutyl pyrazine
21	19.8	Trace	2.17			Trace	1-Octen-3-ol, Unidentified
22	20.9	Trace	3.07	13.39	3.57		A, Acetyl furan, indol
23	22.4	5.84	Trace		24.64	4.15	Benzyl alcohol, dodecanal
24	24.7	Trace	51.02	8.33	Trace	Trace	Unidentified
25	25.8	67.93		Trace			2,4-Undacadienal
26	28.0	Trace	2.34	25.0	Trace		2,4,6-Dodecatrienal, Unidentified
27	31.8	Trace	2.17			6.46	3, Heptanone, methyloctanoate
28	32.7	5.35	Trace		Trace	Trace	3-Octanone, Unidentified
29	33.5						Methyl undecanoate, furfuryl alcohol
30	34.9						3-Nonanone, Unidentified
31	33.0						Unidentified
32	39.4						Unidentified
33	43.1						Unidentified
34	46.0	Trace	Trace			6.41	Guaicol

Table 5: Volatile Components Stored Fish for 135 days (Concentration %).

Peat	t_R	aroma concentrate	neutral acidic	basic	carbonyl	non-carbonyl	Components
1	0.8						Ethanol
2	1.2	15.13	Trace			26.88	Propanal, methylamine
3	1.7	Trace		20.12			Butanal
4	2.2						Unidentified
5	2.8	Trace	3.59			36.72	Ethylamine
6	3.3	Trace	Trace		0.6		Propanol, isopropyl pyrazine
7	4.0	Trace	Trace		1.3		Unidentified
8	4.8	8.74	Trace		0.5	5.39	Pentanal, propyl pyrazine
9	5.6	3.69	Trace				Trimethylamine, 1-methyl pentanal
10	6.1						Hexanal, 2,3-dimethyl pyrazine
11	6.6						Methyl hexanoate, 2,5-dimethyl pyrazine
12	7.4	4.48	6.34		Trace		Heptanal, 2,6 dimethyl pyrazine
13	8.7						1-Hexenol, 2-hexanal, 2,3-diethyl pyrazine
14	10.8	Trace	Trace	8.66	18.74		Octanal, Unidentified
15	11.9						Methyl heptanoate, 2,5-diethyl pyrazine
16	12.6	2.53	Trace	7.07		4.64	1-Penten-3ol, 2,6-diethyl pyrazine
17	14.5	Trace	6.03	7.04	Trace		Nonanal, 1-hexe-3ol, 2,5-diethyl-3-methyl pyrazine
18	16.5	5.6	Trace	4.62	1.58	6.91	Octyl alcohol, furfural, 2,6-diethyl-3-methyl pyrazine
19	18.2						Benzaldehyde, unidentified
20	19.3	5.15	6.66			1.57	Decanol, 5-methyl furfural, dimethyl isobutyl pyrazine
21	19.8	Trace		6.06			1-Octen-3-ol, unidentified
22	20.9	Trace	Trace	12.51		2.73	2, Acetyl furan, indol
23	22.4		14.2	3.85	1.67		Benzyl alcohol, dodecanal
24	24.7	2.8	6.92	10.01	60.94	9.67	Unidentified
25	25.8	6.92	49.82	4.38		1.49	2,4-Undecadienal
26	28.0			11.93		1.93	2,4,6-Dodecatrienal, Unidentified
27	31.8	2.85	6.39	3.7		0.88	3, Heptanone, methyl octanoate
28	32.7						3-Octanone, unidentified
29	33.5	Trace	Trace		4.18	0.34	Methyl undecanoate, furfuryl alcohol
30	34.9						3-Nonanone, unidentified
31	37.0					0.78	Unidentified
32	39.4						Uniedentified
33	43.1	Trace	Trace		10.45		Uniedentified
34	46.0	42.74					Guaicol

By storing concentration of glutamic, histidine and alanine decreased. This decrease is in- accordance with change in flavour. Histamine is formed having the concentrations 2%, and 3% which increase by increasing the period of storage 135 days (4%).

Histamine is formed from the bacterial decomposition of histidine.

Table 6: Changes in amino acid composition of protein of stored fish (concentration %).

Components	105 days	120 days	135 days
Alanine	30.0	24.0	20.0
Valine	7.0	6.0	8.0
Glycine	3.0	4.0	4.0
Methionine	39.0	49.0	52.0
Glutamine	9.0	6.0	6.0
Histamine	2.0	3.0	4.0
Histidine	6.0	6.0	6.0

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