

### RESULTS AND DISCUSSIONS

The following results and discussions show the effects of some manufacturing, cooking, preservation and storage methods on the quality attributes; fatty acids composition; lipids and phospholipids fractions and fat-soluble vitamins of fish oils (conditions of this study) as follow:

# I- Smoking offish:

# A- Moisture, fat, phenols and thiobarbituric acid (TBA) contents:

Data presented in Table (1) show the moisture (%), fat (%), phenols (mg / 100 g) and thiobarbituric acid (TBA, as mg malonaldehyde / kg sample) contents of frozen herring fish (raw material) as affected by smoking methods (liquid, cold and hot smoking) and storage conditions (smoked herring stored at room temperature, 25 °C  $\pm 2$  °C for 30 days and at 4 °C for 90 days).

From the results, it could be observed that the frozen herring fish - used as raw material for processing of smoked herring - recorded 70.69 %, 10.71 % and 0.45 mg malonaldehyde / kg sample for moisture, fat and TBA, respectively (on wet weight basis) while, phenols were not detected.

The moisture content decreased from 70.69% before smoking to 57.55; 54.72 and 56.62% after liquid, cold and hot smoking, respectively. Decreasing percent of moisture for cold, hot-, and liquid-smoked herring were 22.59, 19.90 and 18.58%, respectively. This may be due to the smoking time which  $_{\rm Was}$ 

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longer (8-10 hr.) for cold than that of hot method (2 hr.) and liquid (about 100 minuets), in addition, the high moisture content of liquid-smoked samples may be due to the repeated spraying with liquid smoke containing water during smoking of fish. On the other hand, due to storage either at room temperature (25 °C) or at cold (4 °C), it is evident that the moisture content of liquid-, cold- and hot-smoked herring was decreased with increasing of storage time provided that such loss of moisture was pronouncedly reduced when the storage temperature decreased from 25 °C to 4 °C. When the effect of smoking method was considered, it seems that the rate of moisture loss was higher for hot-smoked herring than that of liquid and cold-smoked herring either at room temperature or at cold storage. For example, after 30 days of storage at room temperature, the percent decrease of moisture for hot-, liquid- and cold-smoked herring were 27.73, 26.16 and 16.46 %, respectively. At the same period (30 days) of storage but at 4 °C, the values were 11.16, 10.87 and 3.33 %, respectively. Moreover, the percent decrease of moisture content after 90 days of cold storage for hot-, liquid- and cold-smoked herring was lower (18.21, 16.92 and 5.39%, respectively) than that stored at room temperature for only 30 days (27.73, 26.16 and 16.46 %, respectively). This indicates the importance of cold storage in reducing the moisture loss of smoked fish compared to storage at room temperature (economic importance). These results were confirmed by the findings of Fredrick and Thomas (1985); Moghazy (1994) and Moghazy et al. (1996).

The fat content of the raw frozen herring was 10.71 and 36.54 % on wet and dry weight basis, respectively. By smoking

either liquid, cold or hot smoking, the fat content was increased on wet weight basis due to the decrease of moisture nevertheless, it was decreased on dry weigh basis as the fat contents decreased from 36.45 % of raw herring to reach 25.87, 29.11 and 25.70 % of liquid-, cold- and hot-smoked herring, respectively. It is evident that the loss of fat was higher for the hot- and liquidsmoked fish than that of the cold-smoked fish and this may be due to the effect of smoking temperature, which was higher in hot (70 °C) and liquid (60 °C) smoking than that in cold (30 °C) smoking, consequently higher melting and dripping of some fat were occurred for hot and liquid smoked samples than cold smoked one. On wet weight basis (W.W.), fat contents of all smoked samples (with slight exception for cold-smoked herring) were increased by increasing the storage time either at room temperature or at cold storage. These increases of fat contents on W.W. during storage periods due to the decrease of moisture contents during the same periods of storage. On dry weight basis, the fat contents of all the samples stored at room temperature or at cold were decreased until the end of storage periods. However, fat contents of liquid-, cold- and hot-smoked herring stored at 4 C were higher than those stored at room temperature. By the end of storage period either at room temperature (30 days) or at 4 C (90 days), the fat content of cold-smoked herring was higher (24.55 and 26.23 %) when compared with liquid- and hotsmoked samples (20.43 and 22.99 and 16.37 and 22.93 % respectively). Also by the end of storage period (on D.W.), the percent decrease of fat for liquid-, cold- and hot-smoked herring stored at room temperature for one month were 21.02, 15.66 and 36.30 %, respectively corresponding 11.13, 9.90 and 10.78 % for RESULTS AND DISCUSSION -----

the same smoked samples stored at 4 °C for three months. It is evident that (with very slight exception) the lowest loss of fat was recorded for cold-smoked herring followed by liquid- and hot-smoked herring, respectively. Loss of fat with dripping or due to escape of some fat breakdown volatile compounds as malonaldehyde may occur as reported by Moghazy *et al.* (1996). Finally, before and after storage, the highest fat content was recorded for the cold-smoked herring. These results are also confirmed by the finding of *Hammed* (1985).

Thiobarbituric acid (TBA, as mg malonaldehyde / kg sample) was used as an important indicator for testing the oxidative rancidity of the samples under this study. From the same Table (1), it could be noticed that the raw frozen herring used as raw material for producing smoked herring- had TBA value of 0.45 mg malonaldehyde (MA) / kg sample, this value of TBA was somewhat higher than that of fresh fish, may be due to that raw material was an imported frozen herring product. By smoking with different methods being liquid, cold and hot smoking, immediately after smoking (zero time), the liquidsmoked herring had lower (0.67 mg MA/Kg sample) than that of the hot- and cold-smoked herring which had values of 0.72 and 0.88 mg MA/ Kg sample, respectively (on W.W. basis). The same trend of TBA calculated on W.W. was recorded for TBA calculated on D.W., being 1.58, 1.66 and 1.94 mg MA/kg sample for liquid-, hot- and cold-smoked herring, respectively. The low TBA value of liquid-smoked samples followed by that of hot-smoked samples then, cold-smoked one may be due to the direct contact between the liquid smoke compounds (some of

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these compounds react as antioxidants) and herring flesh, as well as, the faster penetration of smoke compounds into flesh by liquid and hot smoking than that of cold smoking. Accordingly, lower oxidation of lipids indicating by lower TBA was observed for liquid and hot than that of cold-smoked samples at zero time (Immediately after smoking). By storage at room temperature, the TBA values of all the smoked herring were increased by the increasing of storage time. However, it could be observed that by the end of storage, the cold-smoked herring had lower TBA values either on W.W. or on D.W. basis being 3.49 and 6.43 for cold corresponding 4.63 and 8.05 for liquid nevertheless, hotsmoked one recorded 2.72 and 4.60 mg MA/Kg sample indicating more oxidation and partial breakdown of malonaldehyde. TBA values of smoked herring stored at 4 °C were lower than those stored at room temperature, nevertheless, TBA values of all smoked herring stored at 4 °C were increased up to 60 days then decreased (with exception of hot-smoked samples, which recorded continuous increase of TBA). Anyway, during storage either at room temperature or at cold, according to the values of TBA, the cold-smoked fish was the best followed by the liquid and hot-smoked fish, however, immediately after smoking (zero time), the liquid-smoked fish was the best followed by the hot- and cold-smoked fish, respectively. This trend of cold-smoked herring may be due to higher concentration of phenols occurring by long smoking time and slow penetration of smoke compounds into fish during storage period. The increase of TBA value could be attributed to lipid oxidation specially in the presence of oxygen. These results were confirmed by the findings of Shiau and Chai (1985), Etman RESULTS AND DISCUSSION

(1985), Allam *et al.* (1988), EL-Akeel (1988), Beltran and Moral (1990b) and USDA-FSIS (1996).

Phenols were not detected in raw frozen herring fish. By smoking with different methods, the cold-smoked fish had the higher phenols content than that of liquid- and hot-smoked fish, being: 26.76 and 59.10, 21.36 and 50.32 and 20.20 and 46.57 mg / 100g sample on W.W. and D.W. basis, respectively. Phenols content was decreased to reach 33.82, 17.77 and 9.16 mg / 100 g sample by the end of storage at room temperature (30 days, D.W. basis) for cold-, liquid- and hot-smoked fish, respectively. Values by the end of storage at 4 °C (90 days) were 52.46, 40.07 and 29.07 mg / 100 g, respectively. It could be observed that phenols concentration in smoked herring was related to the TBA values recorded for these smoked samples as, the TBA values were lower when the phenol concentrations were higher (with small exception at zero time). Also, it could be noticed that the loss of phenols was lower for all smoked herring stored at cold compared with that stored at room temperature. According to the TBA values and phenols content, the cold-smoked herring was the best nevertheless, the liquid-smoked herring was the nearest to the cold-smoked one and it may be preferred due to the safety of liquid smoke when compared to the whole smoke used in cold and hot smoking. These results and discussion were confirmed; being in accordance with the findings of Mohamed et al. (1967), Tilgner (1977) and Moghazy (1994).

#### **B- Oil constants:**

The results of oil constants (quality attributes of extracted oil) for frozen herring oil as affected by smoking methods and

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storage conditions (at room temperature for 30 days and at cold for 90 days) are found in Table (2).

From the results of Table (2), it could be observed that refractive index (RI), acid value (AV), free fatty acid (FFA), peroxide value (PV), saponification value (SV) d jodine number (IN) of oil extracted from raw frozen he mg were 1.4702, 1.64, 0.83, 4.32, 203.13 and 135.75, respectiv ly.

Immediately after smoking (zero time) usin methods including liquid, cold and hot smoking, showed that RI, pH and IN decreased while AV, FF SV increased for all smoked samples either the liqui hot-smoked herring. The decrease of RI and IN as increase of AV, FFA, PV and SV means lipids oxi hydrolysis consequently, decrease of lipid unsatura ion. Both hydrolysis (indicated by AV and FFA) and oxidation by the other parameters) of lipids should be consideration since the former promotes the latter (T al., 1981). Some hydrolysis and oxidation were o curred by different smoking methods but, according to the valu of the oil constants at zero time, the liquid-smok d herring mainly recorded more stable oil followed by the  $col_{t-and\ hot-}$ smoked herring as, the former recorded RI, AV, FF and IN of 1.4699, 1.73, 0.87, 4.76, 203.29 an corresponding 1.4700, 1.78, 0.89, 5.70, 203.51 and cold-smoked herring and 1.4692, 1.87, 0.93, 4.63, 2 130.61, respectively. This may be due to the dir between the liquid smoke and the fish flesh and penetration into fish, as well as the shorter smoking ti

different e results PV and -, cold- or ell as the ation and (indicated ken into omizu et obtained PV, SV 133.25 31.33 for 4.15 and t contact he faster e of the

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liquid-smoking method compared with the whole smoke used in both cold and hot-smoking methods.

On the other hand, during storage, gradual de rease of RI and IN was observed by increasing the storage ti e either at room temperature or at 4 °C. The reverse was recor ed for AV. FFA, PV and SV where it was gradually inc ased with increasing of the storage period, This possible d e to lipids oxidation and hydrolysis during storage. However, the rate of lipids oxidation and hydrolysis was lower for all sm ked herring stored at 4 °C than that stored at room temperature. ccording to smoking methods used and storage conditions, t could be noticed that during and by the end of storage ei er at room temperature or at 4 °C, the cold-smoked herring of was more stable when compared with liquid- and hot-smoked erring oils, respectively. Nevertheless, the quality attributes of oil (oil constants) extracted from the liquid-smoked sampl | s were the nearest to the oil constants values recorded for cold-smoked samples (the best) than that of hot-smoked one (the poorest) during and by the end of storage either at 25 °C or at 4 °C. For example, after 30 days of storage at room temperature (the end of storage), the RI, AV, FFA, PV, SV and IN - whic represents the oil constants - were 1.4681, 4.87, 2.35, 30.00, 206.19 206.39 and 115.79 for liquid-smoked herring, and 1 4658, 5.92, 2.95, 13.47, 227.86 and 101.29 for hot-smok d herring. respectively. After the same period (30days) of storage but at 4 C, the values were 1.4695, 2.16, 1.08, 7.64, 203.77 and 130.90; 1.4691, 2.18, 1.10, 9.20, 203.79 and 131.89 and 1.4676, 234,

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1.37, 18.81, 205.94 and 126.22 for cold-, liquid- and hot-smoked herring, respectively. Meanwhile, by the end of storage at 4 °C (90 days), the values were 1.4688, 3.93, 1.97, 22.60, 204.96 and 128.25; 1.4683, 4.28, 2.15, 25.50, 205.46 and 125.41 and 1.4653, 4.72, 2.36, 38.47, 215.46 and 110.50 for cold-, liquidand hot-smoked herring, respectively. It is worthy mentioning that the higher the AV, FFA, PV and SV, the higher the lipids oxidation and hydrolysis but, the lower the IN and RI, the higher the lipids oxidation and hydrolysis as reported by Wally (1981) and Maurice (1990). On the other hand, concerning the pH, the raw frozen herring recorded pH value of 6.40. Immediately after smoking using different methods, the pH value was decreased for all smoked herring, which may be due to some of smoke compounds absorption particularly organic acids. During storage either at 25 °C or 4 °C, the pH values of all smoked samples regardless the cold-smoked samples - were decreased at the first periods of storage (10 days at 25 °C and 15 days at 4 °C) then gradually increased up to the end of storage. The pH value of cold-smoked herring was decreased up to 20 days of storage at room temperature and 30 days of storage at cold then, it was gradually decreased until the end of storage, may be due to the higher concentration and slower penetration of smoke compounds during storage of cold-smoked herring than that of liquid- and hot-smoked herring.

Finally, according to quality attributes of oil, smoking methods and storage conditions, it could be concluded that oil extracted from cold-smoked herring was more stable followed by oil of liquid-smoked herring thereafter oil of hot-smoked one,

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which showed poor quality attributes. However, due to many reasons especially those concerned the health, liquid-smoked herring may be preferred than cold-smoked one. On the other hand, nearly, storage of smoked herring at 4 °C for 90 days may be better than storage at 25 °C for 30 days. For more safety, storage of smoked fish at room temperature should not exceed 20 days under the conditions of this study. However, storage of smoked herring at 4 °C for 90 days may be acceptable, nevertheless, to take smoked herring with high quality and more safety, storage at 4 °C should not exceed 60 days. These results and discussion were within the limits reported by Wally (1981), Ryder et al. (1984), Freeman et a/. (1988), Awatif et al. (1990) and Vinter (1995).

## C- Fatty acid composition and fractions:

Fatty acid composition (as % of total fatty acids) and fractions (%) of raw frozen herring fish as affected by liquid, cold- and hot-smoking methods and storage conditions (including storage at room temperature and at 4 °C) are presented in Tables (3, 4, 5 and 6).

From the results of Tables 3, 4 and 5, concerning the raw frozen herring, it could be noticed that the predominant saturated fatty acid was the palmitic ( $C_{16:0}$ ) acid which was 17.28 % followed by the arachidic ( $C_{20:0}$ ) and myristic ( $C_{14:0}$ ) acids which were 9.93 and 7.56 % of the total fatty acids, respectively. At the same time, the lowest percent (0.04 %) was recorded for the behenic (C22:0) acid. The saturated C15:0,  $C_{17:0}$ ,  $C_{18:0}$  and  $C_{24:0}$  fatty acids represented low percent of total fatty acids being 0.82, **0.14,** 1.10 and 0.10 %, respectively.  $C_{12:0}$  fatty acid was absent in

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Table(3): Fatty acids composition of frozen herring as affected by liquid smoking and storage conditions.

	Frozen			Storage	temperatu	re (°C) ar	nd period	(in days)	
Fatty* acids	herring	Ze ro ** tim e	Room to	emp.(25 ° (	C * 2 °C)		Cold stor	age (4 °C)	
acius	(Raw)	line	10	20	30	15	30	60	90
C12:0	-	-	0.42	-	0.41	0.43	-	-	0.38
C14:0	7.56	14.49	10.54	12.61	14.35	12.84	14.69	12.40	10.64
C15:0	0.82	2.11	0.75	0.41	0.42	0.43	1.54	1.17	3.65
C16:0	17.28	7.59	20.83	24.07	24.99	10.32	14.93	12.16	10.61
C16:1	10.64	7.91	7.85	5.23	4.22	6.66	9.97	7.23	13.87
C17:0	0.14	0.16	0.08	0.08	1.91	0.01	1.05	0.16	0.23
C18,0	1.10	2.19	0.93	6.58	4.77	1.26	3.46	2.51	1.72
C18,1	18.38	22.34	20.40	15.07	13.52	22.95	15.27	15.47	18.69
C18,2	7.06	5.76	1.34	1.26	0.54	6.99	5.57	3.27	3.59
C18:3	2.14	2.08	0.08	0.42	ı	-	0.02	0.05	0.23
C20:0	9.93	10.80	7.53	8.98	11.33	10.39	8.75	15.15	2.63
C20:4	2.82	2.70	0.33	1.25	0.33	2.48	1.58	0.89	0.69
C20:5	10.06	9.31	10.04	10.72	10.99	0.29	6.96	2.61	4.48
C22:0	0.04	0.08	0.08	0.12	0.19	3.93	-	0.05	14.04
C22:6	11.93	12.21	15.79	11.62	9.36	17.11	16.23	23.68	10.31
C24:0	0.10	0.27	3.01	1.58	2.67	3.91	-	3.20	4.24

<sup>=</sup> As % of total fatty acids.

<sup>\*\* =</sup> Immediately after liquid smoking.

Table(4): Fatty acids composition of frozen herring as affected by cold smoking and storage conditions.

	Frozen			Storage	temperati	ure (°C) a	nd period	(in day)	
Fatty* acids	herring	Zero** ti me	Room to	emp.(25°(	C ± 2 °C)		Cold stora	age (4 °C)	
	(Raw)		10	20	30	15	30	60	90
C12:0	-	-	0.87	-	-	-	-	0.08	0.03
C14:0	7.56	12.85	9.78	13.89	15.91	9.68	9.41	13.50	14.30
C18:0	0.82	0.41	0.77	1.36	2.85	0.49	0.44	0.88	0.50
C16:0	17.28	13.39	14.84	13.99	18.75	10.33	9.61	14.46	14.67
C16:1	10.64	7.74	7.11	7.35	7.99	6.00	16.06	14.55	14.52
C17,0	0.14	0.07	0.10	0.10	0.51	0.16	0.15	0.22	0.15
C18:0	1.10	1.16	0.26	0.65	1.35	1.73	1.53	1.02	1.20
C18:1	18.38	24.19	15.69	18.42	19.75	16.01	12.08	21.82	17.95
C18:2	7.06	4.56	2.67	1.36	0.88	5.79	3.77	1.91	2.96
C18 <sub>:</sub> 3	2.14	0.14	0.05	-	-	2.11	0.16	0.07	4.08
C20·0	9.93	5.96	15.87	17.87	13.98	15.36	16.43	12.48	10.95
C20:4	2.82	1.54	1.54	2.42	2.66	1.54	0.59	0.73	1.83
C20:5	10.06	10.89	18.56	9.61	5.42	8.62	13.08	8.05	8.42
C22:0	0.04	-	-	-	0.01	-	3.50	0.07	0.08
C22:6	11.93	11.43	9.59	10.47	8.63	18.56	10.97	7.52	3.74
C24,0	0.10	5.67	2.30	2.52	1.31	3.62	2.22	2.64	4.63

<sup>\* =</sup> As % of total fatty acids.
\*\* = Immediately after cold smoking.

Table(5): Fatty acids composition of frozen herring as affected by hot smoking and storage conditions.

	Frozen			Storage	temperati	ıre (°C) a	nd period	(in day)	
Fatty* acids	heron,	Zero** ti me	Room to	emp.(25 °C	(A 2 °C)		Cold stor	age (4 °C)	
acius	(Raw)	ume	10	20	30	15	30	60	90
C12:0	-	-	0.77	0.26	0.77	-	0.09	1.15	3.01
C14:0	7.56	9.36	13.40	14.21	16.87	10.67	7.64	10.41	14.54
C15 <sub>:</sub> 0	0.82	1.51	1.22	0.93	1.35	0.81	0.73	1.97	4.06
C16:0	17.28	10.31	15.73	9.30	10.66	20.75	16.57	10.77	16.85
C16:1	10.64	6.29	6.70	9.83	6.90	4.08	4.83	7.09	5.91
C17:0	0.14	0.21	0.16	0.90	0.95	0.17	0.13	0.28	2.12
C18:0	1.10	1.32	3.77	4.18	9.18	4.92	2.03	13.52	6.33
C18;1	1838	19.86	14.42	10.80	8.88	25.42	17.00	5.60	13.01
C18;2	7.06	2.22	1.60	1.12	1.22	3.17	3.19	3.17	1.01
C18;3	2.14	2.16	0.22	0.03	-	0.67	0.09	0.08	0.05
C20:0	9.93	23.27	15.61	21.15	22.19	10.25	18.39	18.53	19.00
C20:4	2.82	2.63	2.63	3.85	3.75	6.67	0.35	0.91	0.80
C20,5	10.06	8.64	10.44	9.67	3.44	1.00	8.20	12.71	6.53
C22:0	0.04	-	2.00	-	8.31	0.08	-	0.04	4.01
C22:6	11.93	10.00	10.89	10.11	3.21	9.58	1731	10.09	2.00
C24:0	0.10	2.22	0.44	3.66	2.32	1.50	3.45	3.68	0.77

<sup>\* =</sup> As % of total fatty acids.

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<sup>\*\* =</sup> I mmediately after hot smoking.

Table(6): Fatty acids fractions (%)of frozen herring (raw) as affected by smoking methods and storage conditions.

E 44				Storage	temperat	ture (°C) :	and perio	d (in day)	<u> </u>
Fatty acids	Frozen herring	Zero** time	Room t	emp.(25 ']	$\Gamma \pm 2$ °C)			rage (4 °C	
fractions*	(Raw)		10	1 20	30	15		1 60	
				L	iquid-smo			1	1 70
T. sat.	36.97	37.69	44.17	54.43	61.04	43.52	44.42	46.80	48.14
T. unsat.	63.03	62.31	55.83	45.57	38.96	56.48	55.60	52.31	51.86
T. mono.	29.02	30.25	28.25	20.30	17.74	29.61	25.24	22.70	32.56
T. di.	7.06	5.76	1.34	1.26	0.54	6.99	5.57	3.72	3 59
T. tri.	2.14	2.08	0.08	0.42	-	-	0.02	0.05	0.23
T. tetr.	2.82	2.70	0.33	1.25	0.33	2.48	1.58	0.89	0.20
T. pent.	10.06	9.31	10.04	10.72	10.99	0.29	6.96	2.61	4.48
T. hex.	11.93	12,21	15.79	11.62	9.36	17.11	16.23	23.68	10.31
T. poly.	34.01	32.06	27.58	25.27	21,22	26.87	30.36	29.61	19.30
Ks	1.70	1.65	1.26	0.84	0.64	1.30	1.25	1.12	1,08
					Cold-smok			<del>                                      </del>	1.08
T. sat.	36.97	39.51	44.79	50.38	54.67	41.37	43.29	45.35	46.51
T. unsat.	63.03	60.49	55.21	49.63	45.33	58.63	56.71	45.35 54.65	<del>-46.51</del> -53.50
T. mono.	29.02	31.93	22.80	25.77	27.74	22.01	28.14	36.37	32.47
T. di.	7.06	4.56	2.67	1.36	0.88	5.79	3.77	1.91	2.96
T. tri.	2.14	0.14	0.05	-	-	2.11	0.16	0.07	4.08
T. tetr.	2.82	1.54	1.54	2.42	2.66	1.54	0.59	I 0.73	
T. I ent.	10.06	10.89	18.56	9.61	5.42	8.62	13.08	1 0.73 1 8.05	1.83
T. hex.	11.93	11.43	9.59	10.47	8.63	18.56	10.97	I 7.52	8.42 3.74
То ,	34.01	28.56	32.41	23.86	17.59	36.62	28.57	18.28	21.03
Ks	1.70	1.53	1.23	0.99	0.83	1.42	1.31	1.20	1.15
					Hot-smok		1.51	11,20	1.15
T. sat.	36.97	48.20	53.10	54.59	72.60	49.42	49.30	60.35	70.69
T. unsat.	63.03	51.80	46.90	45.41	27.40	50.59	50.97	39.65	
T. mono.	29.02	26.15	21.12	20.63	15.78	29.50	21.83	12.69	<u> 18.92</u>
T. di.	7.06	2.22	1.60	1.12	1.22	3.17	3.19	3.17	18.92 1.01
T. tri.	2.14	2.16	0.22	0.03		0.67		1.0.08	— 1.01 — 0.05
T. tetr.	2.82	2.63	2.63	3.85	3.75	6.67		1 0 91	
T. sent.	10.06	8.64	10.44	9.67	3.44	1.00		1 12.71	
T. hex.	11.93	10.00	10.89	10.11	3.21	9.58	17.31	10.09	
T01	34.01	25.65	25.78	24.78	11.62	21.09	29.14	26.96	2.00
Ks	1.70	1.07	0.88	0.83	0.38	1.02	1.04		10.39
			3.00	0.00	0.50	1.02	1.04	0.66	0.41

<sup>\*</sup> T. sat. = Total saturated fatty acids

T. di. = Total unsaturated fatty acids
T. di. = Total di-unsaturated fatty acids

T. tetra. = Total tetra-unsaturated fatty acids

T. hexa. = Total hexa-unsaturated fatty acids

Ks = T.unsat. / T. sat.

T. mono. = Total mono-unsaturated fatty acids

T. tri. = Total tri-unsaturated fatty acids

T. penis. = Total penta-unsaturated fatty acids

T. poly. = Total polyunsaturated fatty acids

<sup>\*\* =</sup> Immediately after smoking.

raw frozen herring oil. The abundant monounsaturated fatty acids were the oleic (C18.1, 18.38 %) and palmitoleic (C16.1, 10.64 %) while, the predominant polyunsaturated fatty acids were descendingly arranged as follow: docosahexaenoic (C22:6, 11.93 %), eicosapentaenoic (C20:5, 10.06 %), linoleic (C18:2, 7.06 %), arachidonic (C20:4, 2.82 %) and linolenic ( $C_1 \&_3$ , 2.14 %), respectively. It is evident that the abundant polyunsaturated fatty acids represented the essential fatty acids whereas, Friedman (1980), Linscheer and Vergroesen (1988) and Wolfram (1989) reported that the essential fatty acids can be defined as a group of naturally occurring unsaturated fatty acids with a chain length of 18, 20, or 22 carbon atoms and between 2-6 methyleneinterrupted double bounds. This indicates the health benefit of herring fish oil when herring fish flesh or/and its oil are consumed as it contains high amounts of essential fatty acids particularly eicosapentaenoic, docosahexaenoic and linolenic fatty acids which lead to increase the biological value of herring fish oil, in addition to the health benefits (Hamazaki et al., 1996; Kudo et al., 1997; Nair et al, 1997; Garcia, 1998 and Watkins et al, 2001). Moreover, concerning the raw frozen herring also, it could be observed (Table 6) that the total polyunsaturated fatty acids (including di-, tri-, tetra-, pent- and hexa-unsaturated fatty acids) was 34.01 % of total fatty acids. By adding the percent of the total monounsaturated fatty acids (29.02 %), the total unsaturated fatty acids will be recorded as 63.03 %. At the same time, the total saturated fatty acids were recorded 36.97 %. Accordingly, the Ks - which was obtained by dividing the total unsaturated fatty acids / the total saturated fatty

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acids - of the raw frozen herring was high (1.70) indicating the high percent of the total unsaturated fatty acids versus the low percent of saturated fatty acids. These results nearly went in parallel with those given by Kaitaranta and Linko (1979), Mai and Kensella (1979), Ziino et al (1992) and Kaneniwa et al (2000).

From the same Tables (3, 4, and 6), by smoking with different methods (immediately after smoking, zero time) including liquid, cold and hot smoking, it is evident that the smoking process affected the fatty acids composition as some fatty acids were decreased and others were increased. The more susceptible unsaturated fatty acid for liquid or cold smoking was the palmitoleic acid while, by hot smoking, linoleic, and palmitoleic were the most susceptible unsaturated fatty acids. The most sensitive saturated fatty acid overall the different smoking methods was recorded for palmitic acid. On the other hand, with respect to the essential fatty acids (linoleic, linolenic, arachidonic, eicosapentaenoic and docosahexaenoic acids), the percent of total essential fatty acids (immediately after smoking) were 32.06, 28.56, 25.65 % for herring smoked by liquid, cold and hot smoking, respectively corresponding 34.01 % for raw frozen herring. This indicated that all smoking methods affected the essential fatty acids content, nevertheless, according to the percent of total essential fatty acids in the smoked samples, the liquid-smoked herring was the best followed by cold- and hotsmoked herring. Accordingly, at zero time, higher biological value was recorded for liquid- than cold- and hot-smoked herring. The higher content of essential fatty acids recorded for

liquid- compared to cold- and hot-smoked herring may be due to less oxidation occurred under conditions of liquid smoking than that of cold and hot smoking, this is confirmed by the results of TBA in Table (1) and the results of oil constants in Table (2) immediately after smoking. Also, these results were confirmed by the finding of Table (6) which showed the fatty acids fractions (%) of raw herring as affected by smoking methods, as at zero time, the total saturated fatty acids (TSFAs) were increased while the total unsaturated fatty acids (TUFAs) were decreased overall the smoking methods provided that the level of oxidation (decreasing level of the total unsaturated fatty acids) for the liquid-smoked herring was lower than those of cold- and hot-smoked herring whereas, the TUFAs were 62.31, 60.49 and 51.80 % for liquid-, cold- and hot smoked herring, respectively corresponding 63.03 % for raw herring. Moreover, the Ks (TUFAs / TSFAs) was supported these results. The high the Ks, the high the TUFAs and the less the oxidation, therefore, the Ks values were 1.70, 1.65, 1.53 and 1.07 for raw herring, liquid-, cold- and hot-smoked herring, respectively. These results were supported by the findings of Ziino et a/. (1992), Benjakul and Tayler (1994) and Kaneniwa et al (2000).

By storage either at room temperature (25 °C) or at cold (4 °C), on the whole (Tables 3, 4 and 5), some saturated fatty acids were increased and others at the same time decreased and vice-versa. It is evident that the individual saturated fatty acids were not stable during storage periods may be due to the conversation of some fatty acids to another because of oxidation and/or hydrolysis occurred for fatty acids during storage.

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Concerning the unsaturated fatty acids (UFAs) durin storage, almost UFAs decreased due to oxidation provide that the decreasing rate (oxidation rate) was less when t e storage temperature was decreased from 25 °C to 4 °C. oreover, according to the smoking method and storage to perature, during storage either at 25 °C or at 4 °C, the cold-s oked fish showed lower oxidation than liquid-smoked one. The hotsmoked fish indicated more oxidation during storag (on the same time) as showed by the results of Table (5).

Anyway, the results of Table (6) were more illustrating and confirming for the results of Tables 3, 4, and 5. D ta of fatty acids fractions (Table 6) of smoked herring - as ected by storage conditions and smoking methods - indicated th t the total saturated fatty acids (TSFAs) were gradually increas • until the end of storage either at 25 °C or at 4 °C for all smok o herring either liquid-, cold- or hot-smoked samples. However, i could be observed that the increasing rate of TSFAs was low r at 4 °C than that at 25 °C. The reverse was recorded for the total unsaturated fatty acids (TUFAs) as, it was gradually • ecreased until the end of storage periods of all smoked s. pies. In addition, the decreasing rate of TUFAs was lower at compared with that at room temperature. The inc ent of TSFAs and the decrement of TUFAs may be ascrib • to the lipids oxidation occurred during storage periods but a different rates according to the conditions of storage. For ex pie, by storage at 25 °C, the TSFAs were increased from 37. 6, 39.51 and 48.20 % (at zero time) to reach 61.04, 54.67 and 72.60 % (after 30 days) for liquid-, cold- and hot-smo ed fish,

respectively. At the same time (30 days) of cold storage, the values were 44.42, 43.29 and 49.30 % for liquid-, cold- and hotsmoked fish compared with that recorded at zero time. On the other hand, concerning the TUFAs, it was decreased from 62.31, 60.49 and 51.80 % at zero time to record 38.96, 45.33 and 27.40 % at the end (30 days) of storage at room temperature for liquid-, cold- and hot-smoked fish, respectively. The values after 30 days of storage at cold were 55.60, 56.71 and 50.97 %, respectively. It is evident that during storage, the cold-smoked herring oil was more stable than that of liquid- smoked one as indicated by more lipid oxidation (higher and lower levels of TSFAs and TUFAs, respectively) for liquid- than cold-smoked herring. The hotsmoked herring showed progressive lipids oxidation either at zero time or during storage at room temperature and at cold. The values of TSFAs and TUFAs recorded for liquid-, cold- and hotsmoked herring stored for 60 days at 4 °C referred to less lipid oxidation than that stored for 30 days at room temperature being 46.80, 52.31; 45.35, 54.65 and 60.35, 39.65 % for smoked samples stored at 4 °C corresponding values were 61.04, 38.96; 54.67, 45.33 and 72.60, 27.40 % for those stored at room temperature for 30 days, respectively. This indicates that smoked herring may be stored with high quality at 4 °C for 60 days instead of that stored at room temperature for 30 days (lower quality). Moreover, from the same Table (6), it could be observed that the Ks value (TUFAs / TSFAs) confirmed the previous results and discussion. The higher the Ks, the lower the lipids oxidation. Therefore, it could be reported that according to the Ks value found in Table (6), the cold-smoked fish oil was more stable than those of lipid-and hot-smoked fish. Also, The RESULIS AND DISCUSSION

smoked herring oil stored at 4  $^{\circ}$ C was more stable than that stored at room temperature, as well as, all smoked samples stored at 4° C for 60 days were more stable for lipids oxidation than that stored at room temperature for 30 or 20 days with exception for hot-smoked fish which recorded progressive oxidation indicated by the lowest Ks value. For example, after 10, 20 and 30 days of storage at room temperature, the Ks recorded for lipid-, cold-and hot-smoked herring were 1.26, 0.84 and 0.64; 1.23, 0.99 and 0.83 and 0.88 respectively. The value after 15, 30, 60 and 90 days of storage at C for lipid-, cold- and hot-smoked herring were 1.30, 1.25, 1.12 and 1.08; 1.42, 1.31, 1.20 and 1.15 and 1.02, 1.0 0.66 and 0.41, respectively. Anyway, according to fatty acid fraction, smoking method and storage conditions, the co d-smoked herring was the best followed by liquid-smoked one then hotsmoked fish. However due to many reasons cone ming the health status the whole smoke as in cold and hot smoking method (polycyclic aromatic hydrocarbons) is considered as a disadvantage for smoking (Moghazy, 1994). Thereby the liquidsmoked herring stored at 4  $^{\circ}$ C for 60 days (more safe ) may be recommended. In addition, smoked herring by ditional methods should not be stored more than 20 days at room temperature. These results were confirmed by the nding of Goncharav and Khamadi(1979), Etman (1985), US A-FSIS (1996), Kaneniwa et al. (2000) and Aubourg (2001).

D-L'Wujinstiec:

Data found in Table (7) shows the lipid frac ions (by using thin layer chromatography as % of total lipids) f frozen

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Table(7): Lipid fractions(as % of total lipids) of frozen herring as affected by smoking methods and storage conditions.

				Storage t	 emperatu	re (°C) an	d period (	in day)	
Lipid *	Frozen	Zero**	Room ter	nperature			Cold stora		
fraction	herring	time	10	20	30	15	30	60	90
	(raw)			Lie	quid-smol	ked herrin	g		
1	56.11	54.31	50.53	47.43	42.51	52.42	51.25	49.30	46.25
2	18.60	20.51	18.01	15.32	11.85	19.35	18.20	16.22	14.03
3	2.53	2.69	5.82	8.90	10.35	4.19	6.98	8.05	10.65
4	4.66	5.92	6.89	7.99	9.80	6.43	7.03	7.61	8.46
5	8.98	6.89	5.60	5.01	4.20	6.00	5.05	5.22	4.73
6	5.02	5.25	7.93	10.75	14.62	6.78	7.91	9.55	11.23
7	1.70	1.70	1.41	-	-	1.61	-	-	-
8	2.40	2.73	3.81	4.60	6.67	3.20	3.58	4.05	4.65
				C	old-smok	ed herring	3		
1	56.11	53.77	50.75	47.98	41.54	52.99	50.88	48.48	45.58
2	18.60	20.45	17.76	14.97	11.85	19.47	18.55	17.10	15.57
3	2.53	2.85	5.33	7.02	8.58	3.99	5.67	6.78	8.77
4	4.66	4.44	6.84	6.99	6.78	6.26	6.76	6.74	6.88
5	8.98	6.76	5.39	4.89	3.93	5.79	4.97	4.49	4.26
6	5.02	5.56	7.54	9.88	12.98	6.68	7.52	8.95	8.37
7	1.70	1.58	-		-	1.63	-	-	-
8	2.40	4.59	6.39	8.29	14.34	3.19	5.65	7.46	10.57
					Hot-smok				
1	56.11	53.56	45.54	35.50	22.55	46.35	43.51	40.64	37.22
2	18.60	13.49	11.52	7.26	5.67	13.08	12.45	10.45	9.23
	2.53	2.95	6.22	9.45	11.59	7.15	7.78	8.56	12.65
	4.66	5.08	5.76	8.67	9.97	2.77	2.73	4.47	2.56
	8.98	14.94	15.56	15.66	19.74	17.30	17.56	18.50	18.63
	5.02	5.82	6.66	10.64	18.01	4.56	6.00	8.94	11.47
	1.70	-	-	-	-	-	-	-	-
	2.40	4.26	8.74	12.82	12.47	8.79	9.97	8.43	8.24

<sup>\* 1 =</sup> Triglycerides 2 = Phospholipids 3= Monoglycerides 4= Cholesterol

<sup>5 =</sup> Higlyeerides

<sup>6 =</sup> Free fatty acids 7 = Tocopherol 8 = Hydrocarbons

<sup>\*\*</sup> Immediately after smoking

herring (raw material used to obtain smoked herring) as affected by smoking method and storage conditions (storage at room temperature, 25 °C and cold, 4 °C).

From the results, it could be reported that the w frozen herring revealed eight fractions of lipids as *f flow: 1*) triglycerides (TG), 2) phospholipids (PL), 3) mono lyeerides (MG), 4) cholesterol (CL), 5) diglycerides (DG), 6) free fatty acids (FFA), 7) tocopherol (TO), and 8) hydrocarbons (HC). Raw frozen herring under this study recorded 56.11, 1 .60, 2.53, 4.66, 8.98, 5.02, 1.70, and 2.40 % (of total lipids) o TG, PL, MG, CL, DG, FFA, TO, and HC, respectively. It is e ident that the TG was the main fraction of lipid extracted from w frozen herring followed by PL, DG, FFA, CL, MG and HC, respectively. The lowest fraction of raw frozen he ng was recorded for TO (1.70 % of total lipids). Chanmug m et al. (1983), Hoelscher et a/. (1987) and Abd El-Aziz et al (1998) reported similar results of lipid fractions as a perce t of total lipids.

Concerning the smoked herring immediat ly after smoking process; the percent of MG, HC, FFA and C fractions were increased by using the different smoking methods either liquid, cold or hot smoking while at the same time, th TG was decreased. The lipid fractions which increased by us ng liquid smoking method were also increased by using cold sm king one and vice-versa. Therefore, the PL, MG, CL, FFA and HC fractions were increased while the DG and TG fractions were decreased either by liquid or cold smoking method. With respect to hot smoking, the reverse was recorded for PL and DG when

compared with those of liquid and cold smoking. Anyway, the increment of phospholipids and cholesterol fractions may be attributed to the partial breakdown of lipoproteins complex which is the main reason for this increasing (Aman et al. 1970) while, the decrement of phospholipids probably due to the partial oxidation of unsaturated fatty acids presented with high levels in almost phospholipids (Bell et al., 1996). Also, the increasing or decreasing of DG, the increasing of MG and the decreasing of TG as affected by smoking methods (as showed in Table 7, at zero time)may be due to some lipid oxidation and hydrolysis occurred during smoking process. On the other hand, according to the method of smoking and lipid fractions (especially MG and FFA) of smoked herring at zero time, it could be reported that the liquid-smoked herring had more stable oil (lower MG and FFA) followed by cold-smoked herring then hot-smoked one. Moreover, the TG fraction was higher for liquid- than that for cold- and hot-smoked herring indicating less hydrolysis of liquid-smoked herring than other smoked samples. With respect of TO fraction at zero time, it could be observed that either by liquid or cold smoking, the TO fraction was nearly constant while, it was absent by hot smoking possibly due to higher smoking temperature used in hot smoking. The results of smoked herring (at zero time) may be due to the effect of the different smoking conditions as, the liquid smoking characterized with the following: short smoking time (100 minuets), fast penetration for smoke compounds into fish beside lower (60 °C) smoking temperature than that of hot smoking. Concerning the cold smoking, it needs too long (8-10 hr.) smoking time to obtain cold-smoked fish while, hot smoking apply higher (70 °C) RESULTS AND DISCUSSION

smoking temperature to achieve the processing. These results were supported by the findings of Rhee and Smith (1983), Chanmugam *et al.* (1983) and Wally (2002).

During storage of smoked herring, it could be noticed that the PL and TG fractions decreased by increasing the storage period either at 25 °C or at 4 °C for all the smoked herring included liquid-, cold- and hot-smoked samples. This may be ascribed to the oxidation of unsaturated fatty acids found in PL (Bell et al., 1996) and the lipid hydrolysis (Abd EL-Aziz, et al.,1998), respectively. Concerning the DG fraction, it was decreased by liquid and cold smoking as well as by storage, while increased by hot smoking as well as during storage (at 25 °C and 4 °C). The MG, CL, FFA and HC fractions of all the smoked herring (with exception for CL and HC fractions recorded for hot-smoked samples stored at 4 °C) stored at 25 °C and 4 °C, were increased by increasing of storage times. As mentioned before, the TO fraction was also absent during storage of hot-smoked fish. The TO fraction of liquid-smoked fish was higher (1.70 %) than that of cold (1.58 %) smoked one at zero time. TO fraction of liquid-smoked fish was only found up to the 10<sup>th</sup> day of storage at 25 °C and up to the 15<sup>th</sup> day of storage at 4 °C while it was absent in cold-smoked fish during storage for more than 15 days at 25 °C. It is evident that any increases or a decrease of the previous fractions was less by the storage at 4 °C than at 25 °C. For example, after 10, 20 and 30 days of storage at <sup>25</sup> °C, liquid-smoked herring recorded 18.01, 15.32 and 11.85; 5.82, 8.90 and 10.35; 6.89, 7.99 and 9.80; 5.60, 5.01 and 4.20; 7.93, 10.75 and 14.62; 1.41, 0.00 and 0.00; 50.53, 47.43 and

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42.51 and 3.81, 4.60 and 6.67 % for PL, MG, CL, DG, FFA, TO, TG and HC, respectively. The values recorded at 15, 30, 60 and 90 days of storage at 4 °C were 19.35, 18.20, 16.22 and 14.03; 4.19, 6.98, 8.05 and 10.65; 6.43, 7.03,7.61 and 8.46; 6.00 5.05, 5.22 and 4.73; 6.78, 7.91, 9.55 and 11.23; 1.61, 0.00, 0.00 and 0.00; 52.42, 51.25, 49.30 and 46.25 and 3.20, 3.58, 4.05 and 4.65, respectively. Anyway, during storage, the results of lipid fractions found in Table (7) particularly of MG, FFA and PL fractions may indicate a trend of more stability of lipids extracted from cold-smoked herring followed by liquid-smoked herring then hot-smoked samples which recorded the lowest stable lipids during storage. These results and discussion were in parallel and confirmed by the findings of Bell *et all* (1996), USDA-FSIS (1996) and Abd EL-Aziz, *et al.* (1998).

## **E**\_**Phospholipid** fractions:

Phospholipid fractions - including phosphatidyl serine (PS), Lysophosphatidyl choline (LPC), sphingomyeline (S), phosphatidyl choline (PC), phosphatidyl inositol (PI), phosphatidyl ethanolamine (PE), phosphatidic acid + glyceryl phosphatides (PAG), Plasmalogenes +cardio lipids (P) and glycolipids (G), as % of total phospholipids - of raw frozen herring as affected by smoking methods and storage conditions are presented in Table (8).

From the results found in Table (8), it could be observed that the phospholipid fractions of raw frozen herring were 3.39, 2.27, 10.55, 35.57, 2.77, 27.61, 10.56, 5.32 and 1.96 % for PS, LPC, S, PC, PI, PE, PAG, P and G, respectively. Therefore, it is

Table(8): Phospholipid fractions(as % of total phospholipids) of frozen herring as affected by smoking methods and storage conditions.

		7		Storage t	emperatu	ıre (°C) a	nd period	d (in day)	
Phospholipid	Frozen	Zero* time *	te	mperature	e (25 °C)		Cold stora	age (4 °C	)
fraction*	herring (raw)	time *	10	20	30	15	30	60	90
	(law)			Lie	quid-smo	ked herri	ng		
1	3.39	6.34	8.10	9.05	-	6.75	6.86	8.49	8.58
2	2.27	4.15	6.88	10.12	14.51	5.87	6.85	8.70	10.45
3	10.55	10.42	11.91	8.59	7.75	11.43	9.46	8.54	8.70
4	35.57	25.65	20.64	13.25	10.72	21.51	18.04	14.61	10.44
5	2.77	2.25	3.61	5.36	6.46	3.56	4.50	4.79	6.10
6	27.61	21.74	15.86	10.10	7.30	19.54	16.59	12.56	10.33
7	10.56	15.78	19.96	28.70	31.08	20.07	23.46	24.22	25.01
8	5.32	8.99	8.11	9.47	11.41	6.41	7.46	8.06	8.92
9	1.96	4.68	4.93	5.36	10.74	4.86	6.78	10.03	11.47
			•	C	old-smok	ed herrin	g	•	
1	3.39	5.49	3.73	6.43	8.43	5.67	6.51	6.92	8.47
2	2.27	4.38	3.4.3	5.73	8.15	4.62	4.39	5.50	6.57
3	10.55	7.82	7.40	7.35	6.38	7.57	7.37	6.98	10.41
4	35.57	29.50	24.63	17.49	10.06	25.45	22.33	15.07	11.40
5	2.77	2.58	2.39	3.70	5.39	3.71	4.22	4.70	6.80
6	27.61	23.08	20.40	16.73	10.52	22.07	20.51	19.46	11.33
7	10.56	15.32	23.90	27.41	33.11	18.65	21.79	26.61	28.76
8	5.32	6.40	7.8:5	8.84	11.05	6.16	7.06	7.85	8.75
9	1.96	5.43	6.26	6.31	6.91	6.10	5.82	6.91	7.51
				I	lot-smok	ed herring	g		
1	3.39	7.18	9.18	7.27	10.89	7.28	8.77	9.84	12.55
2	2.27	5.16	6.60	7.44	8.73	5.75	5.03	6.20	9.21
3	10.55	9.80	8.61	7.10	6.14	9.52	7.76	8.41	11.52
4	35.57	22.58	19.39	14.05	9.06	20.27	18.98	9.84	7.54
5	2.77	3.58	3.73	5.07	6.72	2.56	3.81	5.66	5.56
6	27.61	24.98	18.37	16.54	11.53	25.46	19.56	15.52	10.00
7	10.56	18.39	24.41	31.51	32.39	19.54	26.21	30.34	31.38
8	5.32	6.33	6.64	7.28	10.60	6.20	6.39	9.45	7.29
9	1.96	2.00	3.07	3.74	3.94	3.42	3.49	4.74	4.95

<sup>1 =</sup> Phosphatidyl serinc

<sup>3 =</sup> Sphingomycline

<sup>5 =</sup> phosphatidyl inositol

<sup>7 =</sup> Phosphatidic acid + glyreryl phosphatidcs

<sup>9 =</sup> Glycolipids

<sup>\*\*</sup> Immediately after smoking

<sup>2 =</sup> Lysophosphatidyl cholinc

<sup>4 =</sup> Phosphatidyl choline 6 = phosphatidyl ethanolamine

<sup>8 =</sup> Plasmalogenes + cardio lipids

evident that the greatest fraction (35.57 %) was recorded for PC followed by PE (27.61 %). This was in accordance with the finding of **Maurice (1990)** who reported that among the various phospholipids which may occur in fish, PC occur to the greatest extent, with PE being the second most common class. Nearly similar percent was found in raw fish for PS, LPC and PI being 3.39, 2.27 and 2.77 %, respectively. The lowest (1.96 %) amount was recorded for the G fraction.

By smoking of herring, immediately after smoking (zero time), the PS, LPC, PAG, P and G fractions increased while S, PC and PE fractions decreased overall the smoked samples included the liquid-, cold- and hot-smoked herring, but the PI fraction increased by using the hot smoking and decreased by using the liquid and cold smoking. According to the PC and PE fractions as major fractions of phospholipids, the cold-smoked herring seems to be the better than other smoked herring. Liquid-, cold- and hot-smoked herring recorded 15.78, 15.32 and 18.39 (% of total phospholipids) for PAG fraction, respectively. This possibly indicated that hydrolysis of phospholipids was more in hot-smoked samples than that of cold and liquid-smoked herring which nearly had similar values of PAG (15.78 and 15.32 %). On the whole, regardless of PE and G fractions, the higher the percent of phospholipids fractions before smoking, the higher the percent of phospholipids fractions after smoking.

The effects of storage (at 25 °C and at 4 °C) on the phospholipid fractions of smoked herring were also presented in Table (8). From the results, the changes rate of phospholipid fractions was higher in smoked herring stored at room

temperature than that stored at cold. It is clear that the PC and PE fractions were gradually decreased during storage periods but, as mentioned before with higher decreasing rate at 25 °C than that at 4 °C. The decrease of PE and PC during storage may be due to the oxidation of unsaturated fatty acids found in PC and PE (Dawson et aL, 1990 and Bell et al., 1996). Also, some phospholipid fractions were increased during stora e probably due to conversion to others by hydrolysis or/an oxidation during storage periods. In addition, PAG fracti n may be considered an indicator for hydrolysis of the other ph spholipids as the PAG gradually increased during storage p riods. On whole, smoked samples stored at 4 °C was recorded ore stable phospholipids than that stored at room temperature. Generally, liquid-smoked herring is the nearest to be preferred due to many reasons (as mentioned above) followed by cold-smo ed herring then, hot-smoked samples. Similar results of Seg wa (1994), Bell et al. (1996), Abd EL-Aziz et al. (1998) nd Wally (2002) confirmed the previous results (Table 8) and di cussion. F- Fat-soluble vitamins:

Data of Fat-soluble vitamins (as microgram. / g oil) included A, E and K of frozen herring (raw material) affected by smoking methods and storage conditions are give in Table (9). From the results, it could be observed that the fron herring was contained 840.64, 159.71 and 46.34 (i.tg/g oil) o A, E and K vitamins, respectively. Immediately after smoking either by liquid-, cold- or hot-smoking, all the vitamins (A, E K) were decreased but, the vitamins loss was higher of h t-smoked herring than that of liquid-and cold-smoked herring. e latter

RESULTS AND DISCUSSION .....

Table(9): Fat-soluble vitamins (µg/g oil) of frozen herring (raw) as affected by smoking methods and storage conditions.

E o o o o o o o o o o o o o o o o o o o				Storage 1	temperatu	Storage temperature (C) and period (m day)	in perion	(mn mm)	
itamins time it of the item its item it	N L	4: O N	c:4	E	± Z °C)		Cold stor:	Cold storage (4 C)	
tamins  itamins  itam	-				1000		(	0.7	C7
eu 63Z 21 593.91  No o o o o o o o o o o o o o o o o o o	5 -			O N	O en	15	o en	00	
eu 63Z 21 Se 3.91	L.			-	I janid-smoked herring	ked herri	ng		
eu CN					,,,,,,	LC KO	O C e ki	Nt N	219.45
00 ON en ON	, c	6227	-	ti 00 en	176.61	17 ::90	- 1	t	
0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0		100	+	+	1	Cr\	00 N	<b>2</b> 0 <b>z</b>	34.07
Soft Signature of the state of	N	17 <u>X</u>	οz	1	,	1.7.7.6	re 0 ti N	C7'	24.31
en 099 600 N ort en CN en en CN en C	N.	36 7	-	C7\ 00 r.*	1082	50.4	o 0 rj	- 81	
en 099 600 N 000 17.0 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	[		+		5	*r.	b <i>I</i>		
en 090 00 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0						000	0 r	00000	341.89
2000 CN 71. TO 100 CN 900 En CN 900 C		1	067	1-0	r-1 1• 00 en N	590 80	_  0 N n	r. OO:r	200
19.600 en en en St. 17.000 En		1	OZO		0 e	r	*= *	N OD N If)	N N
CN en en en 840.08  tr) 17651  Tr ws ws 000  17651	СТ			.0 •	n 0	J !	) o c	N N	oN er
2 ort en 61 oo 12651	+	-T	er	en 00 <b>N</b>	Ntr. 61	42.6	0	- 1	1
840.64 kg, 49.19 Z ort en 61 % S Z V 00 159.71	6		וו		5 .H		tor)		
840.64 kg, 19.07 Z out eu	di	r)			1	17 V	er	**I• N N	00 N N r-1 i-4
(71. ΣS Σ 00 17.6\$1	840 (	kf)	ort en	70 0 1-4 <b>N</b>	1.	- 1	1	\$:	If
7	010	0	╁	00 er	•	<b>0</b> 00		47.C4	
	159.	0	+			71 Ci	N © N	14.2	1Z
0 2 7	46.3	<b>4</b>	N N O	n*					

Immediately after smoking

one recorded the lowest 1088 of vitamins either A, E, or K. This is possibly due to the effect of smoking temperat which is lower in cold smoking (30 °C) followed by liquid (60 C) and hot smoking (70 °C). By storage (either at room tempera re or at 4 °C) of smoked herring samples, a marked decreasing of vitamins was observed however, the decreasing rate was muc higher in smoked samples stored at room temperature comp d to that stored at cold storage. Concerning the storage at room temperature, by the end of storage (30days), vitamin E was completely absent in liquid-smoked herring while vitamins E and K were not detected in hot-smoked herring but, all vit ins were detected in cold-smoked one. On the whole, according to the vitamins content

and smoking method, the descending order was as follow: cold-, liquid- and hot-smoked herring fish. Moreover, cold storage is better than storage at room temperature of II smoked samples concerning the fat-soluble vitamins. These results were confirmed by the findings of Stepanova et al. (198 Muggli (1994) and Valk and Hornstra (2000) confirmed thes results. G-Statistical analysis:

## 1-Oil constants:

Data presented in Tables (10 and 11) show the . alyses of variance for oil constants of frozen herring as a ected by smoked method and storage at room temperature (25 °  $\pm$  2 °C) for 30 days and at 4 °C for 90 days, respectively. Form the results found in Table (10), the analysis indicated that the differences between smoking methods (liquid, cold and hot smoking) were significant (p < 0.05) for all the oil constants

			_	F values for Oil constants••	constants••		
		III	AV	Vdd	Ad	AS	NI
Replication	Z	0.78 NS	SN IWO	0.04 NS	0.49 NS	1.77 NS	* 8C9
t	Z	* L8'0S	6CL1	* Z0'11	25.70 *	400.25 *	
0	М	Pofta8	708.54 *	* 81'169	2742.50 *	*179'6LZ	IRTL81
gx V	٠.0	3.47 NS	•	*9S'17	754.75 *	142.80 *	£Z111
Error	ZZ						
Total	SE						
on 0	o =	•	E				
c¹ 4" W	IIttg1	Ti.sr s;ma ½4r=					
* = signiticant(P<0.05)	(50.05)	NS = non sign	NS = non significant (P>0.05)				

**RESULTS AND DISCUSSION -**

	· •			F values for Oil constants••	constants.		
aaJnos	ö	U	AV	V3.3	Ad	AS	M
Replication	N	0.78 NS	0.01 NS	0.04 NS	0.49 NS	SMLLI	* 81:9
Q	NI	L8'09	*6CLI	*ZO'171	• OCSZ	* SZTOP	60*Si,
Oa	м	*C1778	708.54 *	* 81169	2742.50 *	*179't5LZ	TIT ~
χV		3.47 NS	S£'17	[*9S 17	754.75 *	(Kati	
Error	ZZ						
Total	SC						
. A = emoling method	thod	R = ctorage ner	B = storage periods of room temperature	arratura			

B = storage periods at room temperature A= smoking method

AV = Acid value(mg KoH/gm oil)
 FFA = Free fatty acids/%, as oleic)
 PV = Peroxide value(meq /kg oil
 PV = Peroxide value(meq /kg oil
 SV = Saponification value per gm of oil).

IN = Iodine number.

NS = non significant (P>0.05) = significant(P<0.05)

				F value for oil constants••	constants••		
.aainos	Ÿ		AV	vu	Ad	AS	Z
Replication		2.15 NS	09.00 NSI	SN	1.25 NS	SN	SN 8E11
		3.76 NS	* tt'ZI	* gni	2328.30 *	* 00 0Z	2554.20 *
		*L0*8	163.53 *i	* r6Tt I	5045.80 *	* 98*01	*0P'S£S1
Elxv	00	*11',1	1.12 NS	1.00 NS	* 08TIZ	SN 961	354.76 *
Error	Z8						
Total	rt						
• A= smoking method	pou	B = storage per	B = storage periods at room temperature	perature			

RI = Refractive index.

AV = Acid value(mg KoH/gm oil)

FFA = Free fatty acids(%, as oleic)

PV = Peroxide value(meq /kg oil .

SV = Saponification value per gm of oil).

IN = Iodine number.

= significant(P<0.05) NS = non significant (P>0.05)

including RI, AV, FFA, PV, SV and IN. Also, the differences between the storage periods at room temperature we significant (p<0.05) for all the oil constants. On the other hand, the interaction between the smoking method and the storage periods at room temperature was significant (p<0.05) for all q constants but with exception of the refractive index (RI) Which was recorded non-significant (p>0.05) differences from data in Table (11), the analysis showed that the differences between smoking method applied under this study were significant (p<0.05) for all the parameters used in measuring the quality attributes of fish oil but regardless the RI which had non-significan (p>0.05) difference. Concerning the differences between e storage periods at cold (4 °C), it was significant (p<0.05) for all oil constants. The interaction between the smoking meth d and the cold-storage periods was significant (p<0.05) for RI, and IN. and non-significant (p>0.05) for AV and FFA.

#### 2- lipid and phospholipid fractions:

The analysis of variances for lipid and ph spholipid fractions of frozen herring as affected by smoking methods (liquid, cold and hot smoking) and storage (either at room temperature for 30 days or at cold for 90 days) are presented in Tables (12, 13, 14 and 15).

Concerning the lipid fraction of herring fish as affected by smoking method and storage at room temperature (Table 12), the analysis or variance indicated that the difference between the smoking methods were significant (p<0.05) for all the lipid fractions. Also, the storage periods at room temperatur recorded the same trend of smoking methods. As well as, the i tractions

ŗ	91.			Ш	valuefor lip	F valuefor lipid fractions••	:		
Factors•	Ð	1	2	м		if	s0	ţe-e	OD
Replication	2	OVO NS	SN 09'0	0.90 NS	* 01'61	3.20 NS	SN CO'0	SNZ	* OC'01
-*L	N	08'96171	* 09'601	* OLTS	ZI'6C	* 0179LZ	* P111'	* 01'9L1	92.50 *
8	en	2390.50 *	OVLSL	Or689	142.72 *	* 06'6	ж-	* 091•CZ	* 017T6
11x V	vc	# OS'66Z	3.80 NS	0111	* 09'91	* Or6S	* 0C 91	170t6	ZO"ZI
Error	ZZ								
Total	SC								

 NS = non significant(P>0.05).

= signifieant(P<0.05).

B = storage periods at room temp.

A= smoking method.

RESULTS AND DISCUSSION

901				L L	value for li	Fvalue for lipidfractions••			
		,•i	4 <b>~</b> 4	4 <sup>0</sup> 1	•er	cfl	NC)	I	00
Replication	4 <b>*</b> 1	0.70 NS	*011	SN 08'E	SN	091'	* 09,	1.80 NS	3.80 NS
,4 <b>t</b>	CM	* ors9	* Or8L01	* OFZI1	* 0VZ69	* 06'09ZZ	* 0L'6Z	* LZ*61 Z	* 06'15
со	• 1.	53030 *	* 011ZZ	473.30 *	* 09'1E	SW. OL'I	438.90 *	373.67 *	* 09'SI
\x\{	со	* 08T1 1	3.30 NS	* OS'ZI	* 6675	* II'81	6E'SE	OLT6	* 01'L
Error	8Z								
Total	rr								

1 = Triglycerides 2 = Phospholipids 3 = Monoglycerides 4 = Cholesterol

Diglycerides Free fatty acids Tocopherol Hydrocarbons

**B** = cold storage periods • = significant(P<O.

A= smoking methods

NS = non signific nt(P>0.05).

RESULTS AND DISCUSSION

3	•				F values for p	F values for phospholipid fractions••	fractions.			
Source.	5		N	ні	el	In	v:	N-	00	ON
Replication	N	*Sr',	2.62 NS	*L1737	3.26 NS	2.43 NS	SN 9r0	0.03 NS	2.95 NS	f6'9
'It	N	398.85 *	* 0rZ9Z	* 08791	286.30 *	* Z0'SZ	* 6S'S6Z	,4 176'6S	ZO'88	*
1:0	NI	*£1 17	435.31 *	* 8P'SZI	* 89780Z	L17'8ZI	* £8'5110I	17£'£011	237.07 *	SN 967
RxV	VD	ZrL91	64.03 *	SSIZ	56'9Z	ZST	,19'1Z	*	* LS'8	« <del>9</del> 517
Error	ZZ									
Total	sc									
>, o :Es o que en	1	1 3 g	) 0, ice	7. 7in 600 000 000 000 000 000 000 000 000 00	5 2 Es, -\alpha 5.7. 7 in o v: t; I o o o o o F, 8 ir	spidiosylp = 6  6. = 4  7 = 4  5 2 Es,	colipids			
BINOILS LV	collogs		<b>a</b> -scolage perious	- significant	.(٢ / ٥.02).	5 }	<u>.</u>	٥		

3000					F values for p	phospholipid	F values for phospholipid fractions—			
Sources		. 1	tql	e.3	"er	en	o	n	00	en
Replication	01	* Or17	SN 01'0	<b>SN</b> 987	SNSCZ	3.37 NS	SN 8E 0	SNL17'0	SN55'0	£8'1I
'4	1*1	4 08'0E1	* 09'9L	16*0L	* 61T16	SN 65'0	394.23 *	* 11151	*	47.75 *
co	Ί,	4 09'001	817' 011	* L0'9f	*LI'5861 *L0'9f	* f0'56	95.0J * 2352.68 *	* ZOTIS	* 86'8t7	48.77 *
fixV	00	* OT8	* 9071	* Z£'17Z	zros	9r9	MIL	* 5r9Z	08171	* 15'6
Error	8Z									
Total	4									
6 o o·	o, C		1 1-1	= Lysopho	Lysophosphatidyl choline		9 = Glycolipids			
g t, E	g t,		7	- Phospha	Phosphatidyl choline		-			
o s' ci II		-75	SO.	I	phosphatidyl ethanolamine	mine				
0. I	+ : <b>•</b> F, El	0	is	It	Plasmalogenes + cardio lipids	io lipids				
	0	B = storage periods		* = significant(P<0.05)	(P<0.05)	NS = non	NS = nonsignificant (P>0 05)	0.05)		

RESULTS AND DISCUSSION -----

between the smoking methods and storage periods were significant (p<0.05) for all lipid fractions with exception for phospholipids fraction which recorded non-significant (p>0.05) differences. On the other hand, concerning the lipid fractions of frozen herring as affected by smoking method and storage at 4 C (Table 13), the analysis or variance showed that there was significant (p<0.05) differences between the smoking methods for all lipid fractions. Also, there was significant (p<0.05) differences between the cold storage periods for all the lipid fractions with exception for diglycerides fraction (nonsignificant (p>0.05)). The interaction between smoking methods and cold storage periods were recorded the same trend of smoking methods regardless of phospholipids fraction -non significant (p>0.05) differences. With respect of phospholipid fractions of herring fish as affected by smoking methods and storage at room temperature (Table 14), the analysis or variance showed that the differences were significant (p<0.05) over all factors for all phospholipids fractions but it was only non significant (p>0.05) for glycolipids fraction concerning the differences between the storage periods. Regarding of phospholipid fractions of herring fish smoked by the same conditions but stored at 4 °C (Table 15), analysis or variance indicated the same trend of table (14) but the exception was recorded for phosphatidyl inositol fraction (non-significant (p>0.05) differences ).

# **H- Cooking offish:**

## **A- Chemical properties:**

Data of chemical properties (moisture, fat, TBA and pH) of some fish (including Nile bolti, aquaculture bolti and marine bouri fish) as affected by some cooking method (frying, grilling and roasting) are presented in Table (16).

Form the results, it could be indicated that the fresh Nile bolti (FNB), fresh aquaculture bolti (FAB) and fresh marine bouri (FMB) fish recorded 79.30, 80.61, and 77.57 % for moisture; 1.85, 2.85 and 5.41 % for fat; 0.13, 0.15 and 0.12 for TBA (thiobarbituric acid as mg malonaldehyde/kg sample) and 6.30, 6.21 and 6.15 for pH, respectively (on wet weight basis, W.W.). The values on dry weight basis (D.W) were 8.88, 14.35 and 24.14 % of fat and 0.62, 0.77 and 0.94 of TBA respectively. Consequently, the FMB recorded the lower moisture and the higher fat contents when compared with FAB or FNB. The lowest (1.85 %) fat content was recorded for the FNB while the highest (5.41 %) was reported for the FMB, the fat content of the FAB was in between (2.85 %). With exception of the FAB, when the FNB compared to the FMB, it could be observed that the higher the fat content the lower the moisture content. With respect of thiobarbituric acid (TBA), it could be noticed that on W.W. and D.W., the FMB had lower (0.12 and 0.53) TBA followed by FNB (0.13 and 0.62) and FAB (0.15 and 0.77), respectively. It is evident that the higher freshness was recorded for FMB followed by FNB then FAB resp. According s the pH value, the descending order of fresh fish was as foil i w: FNB (6.30), FAB (6.21) then FMB (6.15), respectively.

RESULTS AND DISCUSSION -

1 able(16): Chemical properties and oil constants of some fresh fish as affected by some cooking methods.

										1			
ri.:v	ıī		Nile bol	lti fish		Aqu	aculture	bolti fis	sh	M	larine bo	ouri fish	
E	4	Fresh	Fried	Grilled -whole	Roast	Fresh	Fried	Grilled -whole	Roast	Fresh	Fried	Grilled -whole	Roast
% e		79.30	65.17	70.64	65.71	80.61	67.50	68.51	66.91	77.57	57.79	63.53	67.58
Moisture	DW												
70	ww	1.85	6.94	1.31	1.26	2.85	6.00	3.68	2.79	5.41	9.74	5.10	4.27
Fat Vo	<u>wd</u>	8.88	19.12	4.45	3.68	14.35	18.47	11.67	8.42	24.14	23.06	13.98	13.07
1	ww	0.13	0.53	0.41	0.21	0.15	0.53	0.48	0.31	0.12	0.73	0.59	0.33
	<u>DW</u>	0.62	1.52	1.40	0.69	0.77	1.64	1.54	0.94	0.53	1.73	1.63	1.02
P1		6.30	6.02	6.18	6.23	6.21	5.88	5.97	6.15	6.15	5.75	5.83	5.95
						0	il consta	nts					
R.	[	1.4677	1.4667	1.4668	1.4672	1.4651	1.4645	1.4648	1.4650	1.4681	1.4660	1.4670	1.4675
A	V	1.58	1.83	1.69	1.63	1.72	1.99	1.83	1.79	1.44	1.64	1.53	1.48
FI	FA	0.79	0.90	0.85	0.83	0.85	0.99	0.92	0.90	0.74	0.82	0.77	0.74
Р	V	4.72	17.17	7.86	6.86	5.73	19.75	9.46	8.85	3.79	16.36	7.63	5.95
S	V	186.72	201.15	190.87	187.55	188.26	203.44	193.46	189.86	186.64	199.75	189.44	186.42
II	N	128.76	121.55	125.26	126.74	121.43	113.28	118.52	119.80	133.24	125.52	130.59	131.65

<sup>\*</sup>TI3A = Thiobarbituric acid(mg malonaldehydelkg).

RI = Refractive index.

AV = Acid value(mg KoII/g oil).

FFA = Free fatty acids(%, as oleic).

PV = Peroxide value(meq /kg oil).

SV = Saponification value per g of oil.

IN = Iodine number.

The different cooking methods including frying, grilling and roasting decreased the moisture content of cooked fish either Nile bolti, or marine bouri. With exception of roasted aquaculture bolti fish, the roasted or grilled fish showed higher moisture contents than that of fried fish. Also, it could be observed that the fat content (W.W. or D.W.) was increased by frying while it was decreased by grilling or roasting for all the cooked under this study. This might be due to loss of some fat by melting and dripping occurred by grilling and roasting of fish. Concerning the TBA value, it could be illustrated that the TBA value were increased by all the three cooking methods used in this work indicating lipids oxidation occurred by cooking processes. However, oxidation level (as shown by TBA value) was varied according to the applied cooking method. Roasting of fish recorded the lower (0.12-0.33) TBA value followed by grilling (0.14-0.59) then frying which recorded the highest (0.53-0.73 mg MA/KG sample) TBA values (on W.W.). The same trend was observed on dry weight basis. Consequently, the fish oil is more stable by roasting than grilling and frying of fish. On the other hand, the lowest TBA values were recorded for Nile bolti, whatever the cooking method used. It is evident that the lower the fat content the lower the TBA value and vice versa. Fried, grilled and roasted samples had fat contents of 6.94, 1.13 and 1.26; 6.00, 3.68 and 2.79 and 9.74, 5.10 and 4.27 % (W.W.) and TBA value of 0.53, 0.41 and 0.12; 0.53, 0.48 and 0.31 and 0.73, 0.59 and 0.33 mg malonaldehyde/kg sample (W.W.) of Nile bolti, aquaculture bolti and marine bouri fish, respectively. With regarding to pH value, all the cooking methods reduced the

pH value, but provided that the decreasing rate of pH was lower for roasted fish than grilled and fried one, respectively, possibly due to lower level of lipid oxidation and hydrolysis occurred by roasting when compared to grilling and frying of fish, since the compounds obtained by oxidation and hydrolysis particularly free fatty acids decreases the pH value. These results were confirmed and supported by the findings of **Zaitseve** *et al.* (1969), **Mai and Kinsella** (1981), **Moghazy** *et al.* (1996) and wally (2002).

#### **B-Oil** constants:

Results of refractive index (RI), acid value (AV), free fatty acids (FFA), peroxide value (PV), saponification value (SV) and iodine number (IN) as limiting factors for the quality attributes of fish oil are presented in the same Table (16). It could be reported that the fresh marine bouri (FMB) had higher (1.4681) RI when compared with the fresh Nile bolti (FNB, 1.4677) and aquaculture bolti (FAB, 1.4651) fish, respectively. This may be because FMB contains higher amount of unsaturated fatty acids than those of FNB and FAB. Maurice (1990) reported that the higher the unsaturated fatty acids, the higher the RI. However, although the FMB had higher fat content (5.41 %) than that recorded for FAB (2.85 %) and FNB (1.85 %), the FMB recorded lower AV, FFA, PV and SV (1.44, 0.74, 3.79 and 184.64, respectively) followed by FNB (1.58, 0.79, 4.72 and 186.78, respectively) and FAB (1.72, 0.85, 5.73 and 188.26, respectively). This means that the degree of freshness was higher for FMB than FNB then FAB which recorded the lowest degree of freshness. Concerning the IN as an

indicator for the degree of unsaturation, the FMB had higher (133.24) IN when compared with FNB (128.76) and FAB (121.43) indicating that FMB is contained higher amount of unsaturated fatty acids followed by FNB and FAB, respectively. On the other hand, all the cooking methods (flying, grilling and roasting) affected the oil constants of the three 'fish species whereas the RI and IN decreased while the AV, FFA and SV increased, this possible due to the lipid oxidation (indicated by increasing the PV and SV; and decreasing the RI and IN) and the lipid hydrolysis (as indicated by increasing the FFA and AV) of fish oil. However, the oxidation or/and hydrolysis levels of lipids were lower for roasted-fish samples than grilled one, then fried fish samples which recorded the highest level of oxidation and hydrolysis. On the whole, it is clear that the best cooked samples were nearly the roasted and grilled marine bouri fcllowed the roasted and grilled Nile bolti the the roaste d grilled aquaculture bolti, respectively. The lowest quality attributes recorded for fried aquaculture bolti, fried Nile bolti and fried marine bouri, respectively (ascendinglly). These results were in parallel and confirmed by similar results given by Albid EI-Aziz et al. (1998) and Wally (2002).

## C- Fattp acids comnosition and fractions:

Results of fatty acids composition and fraction (as % of total fatty acids) of Nile and aquaculture bolti and m me bouri fish as affected by some cooking methods including fryin grilling and roasting are found in Table (17).

Concerning the fresh fish, from the results
Table (17), it could be observed that the abundant fatty acids in

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Table(17): Fatty acids composition (F.A.C) and fractions (as % of total fatty acids) of some fresh fish as affected by some cooking methods.

Fatty		Nile bo	lti fish		Aqu	acultur	e bolti f	ish	N	larine b	ouri fish	1
acids	Fresh	Fried	<b>Z</b> ::	Roast	Fresh	Fried	caned	Roast	Fresh	Fried	Gw <b>t</b> ei	Roast
C10,0	1.10	-	-	-	0.71	-	1.23	0.87		0.32	0.47	
C12:0	0.50	-	-	0.20	0.94	0.28	0.22	0.44		0.16	0.20	0.01
C140	3.53	7.13	3.62	2.04	10.45	4.40	7.45	3.50	4.76	10.25	10.96	5.25
C16:0	1.10	0.70	0.26	0.45	0.63	0.28	0.58	0.44	0.36	2.18	1.26	0.86
C16:0	16.43	28.61	20.32	20.32	10.42	27.84	28.51	23.64	14.68	23.16	12.62	12.53
C160	19.77	12.25	9.43	4.77	11.53	4.58	9.41	8.31	16.55	15.42	10.62	17.11
C17,0	1.01	0.03	0.05	0.03	0.33	-	0.14	0.03	0.81	0.97	1.26	0.52
018:0	5.05	6.12	11.62	10.81	7.87	2.91	4.70	9.59	2.51	1.94	2.99	11.56
C18;1	7.68	21.22	18.76	22.01	20.29	27.74	21.49	24.64	16.30	12.92	15.07	15.97
C18:2	14.22	10.54	15.60	15.81	18.60	17.06	20.65	22.19	16.84	19.44	16.58	12.44
C18:3	1.25	1.78	0.26	3.70	0.87	0.28	0.36	0.55	0.18	0.32	0.53	3.34
C20:0	4.12	4.82	3.10	4.30	3.30	13.12	2.46	2.40	1.97	7.11	8.52	2.16
C20:4	5.41	1.30	1.26	3.41	1.63	0.19	0.98	0.98	2.45	2.18	4.13	4.32
C20 <sub>:5</sub>	4.21	1.80	3.21	3.80	1.31	0.19	0.51	1.11	7.41	0.48	4.91	4.33
Съ	1.34	0.40	6.71	3.61	4.21	1.12	1.31	1.31	5.21	-	5.29	3.21
C22:t	7.34	1.87	3.29	3.49	5.20	•	1	-	2.91	0.97	2.11	2.11
C22:6	5.34	1.43	2.24	1.25	•	•	1	-	6.49	2.18	1.44	4.28
024.0	0.60	•	0.27	•	1.71	0.01	ı	-	0.57	•	1.04	•
					Fatty ac	ids fra	ctions*					
T.sat.	34.78	47.81	45.95	41.76	40.57	49.96	46.60	42.22	30.87	46.09	44.61	36.10
T.unsat.	65.22	52.19	54.05	58.24	59.43	50.04	53.40	57.78	69.13	53.91	55.39	63.90
T.mono.	34.79	35.34	31.48	30.27	37.02	32.32	30.90	32.95	35.76	29.31	27.80	35.19
T.di.	14.22	10.54	15.60	15.81	18.60	17.06	20.65	22.19	16.84	19.44	16.58	12.44
T.tri.	1.25	1.78	0.26	3.70	0.87	0.28	0.36	0.55	0.18	0.32	0.53	3.34
T.tctr.	5.41	1.30	1.26	3.41	1.63	0.19	0.98	0.98	2.45	2.18	4.13	4.32
T.pent.	4.21	1.80	3.21	3.80	1.31	0.19	0.51	1.11	7.41	0.48	4.91	4.33
T.hex.	5.34	1.43	2.24	1.25	-	-	-	-	6.49.	2.18	1.44	4.28
T.poly.	30.43	16.85	22.57	27.97	22.41	17.72	22.50	24.83	33.37	24.60	27.59	28.71
Ks	1.88	1.09	1.17	1.39	1.46	1.00	1.15	1.37	2.24	1.17	1.24	1.77

= Total saturated fatty acids

T.di. = Total di-unsaturated fatty acids
T.pent. =Tote pent-unsaturated fatty acids
Ks = T.unsat IT.sat.

T.tri. T.hes.

T.unsat. =Total unsaturated atty acids
T.tri. = Total tri-unsaturated fatty acids = Total hexamnsatu sled fatty acids T.mono. T.tetr.

= Total mono-unsaturated fatty acid = Total tetra-unsaturated fatty acids = Total polyunsaturated fatty acids

lipid of Nile bolti (NB) were palmitoleic (C16 1, 19,77 %), palmitic (C16:0, 16.43 %) and linoleic (C18:2, 14.22 %) acids while the oleic (Cisq, 20.29 %), linoleic (C18:2, 18.60 %), palmitoleic (C<sub>161</sub>, 11.53 %), myristic (C14.0, 10.45 %) and palmitic (C16:0, 10.42'%) were the predominant fatty acids in lipid of aquaculture bolti (AB), and linoleic (C18:2, 16.84 %), palmitoleic (C16:1, 16.55 %), oleic (C18:1, 16.30 %) and palmitic (C16:43, 14.68 %) in lipid of marine bouri (MB) fish, respectively. It is clear that the C16:1 and C16:0 fatty acids were considered the predominant in the lipids of the three fresh fish species while, the Cig.I was the abundant fatty acid of AB and MB fish species. The main fatty acid recorded for the fresh NB, AB and MB was the C16:, (19.77 %), C18:1 (20.29 %) and  $_{\text{C18:2}}$  (16.84 %), respectively. On the other hand, it could be noticed that the Clo:o and C12:0 fatty acids were not detected in the lipid of fresh MB fish, as well as, the  $_{\text{C22:6}}$  (docosahexaenoic acid) was absent in lipid of fresh AB fish. The latter case may be reduced the health importance (associated with  $_{\text{C22:6}}$  fatty acid) for lipid of AB fish compared to the other species tested under this study which recorded 6.49 and  $5.34~\%~of_{C22:6}$  for fresh MB and NB fish, respectively. Beside C22.6 fatty acid, the eicosapentaenoic fatty acid (C2 0.5) posses health benefits (Goodnight et al., 1981; Gerster, 1995; Connor et aL,1996; Rampjor et aL,1996; Volker et al., 2000 and Watkins et al., 2001). The total essential fatty acid (included C18:2, C18:31 C20:4, C20:5 and C22:6) were higher (33.37 % of total fatty acids) in lipid of fresh MB followed by that (30.43 %) of fresh NB, then fresh AB fish which recorded the lowest percent (22.41 %) of total essential fatty acids. As can be seen in the

same Table (17), it is evident that the fresh fish species under this study had higher percentages of total unsaturated fatty acids than that of total saturated fatty acids. This was expected and confirmed by the findings of many researchers (Maximoves and Tresheva, 1967; Kaitaranta and Linko, 1979; Fellat-Zarrouck and Maurin, 1986; Ziino et al., 1992 and Kaneniwa et al., 2000). Generally, the fresh MB recorded higher percent (69.13 %) of total unsaturated fatty acids followed by the fresh NB (65.22 % and AB (59.43 %) fish, and the reverse for the total saturated fatty acids, respectively. Moreover, the Ks - as an indicator for the degree of unsaturation confirmed the above results whereas, the fresh MB recorded higher (2.24) Ks followed by fresh NB (1.88) and AB (1.46), respectively. The higher the Ks the higher the degree of unsaturation.

Concerning the effect of cooking methods (frying, grilling and roasting) on the fatty acids composition and fractions, the results found in Table (17) indicated that all the cooking methods affect the fatty acids composition and fractions. It could be observed that some fatty acids (FAs) increased and other decreased, beside that some FAs were absent by some cooking techniques while, the same FAs were found using other cooking techniques. This may be due to the oxidation and thermal effects leading to convert some FAs to other as well as degradation of FAs (Wally, 1981; Abd EL-Aziz,1998 and Wally, 2002). Fore example, concerning the fried Nile bolti fish (FNBF), Cio:o, C12:0, and C24:0, fatty acids were not found while, C10:0, and C12:0, FAs were absent in lipid of grilled Nile bolti fish (GNBF) but, C10:0, and C24:0, FAs were not detected in lipid of roasted Nile bolti fish

(RNBF). Fried-aquaculture bolti fish (FABF) recorded no amounts of C10:0, C1711, C22:1, and C22:6, as well as, grilledaquaculture bolti fish (GABF) and roasted aquaculture bolti fish (RABF) recorded no amount of  $_{\text{C22:15 C22:6}}$ , and  $_{\text{C24:0-}}$  On the other hand, fried-marine bouri fish (FMBF) had no amounts of C22:0 and C24:0 while, grilled-marine bouri fish (RMBF) contained all the fatty acids tested under this study. As reported by many researchers the eicosapentaenoic (C 20:5) and docosahexaenoic (C22:6) fatty acids represents certain health benefits (Goodnight et al., 1981; Gerster, 1995; Connor et al., 1996; Volker et al., 2000 and Watkins et |al., 2001), therefore, accordig to the total percentage of C20:5 nd C22:6, it could be indicated that the RMBF had higher (8.61 % of total FAs) percentage followed by GBF (6.35%), GNB (5.45 %),RNBF (5.05 %), FNBF (3.23 %), FMBF (3.66 %), **BF** (1.11 %), GABF (0.51 %) and FABF (0.19 %), spectively. Therefore, the previous arrangement of cooked s ple was recorded for possible health importance. It is evident at RMBF and GBF may be health preferred than those of NBF, GNBF, RABF and GABF, respectively. The lowest health enefit was recorded for fried fish samples when compared with roasted or grilled sample. This may be confirmed by the total es ential fatty acids percent whereas the FNBF, GNBF, RNBF, F F, GABF, RABF, FMBF, GBF and RMBF showed 16.85, 22 57, 27.97, 17.72, 22.50, 24.83, 24.60, 27.59 and 28.71 % of total fatty acids, respectively.

With respect to the fatty acids fractions, the re ults found in Table (17) indicated that all the cooking meth ds applied

under this study-increased the total saturated fatty acids (T.S) percent when compared with the fresh fish provided that the increasing rate of T.S was lower for roasted fish followed by grilled fish, then fried fish which recorded the highest rate of increasing the T.S. As regards the total unsaturated fatty acids (T.U.S) the reverse was observed whereas, the TUS percent was decreased overall the cooking techniques when compared to the fresh fish, but the decreasing rate of TUS was lower in roasted than grilled and fried fish. The increment of TS and decrement TUS may be due to lipids oxidation occurred during the different cooking methods leading to change the fatty acids composition and fraction. In this concern, the Ks (T.U.S/T.S) that indicates the degree of unsaturated of lipid supported the previous results, whereas, the higher the Ks the higher the degree of unsaturated and the lower the oxidation level. Therefore the lower oxidation level was recorded for roasted samples than grilled and fried samples, respectively. For example, the FNBF, GNBF, RNBF, FABF, GABF, RABF, FMBF, GBF and RMBF recorded Ks value of 1.09, 1.17, 1.39, 1.00, 1.15, 1.37, 1.17, 1.24 and 1.77, respectively. According the cooking methods tested, it is evident that the roasting was better than grilling and frying methods, respectively. Anyway, the best product was recorded for roastedmarine bouri fish (RMBF) overall the tested cooked fish. Similar results given by Kaitaranta and Linko (1979), Wally (1981), Pamela (1991), Walter and George (1991), Abd El-Aziz et al. (1998), Echarte et al. (2001) and Wally (2002).

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Data presented in Table (18) show the li which were triglycerides (TG), phospholi ids (PL), monoglycerides (MG), cholesterol (CL), diglyceride fatty acids (FFA), tocopherol (TO) and hydrocarbon of total lipids - of some fresh fish (Nile bolti, aqua and marine bouri) as influenced by some cook including frying, grilling and roasting. From the res be observed that the predominant fraction was the 45.10 %) followed by the PL (32.28 %) overall th species. Also, concerning the fresh fish, the lowest was recorded for the MG fraction among the various lipids. Fresh fish of Nile bolti, aquaculture bolti and m were recorded, 2.62, 2.34 and 3.48 % of corresponding, 4.36, 4.90 and 4.14 for free fatty aci respectively. This may illustrates that the higher the

id fractions (DG), free (HC), as % ulture bolti g methods Its, it could G (54.40three fish percentage ctions of e bouri fraction s fraction, cophero

content the lower the free fatty acids content. Furthermore, fres l aquaculture bolti had higher (8.62 %) percent of H fraction when compared with fresh marine bouri (5.87 %) or resh Nile bolti which recorded the lowest (2.17 %) percent of H fraction. On the whole, PL, MG, CL, DG, FFA, TO TG and H fractions were 28.57, 0.00, 3.11, 4.77, 4.36, 2.62, 54.40 and 2 17 % of fresh Nile bolti; 21.51, 1.71, 4.24, 7.34, 4.90, 2.34, 9.34 and 8.62 % of fresh aquaculture bolti and 32.28, 0.78, 3 4.14, 3.48, 45.10 and 5.87 % of fresh marine b uri fish, respectively.

By different cooking methods applied under t is study including frying, grilling and roasting, it could be noti ed that

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Table(18): Lipid fractions (as % of total lipids) of some fresh fish as influenced by some cooking methods.

A		Nile bol	ti fish		Aqua	aculture	bolti fis	sh	Ma	arine bo	ouri fish	
7,			<u></u> 50	es es	vi ;Z.	-o ri		es ct	,= ri	1	= t.)	A 64
	54.40	55.71	45.19	50.43	49.34	51.94	41.00	47.61	45.10	56.57	40.43	46.88
2	28.57	21.44	25.76	33.30	21.51	10.44	21.46	24.57	32.28	20.24	25.64	32.74
3		1.76	1.43	1.05	1.71	2.09	1.87	1.80	0.78	1.64	1.35	1.15
4	3.11	3.85	3.70	3.38	4.24	4.64	2.31	3.34	3.39	3.30	1.39	4.44
5	4.77	2.61	10.92	3.32	7.34	5.13	18.20	10.76	4.96	4.35	15.37	5.43
6	4.36	5.51	8.42	4.80	4.90	5.44	5.07	4.51	4.14	4.34	5.33	4.21
7	2.62	2.38	1.98	2.18	2.34	2.09	2.11	2.23	3.48	2.25	2.11	2.26
8	2.17	6.75	2.60	1.54	8.62	15.03	7.98	5.18	5.87	7.31	8.38	2.89

Triglycerid es

rhospholipids

Monoglycerides

Cholesterol

5 = Digly cerides 6 = Free fatty acids 7 = Tocopherol 8 = Hydnoccamtbons

the fried and grilled samples recorded lower percent PL, at the same time, the roasted samples recorded higher percent of PL compared to the raw samples. Concerning the action, with exception of grilled aquaculture bolti and grilled arine bouri, the percent of CL fraction was increased overall e different cooking methods and fish species used in this study. Dashlouty et al. (1984) reported that the increase of PL and CL were attributed to the partial breakdown of lipoproteins complex which is considered the main reason of increasing. Moreover, Bell et al. (1996) revealed that the reason of decreasing of PL may be due to the oxidation of phospholipids which have high amounts of unsaturated fatty acids in its composition. With respect of MG fraction, all the cooking methods increased the percent of MG compared to fresh fish samples provide that the lowest increment rate was recorded for the roasted samples followed by grilled and fried samples, respectively. Moreover, according to the fish species, the roasted samples were ascendingly arranged (on MG percent basis) as follow: roasted-Nile b o ti (1.05) roasted-marine bouri (1.15) an roastedaquaculture bolti (1.80), respectively. Different rates of decrease and increase were observed for DG fraction in all e cooked samples nevertheless, the grilled samples recorded t e higher percent of DG than roasted and fried samples, respectively. FFAs fraction increased by all the different methods ocooking but, the roasted fish had the lowest percent of FFA fraction followed by the grilled and fried fish, respectively. All the cooking methods effected the TO fraction whereas, it was decreased when compared to the of fresh fish however, among

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the different methods of cooking used in this work, the lowest rate of decreasing of TO fraction was recorded for roasted fish. With regarding to the TG fraction, it could be observed that the frying technique increased the percent of TG while the grilled and roasting techniques decreased the percent of TG, this may be due to penetration of some frying oil into samples during frying process and loss of some oil from grilled and roasted samples through grilling and roasting process. On the other hand, among all the cooked samples with very small exception (only grilled-aquaculture bolti), the hydrocarbons (I-IC) fraction increased by frying and grilling process while decreased when the roasting method was applied. Anyway, these results were confirmed by the data of Rhee and Smith (1983), Hoelscher et al. (1987), hearn et al. (1987), Abd El-Aziz et aG (1998) and Echarte et al. (2001).

# **E- Phospholipid fractions:**

The data given in Table (19) show the phospholipid fractions (as % of total phospholipids) of some fresh fish-including Nile bolti, aquaculture bolti and marine bouri-as affected by some cooking methods (frying, grilling and roasting).

Form the results, it could be reported that the phospholipids of fish muscles were fractionated to nine fractions as follow: phosphatidyl serine (PS), Lysophosphatidyl choline (LPC), sphingomyeline (S), phosphatidyl choline (PC), phosphatidyl inositol (PI), phosphatidyl ethanolamine (PE), phosphatidic acid + glyceryl phosphatides (PAG), Plasmalogenes + cardio lipids (P) and glycolipids (G). It is evident that the main fractions ( highly percentages ) were

Table(19): Phospholipids fractions (as % of total phospholipids) of some fresh fish as influenced by some cooking methods.

olipids	× suc	Nile	bolti fisl	h	4	quacult	ure bolti	fish		Marine	bond f	ish
Phospholipids	fractions *	ri ied	= 0		E		°. C7 3	Roast	Fresh	Fried	c7 3	Roast
1	1.26	lOõ	4.50	0 4.34	2.70	3.42	5.51	7.61	0.72	0.96	11.71	4.41
2	0.79	1	1.04	3.40	1.24	5.50	7.30	4.38	0.88	0.97	1.54	11.7
3	5.56	7.99	5.89	4.38	4.33	8.24	4.29	4.80	7.22	4.54	8.41	
4	46.8	40.71	35.74	40.5	39.70	21.55	25.61	15.49	43.36	40.05	45.42	21.74
5	0.46	1.64	0.87	1.90	2.82	18.58	6.41	6.80	1.31	4.61	1.59	4.50
6	33.3	29.44	24.28	20.2	35.46	33.11	26.16	28.33	38.13	24.81	15.68	10.38
7	7.79	10.37	15.44	18.6	7.34	4.36	17.92	12.43	6.06	12.73	5.59	7.38
8	2.69	3.08	3.28	4.62	4.84	2.50	4.95	9.54	0.87	5.80	8.62	14.34
9	1.26	2.77	8.96	2.01	1.59	2.74	1.85	10.64	1.45	5.53	1.44	22.03

<sup>\*</sup> 

 $<sup>^{1} = \</sup>text{Phosphatidyl mine}$  .

<sup>3 =</sup> Sphingom)eline.

<sup>5 =</sup> phosphatidyl inositol

<sup>7 =</sup> Phosphatidic acid + glyceryl phosphatides.

<sup>9 =</sup> Glycolipids

<sup>2 =</sup> Lysophosphatidyl cholinc.

<sup>4 =</sup> Phosphatidyl choline.

<sup>6 =</sup> phosphatidyl ethanolamine.

<sup>8 =</sup> Plasmalogenes + cardio lipids .

recorded for PC and PE overall the three fish species (fresh) as the PC was 46.86, 43.36 and 39.70 while the PE was 33.33, 38.13 and 35.46 % for Nile bolti, marine bouri and aquaculture bolti fish, respectively. On the other hand, the lowest amount of phospholipid fraction varied among the three species of fresh fish being LPC in Nile bolti (0.79 %), aquaculture bolti (1.24 %) and marine bouri (0.88 %), while PS was lowest in marine bouri (0.72 %) fish. **Bell et al. (1996)** reported that the essential phospholipids are PC, PE, PS and PI. Under this study, the total percentage ages of PC, PE, PS and PI were 83.52, 81.91and 80.68 for fresh marine bouri, Nile bolti and aquaculture bolti fish, respectively.

Concerning the effect of cooking methods used in this investigation, it could be noticed that the PS and LPC fraction increased with different rates depending on the different methods of cooking included frying, grilling and roasting, this when comparison was attributed to that of fresh fish. Regarding to the PC fraction, it could be observed that this fraction decreased in all the cooked sampled (15.49-40.71 %) with exception of grilled marine bouri (45.42 %) when compared to that of fresh fish (39.70-46.86 %). On the other hand, the PE fraction decreased overall the different cooked samples. Regarding the S fraction, it was decreased by using especial cooking techniques while increased by using others. Nearly, PI, PAG, P and G fraction increased (with different level) by frying, grilling and roasting of Nile bolti, aquaculture and marine bouri fish. Anyway, these results were confirmed by the finding of Gall *et al.* (1983),

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Maurice (1990), Abd El-Aziz (1998), Marathe  $\ et\ al.\$  (2001) and Wally (2002).

#### <u>F\_ Fat\_soluble vitamins:</u>

Results of fat-soluble vitamins (A, E and K) of some fresh fish (Nile bolti, aquaculture and marine bolti fish) influenced by some cooking methods (frying, grilling and asting) are given in Table (20). As can be seen, the fresh marine bouri fish recorded higher amounts of vitamins A, E and K (280.42, 165.49 and 46.93 i.tg/g) than that of aquaculture bolti and Nile bolti fish. However, fresh aquaculture bolti had higher (16286 ttg/g) amount of vitamin A and lower amounts (110.90 and 26.56 Itg /g) of vitamins E and K than that of Nile bolti fish which were 158.34, 182.68 and 38.61 lig/g of A, E and K, respectively. As recorded before, bouri had highest amount of fat than aquaculture bolti and Nile bolti. In this concern, Novikov (1983) reported that oily fish contains higher amounts f vitamins particular A than that of lean fish. All the cook g methods affected the vitamins content of fish. It is evident the loss of vitamins was lower in roasted fish followed by grilled then fried fish and this may be due to the effect of different cooking temperatures.

## **G- Statistical analysis:**

#### 1-Oil constants:

Analysis of variances for oil constants of some fresh fish (Nile bolti, aquaculture bolti and marine bouri fish) as affected by some cooking methods (frying, grilling and r. asting) are given in Table (21). The analysis indicated that the differences between the fish types as well as between the treatments *RESULTS AND DISCUSSION* 

Table(20): Fat-soluble vitamins (as pig g oil) of some fresh fish as influenced by some cooking methods.

a		Nile bo	lti fish		Aqu	acultur	e bolti fi	ish	М	arine b	ouri fish	1
cn tx	1 4.0 L.	-0 6/ <b>T.</b> :;	-0 ;;; 61 ;;; .; • O	<b>₩.</b> <b>C</b> A	. <b>O</b> (co) 41 I	10 61 1: W	• 6 c	⊪ ₁≅oa	. <b>o</b> n 61 e!.	7: W	اري اهادا	ਹ ਹ
А	158.34	09T01	127.88	It'6£1	98'Z91	£0't6	1£'811	SL'6Z.1	280.42	81'9Z1	214.45	Eľ6£Z
E	89'Z81	LI'l.6	91'8ZI	133.68	06'011	6L'ZI	SZ'ZS	S9'89	6,1 'S91	Z91 6	86TI1	197Z1
К	19'8£	6r81	Z6'97:	6£'6Z	99 9Z	8Z'S	4"4 .1.	tn 'xi' -,	fn cs ,45 ,,r	r- r- et et	<b>N</b> c*? P.;	et tr) tri

<sup>\*</sup> Fat-soluble vitamins

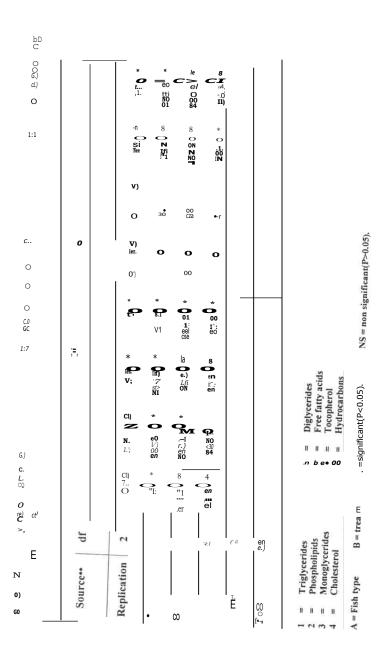
Source.				F values for oil constants••	il constants••		
				;.T		ı	
Replication	N	00	N If/	(,) r. ·c;	31.78 *	6.20 *	4
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			8 <b>2</b> 2 8	N °C' '40	00 <b>c</b> i	00 <b>vi</b>	Z
		sc?		00 Z	<1. ON	N 10	
c L							
Fotal	35						
• R = Fish type  AV = Act FFA = Fr PV = Per SV = Sap IN = Iodi	h type B = treat  = Refractive index.  = Acid value(mg Kol  = Free fatty acids(%  = Peroxide value(me  = Saponification value  = Indine number.	Fish type B = treatments  RI = Refractive index.  AV = Acid value(mg KoH/g oi)).  FFA = Free fatty acids(%, as oleic).  PV = Peroxide value(meq /kg oil ).  SS = Saponification value per g of oil).	= significant(P<0.05).		00 C C (.0	In 0.	

RESULTS AND DISCUSSION \_\_\_\_\_\_

(cooking methods applied) were significant (r0.05) for all the **oil** constants measured (RI, AV, FFA, PV, SV and IN) but, the differences in concern to interactions between the fish species and the cooking methods (treatments) were non-significant (p> 0.05) for the AV, FFA and IN and significant (r0.05) for the RI, PV and SV.

# 2- Lipid and phospholipid fractions:

Data presented in Tables (22and 23) show the analyses of variance for lipid and phospholipid fractions of some fresh fish as influenced by some cooking methods. From the data of Table (22), it could be noticed that the differences between all the factors (fish species, cooking methods or treatments and interaction between the former and the latter) were significant (r0.05) for all the lipid fraction. Also, from data of Table (23), with exception the difference between the fish species which was non-significant difference (p>0.05) for sphingomyeline fraction, all the differences between all the factors were significant (r0.05) for all phospholipid fractions tested under this study.



					F values for	F values for phospholipid fractions•	fractions•			
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Replication		SN OVZ	ZVO NS Z'10 NS	SN OL'1	0.90 NS	SN 08'0	2.40 NS	2.40 NS 1 2.80 NS	SN OE'I	S,30*
		* OE'69I	* 08'196	3.50 NS	* 10'917S	* 06'96SE	270.10 *		017'501	*86'St
		* OLTSZI	*	05'9f	* 09'8IE	*01 TISI	584.60 *	* 06669	* 06'ZLI	* Ol'OSI
8xV		09'L9E	*01;8001	33.60 *	* OVS6	* 09'8SL	*0S'U.	* 05'8Z9	* 06.84	* 66'88
Error	ZZ									
Total	SE									

# Effecte of dry-salting conditions durinif processing of fermented saltedbouri (Feseekh):

# **A- Chemical properties:**

Results found in Table (24) show some chemical properties of fresh bouri fish as affected by dry-salting conditions (heavy, medium and light-salted bouri on salting periods of 15, 30, 60, 90 and 120 days for each) during processing of fermented-salted bouri fish (Feseekh). Form the results, as expected; the fresh bouri recorded the same chemical properties including moisture, fat, TBA and pH as reported in Table (16) for fresh bouri. Additionally, fresh bouri fish contained 0.57 % of sodium chloride on wet weight basis while recorded 2.54 % on dry weight basis. Moreover the salt concentration % (% Nacl / % Nacl + % moisture x 100) was 0.73 in fresh bouri fish flesh.

Concerning the effected of dry-salting conditions, it could be observed that all the different systems of dry salting-included heavy (1:1, fish: salt), medium (2:1, fish: salt) and light (3:1, fish: salt) salting-decreased the moisture content in all samples compared to the fresh fish. Of the heavy-salted samples, moisture content decreased until 30 days and increased on 60 days but thereafter, it decreased again till the end of salting period (120 days). On the other hand, with respect of medium-salted samples, it could be observed that the moisture content was decreased up to 60 days then increased on 90 days and decreased again by the end of salting period (120 days). But, concerning the light-salted samples, the moisture content decreased up to 30 days then little and gradual increase was *RESULTS AND DISCUSSION* 

						Saltin	ig system	(ratio	f fish: s	Salting system (ratio of fish: salt) and period (in day) of dry-salting	period (i	n day) o	<u>f</u> dry-sal≀	ting			
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		c 2		or	09	06		S	of	09	06	<u>OZI</u>		or	09	96	OZi
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FFA = Free fatty acids(%, , as oleic).

SV = Saponification value per g of oil .

AV = Acid value(mg KoH/g oil).

Salt conc. % = |% NaCl / % NaCl + % Moisture|×100 (Zaitsev et al., 1969).

\*TBA = Thiobarbituric acid(mg malonaldehyde/kg).

PV = Peroxide value(meq /kg oil).

RI = Refractive index.

IN = Iodine number.

recorded up to the end of salting period (120 days). It is worthy to mention that salting of fish can be subdivided into three stage, in the first stage, fish is exposed to high osmotic pressure and the active movement of water from the fish into surrounding brine. Therefore, in this stage, a considerable decline occurs in moisture content of fish. At the second stage, there is no great difference in the rate of salt moving into fish, or f the water leaving the fish, and by the end of fish stage, th movement ceases and no further decrease in moisture content o urs. In the third stage minor salt quantities move into fish and as a consequence, the fish moisture content increases s ightly. The increase of moisture content and the weight of fish has been explained in terms of swelling and as an absorption phenomenon, where it induces just a movement of water from brine into fish, however, it can be assumed that myosin and actomyosin in the presence of high salt content are deprived of bound water. Anyway, by the end of salting period, the heavysalted bouri fish recorded lower (51.23 %) moisture content followed by medium (55.49 %) then light-salted (63.31 %) samples. On the other hand, it could be noticed that the fat content increased to reach 7.83 and 9.29 % for heavy and medium-salted samples while it recorded 3.66 % (no wet weight basis) by the end of light salting compared to fresh fish (5.41 %). On dry weight basis, all the salted samples recorded lower (22.97-9.94 %) fat contents when compared with fresh (24.14 %) fish, the heavy-, medium- and light-salted bouri fish ad 16.06, 20.86 and 9.94 % of fat, respectively. It is evident that the loss of fat was lower in medium salted samples followed y heavysalted samples then light-salted one. This may be due to more lipolysis and more oxidation for heavy-salted than mediumsalted fish. Cuppett et al. (1989) and Maurice (1990) reported that adding of salt leads to increase of oxidation level, as well as, the lipolysis of fat enhances the lipid oxidation. Concerning the salt content and concentration of salted samples, increasing and decreasing were observed during the different periods of salting. Anyway, the salt content and salt concentration by the end of salting period (120 days) was 13.75 and 21.16, 11.77 and 17.5 and 5.56 and 8.07 % for heavy-, medium- and light- salted samples, respectively (on wet weight basis). The values of salt content on dry weight basis were 28.19, 26.44 and 15.15 %, respectively. The TBA values were gradually increased with increasing the salting time provided that the higher level of TBA Values was recorded for light-salted fish followed by heavysalted fish then medium-salted fish which recorded the lowest TBA values. Therefore, it is clear that the medium-salted bouri fish is recorded the lower oxidation of lipids than that of heavyand light-salted samples. By the end of salting time, the pH values decreased for such heavy (5.83) and medium (5.65)-salted fish while increased for light-salted one (6.82).

#### **B-** oil constants:

Concerning the oil constants, data presented in the same Table (24) show the oil constants of fresh bouri fish as affected by dry salting conditions during processing of fermented-salted bouri fish "Feseekh". From the results, it could be observed that refractive index (RI) was decreased from 1.4648 and 1.4646 at 15 days to reach 1.4617 and 1.4571 by the end of heavy and light

salting period (120 days), respectively. At the same time, the RI decreased from 1.4661 to reach 1.4643 by the end of medium salting period. The higher the RI the lower the rate of lipid oxidation as mentioned by Wally (1981) and Maurice (1990). Consequently, the medium-salted samples will be rec rded more stability against the lipid oxidation. At any time of salting process, the light-salted samples recorded the highes values of acid value (AV) and free fatty acids (FFA) folloWed by the medium-salted samples then the heavy-salted one which recoded the lowest values of AV and FFA. It is clear that there is a negative relation between salt concentration and AV and FFA of salted fish whereas, it was observed that the higher the salt content the lower the AV and FFA values. Also, it is worthy mentioned that the increase of AV and FFA means more lipolysis and enhancing of lipid oxidation as mentioned before. In view of PV, the heavy-salted samples recorded igher PV than that recorded for the medium-salted samples whi h may be due to high salt content (in heavy-salted samples) tha enhances the lipid oxidation expressed as PV. The light-salted samples recorded the highest PV probably due to more lipolysis occurred in these samples leading to enhancing the lipid oxidation. Saponification value was recorded the same trend of PV. With respect of iodine number (IN) as an indicator of the unsaturation degree, the medium-salted fish recorded higher IN when compared with heavy- and light-salted fish. This may be due to the lower oxidation level of unsaturated fatty acids for mediumsalted fish than that for heavy- and light-salted fish. For example, at 15, 30, 60, 90 and 120 days of salting, the IN values were 126.59, 125.67, 124.35, 122.61 and 122.41; 127.39, 126.81, RESULTS AND DISCUSSION

125,57, 124.73 and 122.40 and 125.09, 123.61, 120.14, 119.84 and 116.4.5 for heavy-, medium- and light-salted fish., respectively. On whole, these results were cofermed by the findings of Hall *et al.* (1962), CasteII *et al.* (1965), Wally (1981), Cuppett *et al.* (1989), Hazra *et al.* (1998) and Wally (2002).

#### **C-** Fatty acid composition:

The results of fatty acids composition (as % of total fatty acids) of fresh bouri fish as affected by dry-salting condition (heavy, medium and light salting forl5, 30, 60, 90 and 120 days each) during processing of fermented-salting bouri fish (Feseekh) are presented in Table (25). The fatty acids composition of fresh bouri fish was illustrated as mentioned before in Table (17), as noticed before, the major fatty acids were linoleic ( $C_{18,2}$ ), palmitoleic ( $C_{16,1}$ ), oleic ( $C_{18,1}$ ) and palmitic ( $C_{16:0}$ ) acids, respectively. The percent of the previous fatty acids were 16.84, 16.55, 16.30 and 14.68 % of total fatty acids. Eicosapentaenoic ( $C_{20:5}$ ) and docosahexaenoic ( $C_{22:6}$ ) fatty acids recorded intermediate percentage being 7.41 and 6.49 %, respectively. The lowest percent (0.18 %) was recorded for the linolenic ( $C_{18:3}$ ) acid.

The different salting method-either heavy, medium or light salting-affected (with different levels) the fatty acids composition during salting period, it could be observed that there are increments of some fatty acids, at the same time, decreases of other, meanwhile in addition to some fatty acids were absent at different periods of salting. Nevertheless certain fatty acids such as C10:0 and C12:0 acids were initially absent but appeared at

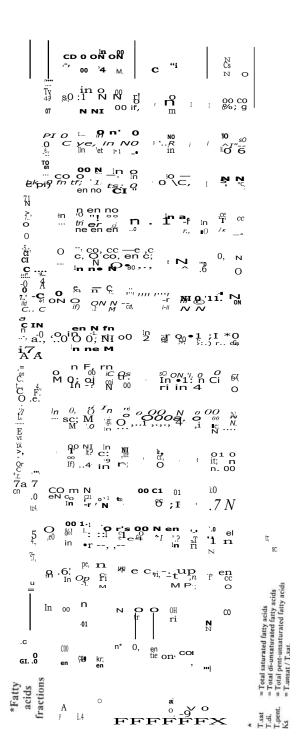
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different times of sailing Moreover, in one of the salting methods, one of fatty acids may decrease at especial time then increased at 'anther time of salting. This may be due to oxidation or/and lipolysis of lipids, accordingly changing the fatty acids composition. On the other hand, according to the total percent of the essential fatty acids (EFA), by the end of salting period (120days), the medium-salted fish recorded the highest (11.19 % of total fatty acids) total percent of EFA followed by the heavysalted fish (4.59 %) then the light-salted one which recorded the lowest (2.97 %) total percent of EFA. Furthermore, due to the more health importance of eicosapentaenoic (C20:5) docosahexaenoic acids (Goodnight et aL, 1981; Gerster, 1995 ; Connor et al., 1996; Volker et al., 2000 and Watkins et al., 2001), it is worthy to mention that by the end of salting period, the medium-salted fish recorded total percent (1.82 %) of C20:5 + C22:6 which were absent in the heavy and light-salted samples. Anyway, according to the fatty acids composition as affected by salting condition, the medium-salted fish was the best followed by the heavy-salted fish then the light-salted one, which had a more poor fatty acids composition.

## **D-** Fatty acids fractions:

Data of fatty acids fractions (% of total fatty acids) of fresh bouri fish as affected by dry-salting condition (heavy, medium and light salting for 120 days) during processing of fermented-salted fish (Feseekh) are presented in Table (26).

From the results, it could be noticed that the data confirmed and supported the previous conclusions obtained from results of Table (25). It is clear that the total saturated fatty acids *RESULTS AND DISCUSSION* 



(TSFA) were increased by increasing of salting time nevertheless the increasing rate was lower for medium-salted fish than that of heavy-and light-salted samples (with exception of the heavysalted fish only at 120 days). The reverse was observed concerning the total unsaturated fatty acids (TUFA) as, the TUFA were decreased with increasing the salting time provided that the total loss of TUFA was lower of medium-than heavy-and light-salted fish. By the end of salting (120 days), the percent of total polyunsaturated fatty acids was 4.59, 11.19 and 2.97 % for heavy-, medium-and light-salted samples, respectively. Moreover, the Ks (as an indicator of the unsaturation degree, calculated as TUFA / TSFA) was decreased when the salting time was increased. The higher the Ks the lower the oxidation of lipid. It is clear that the medium-salted samples had higher (0.72) Ks than heavy-(0.70) and light-(0.20) salted samples (at the end of salting). Anyway, according to the fatty acids fractions, the medium-salted fish was better than heavy-and light-salted fish.

## E- Lipid fractions:

Data presented in Table (27) show the lipid fractions-including triglycerides (TG), phospholipids (PL), monoglycerides (MG), cholesterol (C), diglycerides (DG), free fatty acids (FFA), tocopherol (TO), and hydrocarbons (HC)- of fresh bouri fish (as %of total lipids) as influenced by dry-salting conditions through processing of fermented-salted bouri (Feseekh). From the results, it could be revealed that the main lipid fractions of fresh bouri were the TG and PL fraction. During the salting process, after 15, 30, and 60 days of heavy or medium salting, the main lipid fractions still recorded for TG

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and PL while after 90 and 120 days of heavy or medium salting, the main fractions were the TG and DG fractions. Concerning the light salting, the TG and PL recorded the great amounts only up to the 15 <sup>th</sup> day thereafter, the TG and DG became the

predominant fractions till the end of salting period (120 days). As can be seen from the results, the PL fraction decreased with increasing of the salting time but, the decreasing rate of the PL was higher in light-salted fish than that of medium-and heavy-salted fish. Bell et al. (1996) reported that the decreasing of PL may be due to the oxidation of PL that contains high level of unsaturated fatty acids in its structure. As well as, Maurice (1990) mentioned that the lipolysis of fish lipids enhances the oxidation of lipids, accordingly the PL is decreased. This was confirmed by the values of FFA whereas the light-salted fish showed higher percent (18.73) of FFA than the of the medium (12.41) and heavy (10.60) salted fish (by the end of salting period). Also, the TG fraction deceased by increasing the salting time provided that the decreasing rate was higher for light-salted samples followed by heavy-and medium-salted samples (with very little exception). On the other hand, total loss of tocopherol (TO) was observed after 15, 60 and 90 days of light, heavy and medium salting of samples. MG fraction increased in different ratios overall the salted samples when compared with fresh fish. By the end of salting period, the C fraction decreased in the heavy (1.49 %) salted fish while increased (3.41 %) in the lightsalted fish compared to that of fresh fish (3.39 %). With respect of DG fraction, progressive increases were found over all the salted samples, whereas, the values were 20.67, 25.31 and 31.50

% (at the end of salting time) for the heavy-, medium-and light-salted fish. The HC recorded the same trend of DG, and the percent of HC by the end of salting period was 7,33, 9.55 and 14.74 % for heavy-, medium-and light-salted fish. Anyway, the results were partially confirmed by the finding of **E**-Sebaiy and **Metwalli** (1989).

## F- Phos holi id fractions:

Results of phospholipid fraction (as %of total phospholipids) as influenced by dry salting con ition during manufacturing of fermented-salted bouri fish are gi en in Table (28). The phospholipids were fractionated usin thin layer chromatography into nine fractions as follow: hosphatidyl , Lysophosphatidyl choline (LPC), sphingomyeline (S), Phosphatidyl choline (PC), phosphatidyl inositol (PI), phosphatidyl ethanolamine (PE), phosphatidic acid + glyceryl p osphatides (PAG), Plasmalogenes + cardio lipi s (P) and glycolipids (G). From the results, with exception of 1 ght salting for 120 days, the PC and PE fractions formed the maj r fractions either of res bouri fish or for all the salted fish at any time of the different salting periods. In this concern **Maurice** (1990) reported that among the various phospholipids that occur in fish, the PC occur to the greatest extent, with PE being the second most common class. In addition, Segawa et at (1994) reported that the PC and PE enhance the role of tocopherol, as tioxidant v be due to they regenerate the tocopherol. By alting, in comparing with fresh fish, The PS and LPC fractions increased with increasing the salting time up to the end of salting period (120 days). The percent of PS and LPC increased from

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		06	00 41 CC* 		17 <del>-&amp;T</del>	L9'51	09'S	Z1;87 Î	.5E11	411 , <b>4</b>	
		09		OL'L	0177—	OL'6I	9£'9	[1717 ST]		I <b>₹</b> ZL	
	ism n'Ar	OE	$\mathbf{ri}\mathbf{\pounds}_{\mathcal{P}}$		5 <del>9</del> 5	8VEZ			68 11 1	7Z# 1	
		Si	FT.17£	0;'Z	1707 <b>5</b> <del>1</del> <del>T</del>	L811	65'9 ~				
( m		OZI		0;'ZS171.7	$51$ $^{+}$	I t'LZ	65'9 굳 1 17 1				I8'S
m) oouad <b>DUB (Ws :</b> qsu Jo opea)i	iss:usgʻll:Z <u>H</u> ɒ ji βSwawa	06	£E'L		LS"L,	9L'ZE	097	09'5Z	10'01	ZrZ	
യ ജവവ		09	Z9'S	It7T	£Z*9	36,60	01 <b>7</b> T	$\mathrm{L}'\mathfrak{L}$	8Z'L	66'1	
<b>/s :</b> qsu เ	3Swawa	30		66'1	99'9	Or6£		91'L£	617'9	96'0	
Jo opea)i		S	08'0	96'0	En,	S17'017	9£'1	ZL'9£	98'9	16'0	
		0ZI	Z9'S	89'9	SS p	Orn	Z0'Z	rya	,1 8'61 175'91 LV,t t	± s±	
	Heavy salted(1:1.1 nsn:salt	. 06	٣	irs	160	zs Lz	697	ŽOAZ	175'91	ZP't	6E17
	ted(1:1.1	09	Lt7T	£177	ZO'S	Z67£	0.7	1717££	L <b>v</b> ,t t	ZP't 007 68'0 91"	96T
	leavy sal	30	L9'E	ZS'Z	ZS'S	£6M	8S Z	61T1:	Ertl	68'0	£8T
	ji.	tr	١.	SSO	931 1.	6r017	10.2.	11'Vt.	fa'L	0 T6	L5'0
	.e • • • • • • • •	,-: <b>Q</b> XI	L.L.	U	=	9£TP	It.	±1 at	90'9	Lav	S17'I
	Phospholipid	fractions*		٢	<b>J</b> to	ol 7	V	) s	o N	0	0 Os

1 = Phosphatidyl serine.
3 = Sphingomyeline.
5 = phosphatidyl inositol.
7 = Phosphatidic acid + glyceryl phosphatides.
9 = Glycolipids.

0.88 % of fresh fish to reach 5.62 and 6.68, 7.38 and 7.45 and 11.75 and 11.44 % (120 days) of heavy-, medium,- and lightsalted fish, respectively. Sphingomyeline (S) fracti n increased only after 15 days of heavy and medium salting o fish while decreased over all the other treatments. Concern ng the PC fraction, it decreased when the salting time was inc eased. The PE fraction recorded the same trend of the PC fra tion. With respect of PAG, it was progressively increased in light-salted fish followed by the heavy-salted fish then, the medium-salted fish which recoded the lowest percent of PAG. Additionally, the P and G fractions were in creased (with very little exception) by increasing of the salting time over all the salted fis either the heavy-, medium-or light-salted bouri fish. It is worthy mentioning that the increasing of LPC may be sue to the oxidation of low-density lipoprotein complex (Ma the et aL, 2001). As well as, the increasing of PAG may be t ue to the lipolysis of some phospholipids. Furthermore, A indicated that the increasing of phospho pids was attributed to the partial breakdown of lipoproteins complex, meanwhile Bell et al. (1996) noticed that the dec easing of phospholipids is possibly due to the oxidation of ph e , pholipids which contain high levels of unsaturated fatty ac ds in its structure. Anyway, in addition to the previous refer nces, the results were confirmed by the finding of Castell et a (1965), Cuppett et al. (1989), EL-Sebaiy and Metwal i (1989), Ohshima et al. (1998), Marathe et al. (2001) a d Wally (2002).

Finally, according to the previous analysis including the chemical properties, oil constants, fatty acids composition and fractions and lipid and phospholipid fractions, it could be suggested that the medium-salted bouri fish for 120 days was the beast followed by the heavy-salted bouri fish while, the light-salted one recorded very poor characteristics.

#### G\_ Fat\_soluble vitamins:

Data presented in Table (29) show the fat-soluble vitamins (pg / g oil) of fresh bouri fish as influenced by drysalting conditions (period of salting and the rate of fish to salt used in salting process) during manufacturing of fermentedsalted bouri (Feseekh). The total loss of fat-soluble vitamins (FSV) was lower for medium-salted fish than that for heavysalted or light-salted fish, which recorded the highest total loss of FSV at any time of salting period. This may be due to the high oxidation occurred of the heavy-salted fish and the high lipolysis of light-salted fish. In this concern, Eriksson (1987) mentioned that lipids oxidation leads to nutritional damage including the loss of the essential fatty acids and fat-soluble vitamins. Further, Cuppett et al. (1989) and Maurice (1990) reported that increasing of salt level causes increased the oxidation level, provided that lipolysis enhanced the lipid oxidation. It is evident that gradual loss of FSV was observed by increasing the salting time till the end of salting period (120 days). Also, it is worthy mentioning that vitamin E was not detected in the heavy-and light-salted fish after 120 days of salting while it was found (18.64 pg / g oil) in the medium-salted fish. Also, vitamin K was absent at 90 days and till the end of salting period for heavy-and

	0		<b>4'1</b> -re 00										
ı dav)	O C7N	ä	0			- ci			8 <b>Z</b> 'U	alt)	p Imo		
Dry-salting period (in day)		0k 4.4 c1 1,3	-r In	<b>N</b> 00	N cr	ro E	Z	00		Light salted (3:Lfish:salt)		00	00
Dry	0	11	00	N r•i		Ok	ZZ 08	ON	<sup>4</sup> ? 00 N	Ligh		ON N •er	
			N	so	N 00 <b>N</b>		in	ON —r N.6	72		0	ON eI CO	N
					01		N C	CI)			Z 0 <b>%</b>	it	

light-salted bouri fish while it was only absent after 120 days of salting for the medium-salted one. According to the results obtained for FSV level, the descending order of products was: medium-, heavy-and light- salted bouri fish.

#### F- Statistical analysis:

#### 1- Oil constants:

The results of analysis of variances for oil constants of fresh bouri fish as influenced by salting conditions (including salting period for 120 days and fish: salt ratio used during salting) during manufacturing of fermented-salted bouri fish (Feseekh) are found in Table (30). The analysis or varience indicated that the differences between the salting styles methods(A) -either heavy, medium or light salting- were significant (p<0.05) for all the oil constants with exception for RI (non-significant (p>0.05) difference). Also, the differences between the salting periods (B) as well as the interactions between the salting styles and salting periods (AxB) had the same trend recorded for salting styles (A).

## 2 Lipid and phospholipid fractions:

Data presented in Tables (31 and 32) show the analyses of varience for lipid and phospholipid fractions of fresh bouri as affected by salting conditions (mentioned above) during processing of fermented-salted bouri fish (Feseekh). From the results, it could be noticed that the analysis or variance indicated that the differences between all the factors were significant (p<0.05) for all the lipid and phospholipid fractions, respectively.

· S	Df			F values for oil constants—	oil constants—	ř	
		RI	AV	ΗFA	PV	SV	Z
Replis 'on	Ν	0.9FNS	SN NO	co) O	co,	*	3. Z NS
A	2	1.11 NS	137o 00 a	1333.00 *	2679.00 *	*	* 0025.00
со	4	cf) 00	* 00 N -T	144.03 *	* 0 LC; 0Z	* O	* 00 285
A×B	00	1.01 NS	* OO If) 0/7	15Z %	370 00 *	a scc oc oc	34 90 *
Error	200						0000
Tot3	4						

A = fish : salt ratio used during salting

B= salting period

NS = non significant (P>0.05).

•• RI = Refractive index.

AV = Acid value(mg KoH/g oil).

FFA = Free fatty acids(%, as oleic)

PV = Peroxide value(meq /kg oil ).

SV = Saponification value per g of oil).

IN = Iodine number.

RESULTS AND DISCUSSION

Table (31): Analysis of variances (P=0.05) for lipid fractions of fresh bouri fish as influenced by salting conditions during processing of fermented-salted fish (Feseekh).

				щ	values for li	F values for lipid fractions-			
. °S	DL	1.4	N	3	4	5	se0	N	со
Replication	N	00 Z	00 sms1 6	00 Z.	* 41 tr;	S csi	CI Z Lel	* 444 00 Vl	6.21
	61	10804 *	649.22 *	4e Ose N	* 1.0 00 es,	129 ⋈ *	4 00 et N	611.9% *	1. In .1. 1 e
cc	els	ts•	923.15 *	* \$ 000	* z }	N es4 ti	323.98 #	% 4.64 *	3 In N OZ in
fx:	00	9.30 *	* N C	\$5.56 *	* 00 N	171.87 *	* Os estis	* M	* ON '1 ON <b>N</b>
O	00 N								
Toal	4								

NS = non significant(P>0.05).

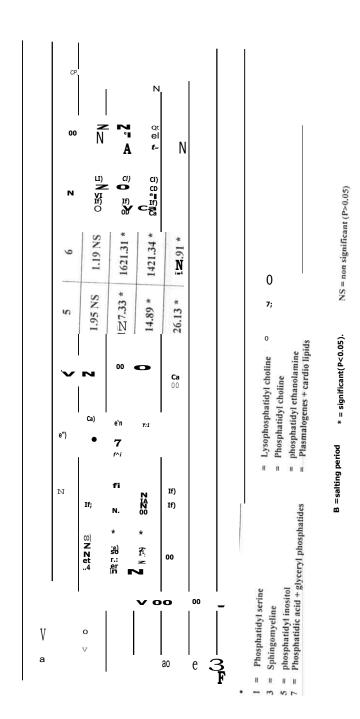
Cri O

to DD

B = salting period

 $\bullet \bullet$  A = fish : salt ratio used during salting

Diglycerides Free fatty acids Tocopherol Hydrocarbons



**RESULTS AND DISCUSSION** 

# IV- Effect of pretreatment (glazing with antioxidants) and frozen storage (at - 18 - C for 6 months) on fish oil attributes:

## **A- Chemical properties:**

The results of some chemical properties of fresh bolti and bouri fish as affected by glazing with antioxidants (tocopherol and BHT) and frozen storage at - 18 °C for 6 months are given in Table (33). The results indicated that the fresh bolti had higher (79.30 %) moisture and lower (1.85 %) fat contents than that of fresh bouri fish (77.57 and 5.41 %, respectively). Generally, the chemical properties of fresh bolti and bouri fish were illustrated as mentioned before in Table (16).

Glazing with antioxidants - either tocopherol (as a natural antioxidant) or BHT (as a synthetic antioxidant) - and frozen storage affected the chemical properties of fish as, it could be noticed that the moisture content was slightly increased only immediately after glazing with tocopherol or BHT of bolti fish, nevertheless, it was gradually decreased during frozen storage period (6 months). But as can be seen, the moisture content of bouri fish glazed with antioxidants decreased either immediately after glazing or during storage period. It is worthy to mention that the loss of moisture was higher for untreated samples (controls) than that for treated samples either of bolti or bouri fish. By the end of frozen storage period, the moisture contents of control, fish glazed with tocopherol (FGT) and fish glazed with BHT (FGBHT) were 77.48, 78.89

Table(33): Some chemical properties of fresh bolti and bouri fish as affected by glazing with antioxidants and frozen storage (-18  $^{\circ}$ C) for 6 months.

	#± 8	æ	Fre		-	reatme	ents and	l storag	e perio	d (in m	onth)		
	onent	(Raw)*	sh fis	Cont	rol		Toc	ophero	I)			внт	
	Components		2	4	6	0**	2	4	6	0**	2	4	6
	1						E	Bolti					
% Moisture	ww	79.3	78.6	7 78.51	77.48	79.34	79.19	78.99	78.89	79,31	79.21	79.05	T 70.0
шге	DW	-	-	-	1							73.00	78.9
%	WW	1.85	1.15	0.93	0.46	1.76	1.70	1.55	1.45	1.81	1.75	-	-
% Fat	DW	8.88	5.39	4.42	2.04	8.54	8.17	7.04	6.56		1.75	1.63	1.55
=======================================	ww	0.13	0.53	0.95	1.22	0.15	0.19	0.38	0.55	8.75	8.42	7,78	7.34
TBA	DIV	0.62	2.48	4.42	5.42	0.73	0.91	-		0.14	0.18	0.25	0.65
pH		6.30	6.26					1.81	2.61	0.70	0.87	1.19	3.08
		0.00	0.20	6.17	6.55	6.30	6.34	6.19	6.58	6.32	6.38	6.28	6.59
>							130	ouri					
% Moisture	ww	77.57	77.32	76.54	74.23	77.52	77.40	77.20	76.44	77.46	77.44	76.45	75.75
re	DW		-	-	-	-	34		-	-		-	
%	ww	5.41	4.85	3.94	2.66	5.37	5.15	4.84	4.25	5.43	5.37	5.10	
Fat	DW	24.14	21.38	19.79	10.32	23.89	22.79	21.23	18.04	24.09	23.89	21.68	4.51
	ww	0.12	0.75	0.81	1.66	0.25	0.41	0.59	0.77	0.24	0.36		18.60
ТВА	DW	0.53	3.31	3.45	6.44	1.13	1.81	2.59	3.27	1.07		0.55	0.75
Н		6.15	6.10	5.91	6.40	6.16	6.12	6.06	-	6.17	6.15	6.13	6.18

<sup>&</sup>quot; Fresh fish without any treatments (zero time of control).
" Immediately, after glazing of fish with antioxidants.

TI3A = thiobarbituric acid (nig malonahlehyde / kg).

1VW = wet weight basis.

DW = dry weight basis.

and 78.91 % for bolti corresponding 74.23, 76.44 and 75.75 % for bouri fish, respectively. The decrement of moisture loss rate of treated samples compared with control was possibly due to the effect of glazing which may be reduced the rate of moisture loss. Concerning the fat content, either on wet or dry weight basis, it could be noticed that the fat content decreased during storage for all the samples tested under this work provided that decreasing rate was lower for FGBHT than that for FGT then, control samples which recorded the highest loss of fat during and by the end of storage period. This may be due to the effect of antioxidants (used through glazing) that reduce the oxidation rates of lipids, consequently, the loss of fat for treated fish. The results of TBA confirmed the previous results recorded for fat whereas, the TBA values increased by increasing time of frozen storage provided that the controls recorded the higher TBA values after 6 months followed by that of FGT then FGBHT. For examples, by the end of storage the TBA values (on wet and dry weight basis) of control, FGT and FGBHT were 1.22 and 5.42; 0.55 and 2.61 and 0.65 and 3.08 for bolti corresponding 1.66 and 6.44, 0.77 and 3.27 and 0.75 and 3.09 mg MA/kg sample for bouri fish, respectively. Anyway, the antioxidants used through glazing of fish decreased the lipid oxidation as shown by TBA values changes, moreover, the BHT antioxidant was more effective against lipid oxidation than the tocopherol, nevertheless, due to many reasons particularly the trend of world to use the natural substances instead of synthetic one(the latter may be carcinogenic), the tocopherol as a natural antioxidant may be preferred. In this concern, **Shahidi (2000)** reported that due to safety concerns, interest in natural antioxidants has intensified, and therefore, mixed or individual to phenol and herbal extracts have been commercialized fo food and nutraceutical applications. Also, these results wer in parallel with the findings of Pawar and Magar (1966), Ja obsson and Sivik (1994) and Husveth et al. (2000). On the other hand, these results disagree with the finding of Wasson et al. (1991) and Mitsumoto et al. (1991) as they reported that the tocopherols are more effective as antioxidant than BHT.

#### **Boil constant:**

The data of Table (34) show the oil cons t (quality attributes of oil) of fresh bolti and bouri fish as in uenced by glazing with antioxidants (tocopherol and BHT as a natural and synthetic antioxidant, respectively, in separated form and frozen storage at -18 degree C for 6 months.

The quality attributes of oil of fresh fish ei er bolti or bouri were discussed as mentioned before. Concerni g the effect of glazing with tocopherol or BHT and frozen sto age on the quality attributes of oil (oil constants) of fish species used under this study, the results indicated that the refractive ind x (RI) was decreased during frozen storage period either for the ntreated or treated samples of bolti and bouri fish but, the decreasing rate of RI was higher for unglazed samples (controls) compared to the glazed samples either with tocopherol or BHT. M reover, the decreasing rate of RI nearly was higher in fish lazed with tocopherol than that of fish glazed with BHT. Anywa the lower the RI the higher the oxidation of fish oil as report by Wally (1981) and Maurice (1990). The iodine number ) as an RESULTS AND DISCUSSION

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 $Table(34): \begin{tabular}{ll} Oil constants of fresh bolti and bouri fish as affected by glazing with antioxidants and frozen storage (-18 \ ^\circ C) for 6 months. \end{tabular}$ 

				т	reatmen	ts and st	orage pe	riod (in ı	months)			
4t Wi 1,- 0.1	Fresh	(	Control			Tocopi	herol			ВН	T	
4 <u>+</u> 2 a Is	fish* (Raw)	2	4	6	0**	2	4	6	0**	2	4	6
Is.							Bolti					
RI	1.4677	1.4664	1.4660	1.4654	1.4667	1.4665	1.4665	1.4664	1.4667	1.4666	1.4665	1.4665
AV	1.58	1.81	2.10	2.88	1.60	1.67	1.77	1.84	1.58	1.60	1.64	1.72
FFA	0.79	0.92	1.10	1.44	0.81	0.83	0.89	0.94	0.76	0.80	0.82	0.85
PV	4.72	8.65	12.49	15.11	4.88	4.93	4.99	5.91	4.75	4.59	4.61	4.77
sv	186.72	186.82	187.41	188.88	186.73	187.09	187.36	187.64	186.70	186.96	187.15	187.30
IN	128.76	128.55	128.1	125.75	128.75	128.70	128.62	128.25	128.79	128.75	128.70	128.49
					•		Bouri					
RI	1.4681	1.4655	1.4650	1.4646	1.4663	1.4660	1.4660	1.4650	1.4664	1.4663	1.4660	1.4660
AV	1.44	1.99	3.14	3.99	1.59	1.70	1.80	2.90	1.50	1.75	1.88	1.99
FFA	0.74	0.95	1.60	1.94	0.79	0.85	0.90	1.40	1.25	0.85	0.95	0.99
PV	3.79	10.40	14.65	18.51	3.99	6.88	8.41	10.38	3.80	4.95	5.65	9.33
sv	186.64	186.97	187.91	188.59	186.81	187.21	187.66	188.01	186.76	187.06	187.39	187.80
IN	133.24	132.79	130.31	127.67	133.33	133.22	133.39	132.74	133.21	133.10	133.01	132.80

<sup>\*</sup> Fresh fish without any treatments (zero time of control).

RI = Refractive index. AV = Acid value (mg KoII/g oil).

FF = Free fatly acids (%, as oleic).

PV = Peroxide value (mcq /kg oil).

SV = Saponification value per g of oil.

= Iodine number.

<sup>&</sup>quot;\* Immediately, after glazing of fish with antioxidants.

indicator of the unsaturated double bonds recorded the same trend of RI. It is worth mentioned that the lower the IN the lower the degree of unsaturated and the higher the lip d oxidation. Therefore, according to the IN, oxidation rate occ ed in fish glazed with BHT (FGBHT) was lower than that o fish glazed with tocopherol (FGT) followed by control fish whech recorded the highest rate of lipid oxidation during storage p iod of fish species tested provided that bouri fish had higher Oxidation of lipid than that of bolti, possibly due to higher fat con ent of bouri than that of bolti as found in Table (33). Peroxide va ue (PV) and saponification value (SV) confirmed the previou results. It could be observed that the PV increased during fr zen storage period over all the tested samples either contra 1, FGT or FGBHT. For example, the PV at the end of froze storage (6 months) of control, FGT and FGBHT were 15.11, 5.:1 and 4.77 for bolti corresponding 18.51, 10.38 and 9.33 for bouri, respectively. With respect of free fatty acids (FF) and acid value (AV), both increased over all the tested sample stored at -C for 6 months may be due to hydrolysis o fish lipids occurred during storage period. The FFA and AV inc eased with increasing of storage time provided that the increas g rate was higher for bouri than bolti fish, as well as, it was higher for control than treated samples either FGT or FGBHT. Furthermore, it is worthy reporting that the hydr lysis may enhance the oxidation of fish lipids (Toyomizu et 1., 1981). Anyway, either by using tocopherol or BHT the oxidation rate of lipids of the fish tested was reduced but, the FGBH recorded the best effect, nevertheless, due to many reasons co cerned the

health, FGT should be selected. Similar results were reported by Takahashi *et al* (1978), St. Angelo (1996), Chapman and Regenstein (1997) and Hamilton *et* (1998).

## **C**- Fatty acids composition:

Results of fatty acids composition (as % of total fatty acids) of fresh bolti and bouri fish as affected by glazing with antioxidants and frozen storage at -18 °C for 6 months are given in Tables (35 and 36).

From the results, it could be observed that glazing with antioxidants (either tocopherol or BHT) and frozen storage for 6 months affected the fatty acids composition of bolti and bouri fish whereas some fatty acids were absent, others were increased, some were decreased, some fatty acids were decreased then increased and vice-versa (at different periods of frozen storage). This may be due to the hydrolysis or/and oxidation occurred for fish lipids during storage period. For example, C 10:0 and  $_{\mathrm{C12:0}}$  found in small amount (1.10 and 0.50 % respectively) in fresh bolti fish lipid (Table 35) were absent at any time of storage period (with very little exception), this was possibly due to hydrolysis of these saturated fatty acids. On the other hand, the reverse was recorded for Cmo and C12:0 in fresh bouri (Table 36) as these acids were not found in fresh bouri lipid and appeared at different times of storage particularly for untreated sample (control) and fish glazed with BHT (FGBHT). This was probably due to lipid hydrolysis and conversion of some fatty acids to other fatty acids. Myristic (C 14:0) acid of bolti and bouri fish lipids increased during frozen storage period either for controls, fish glazed with tocopherol (FGT) or fish glazed with

Table(35): Fatty acids composition (% of total fatty acids) of fresh bolti fish as affected by glazing with antioxidants and frozen storage (-18  $^{\circ}\mathrm{C})$  for 6 months.

Fatt	Fresh			Treatm	ents and	storage p	period (in	months	)	
Fatty acids composition	bolti (Raw)		Contro			Tocophe	rol		ВНТ	
on On	(14411)	2	4	6	2	4	6	2	4	6
C <sub>10:0</sub>	1.10	-	-	-	-	17.0			-	<u> </u>
C <sub>12:0</sub>	0.50	-		-		-	, Jian		0.58	-
C <sub>14:0</sub>	3.53	13.00	18.83	14.91	11.94	12.14	14.02	8.46	12.89	16.81
C <sub>15:0</sub>	1.10	1.34	0.60	1.92	0.13	0.20	0.47	0.28	1.70	2.02
$C_{16:0}$	16.43	23.47	31.70	37.23	26.54	34.40	30.75	25.31	19.55	20.92
C <sub>16:1</sub>	19.77	19.28	25.04	25.19	29.40	34.00	32.64	37.53	19.55	
C <sub>17:0</sub>	1.01	1.34	2.63	3.41	-	lu lu	-	-	5.43	30.26
C <sub>18:0</sub>	5.05	1.87	1.20	4.61	1.27	0.90	2.10	0.99	2.78	1.00
c,s,,	7.68	12.00	9.20	6.21	8.64	2.67	7.41	4.54	- 20	1.68
C <sub>18:2</sub>	14.22	6.35	1.31	1.10	8.46	8.93	6.80	8.92	17.45	1.01
C <sub>18:3</sub>	1.25	-	0.49	0.33		-	-		5.16	7.56
C <sub>20:0</sub>	4.12	4.44	1.97	3.61	0.67	1.59	2.81	0.66	0.48	1.01
C <sub>20:4</sub>	5.41	-	0.44	-	5.08	1.69	2.01	2000	1.49	3.36
C <sub>20:5</sub>	4.21	4.05	2.97	0.43	4.27	1.67	2.00	-	0.34	2.02
C <sub>22:0</sub>	1.34	3.52	-	0.55	- 1		2.09	6.44	4.20	2.75
C <sub>22:1</sub>	7.34	4.03		0.50			-	1.55	1.22	3.75
C <sub>22:6</sub>	5.34	4.31	3.61		2.00	-	-	•	2.58	5.60
C <sub>24:0</sub>	0.60		3.01	-	3.60	1.81	0.91	5.33	4.60	1.25
-24:0	0.00	-	-	-	- 41	-	4,	;-:	-	-

Table(36): Fatty acids composition (% of total fatty acids) of fresh bouri fish as affected by glazing with antioxidants and frozen storage (-18  $^{\circ}$ C) for 6 months.

			7	Γreatmer	its and sto	orage pe	riod (in m	onths)		
,5;	Fresh boo ri	(	Control		То	copherol			BUT	
° rg	(Raw) _	2	4	6	2	4	6	2	4	6
C <sub>10:0</sub>		0.87	0.90						0.70	
C12:0			0.35					1.00	0.17	6.74
C14:0	4.76	8.63	9.00	11.67	4.81	4.71	6.73	4.51	6.58	2.96
C15:0	0.36	2.04	1.66	2.65	1.14	1.41	2.79	1.09	2.14	
C16:0	14.68	15.45	20.27	40.15	25.05	29.91	24.03	21.26	10.20	25.43
C16:1	16.55	25.36	16.06	17.14	15.88	15.31	25.43	20.31	17.92	18.75
C17:0	0.81	0.36	0.83	0.53	0.27	0.34	0.63	0.35	1.69	1.62
C18:0	2.51	1.07	6.34	1.06	0.80	0.91	1.14	0.99	11.08	1.35
C18:1	16.30	18.04	26.75	14.85	20.29	15.80	14.43	16.17	16.28	10.33
C18:2	16.84	5.42	6.55	6.96	14.57	14.31	7.87	13.21	3.23	17.01
C18:3	0.18	0.40	0.21	0.27		0.51	0.38	0.35	10.93	0.54
C20:0	1.97	9.16	3.60	3.71	0.30	0.25	4.83	0.30	1.30	4.41
C20:4	2.45	0.76	4.83	1.0	3.18	4.93	2.57	2.19	2.70	0.27
		7 77			7.27	6.51	1.61	7.56	6.28	4.33
C22.0	5.21	-	0.42	-	-	-	5.30	2.31	2.37	0.54
C22:1	2.91	1.68	1.68	-	-	0.49	-	1.91	-	1.62
C22.6	6.49	3.54	-	-	6.45	4.61	2.26	6.49	6.44	4.10
C24 :0	0.57	-	-	-	-	-	-		-	-

BHT (FGBHT) compared with that of fresh fish s pies. Also, from results of Tables (35 and 36), it could be noticed that progressive increase of C 16:0 was observed during frozen storage of all the tested samples either for bolti or bouri fish but, the increasing rate in control samples was higher wh compared with FGT and FGBHT. Also, the increasing of C16: was higher for control and FGBHT of bouri fish than that of bol i fish while, the reverse was given in concern the FGT as the i creasing of <sup>Cl</sup> 6:0 was higher for bolti than bouri fish (by the end of storage). Of bolti fish (control or treatments) stored at -1 months, C18:0 and  $_{\rm C20:0}$  nearly decreased by compari g with that of fresh bolti fish. Stearic acids (Cts:o) recorded the same trend for all bouri samples with exception of control d FGBHT samples at 4 months of storage. Also, concerning th bouri fish, C20:0 (arachidic acid) increased in control samples at y time of storage while increased for FGT and FGBHT samp es only by the end of frozen storage. Different changes of C acid) were observed either for bolti or bouri sample stored at - $^{\circ}$ C for 6months. It is clear that  $_{\text{C24:0}}$  was absent overall the stored samples of bolti and bouri fish.

Regarding the unsaturated fatty acids of all bolti fish samples (Table 35), it could be indicated that palmi • leic (C 16:1) acid almost in creased in all the tested samples eith control or treatments during frozen storage period, as well as the same trend was nearly observed for that of bouri fis samples presented in Table (36). The reverse was recordea for whereas it decreased in all the tested fish samples (controls and treatments) during frozen storage of bolti and bouri (regardless

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Table(37): Fatty acids fractions (as % of total fatty acids) of fresh bolti and bouri fish as affected by glazing with antioxidants and frozen storage (-18  $^{\circ}\text{C})$  for 6 months.

Fatty*	Fresh			Treatm	ents and	storage 1	period (in	months		
acids	fish		Contro	<u> </u>		Tocophei			ВНТ	
fractions	(Raw)	<u>2</u>	<u>i 4</u>	<u>i 6</u>	2	4	I 6	2		6
	(==)					Bol ti				
T.sat.	34.78	48.98	56.93	66.24	40.55	49.23	50.15	37.25	45.64	48.54
T.unsat.	65.22	51.02	43.07	33.76	59.45	50.77	49.85	62.76	54.36	51.46
T.mono.	34.79	35.31	34.24	31.90	38.04	36.67	43.05	42.07	39.58	36.87
T.di.	14.22	6.35	1.31	1.10	8.46	8.93	6.80	8.92	5.16	7.56
T.tri.	1.25	-	0.49	0.33	-	-	-	-	0.48	1.01
T.tet r.	5.41	-	0.44	-	5.08	1.69	-	-	0.34	2.02
T.pent.	4.21	5.05	2.97	0.43	4.27	1.67	2.09	6.44	4.20	2.75
T. h ex.	5.34	4.31	3.61	-	3.60	1.81	0.91	5.33	4.60	1.25
T.poly.	30.43	15.71	8.82	1.86	21.41	14.10	9.80	20.69	14.78	14.59
Ks	1.88	1.04	0.76	0.51	1.47	1.03	0.99	1.68	1.19	1.06
						Boo ri				
T.sat.	30.87	37.58	43.37	59.77	32.37	37.53	45.45	31.81	36.23	43.05
T.unsat.	69.13	62.42	56.63	40.22	67.63	62.47	54.55	68.19	63.77	56.96
T.mono.	35.76	45.08	44.49	31.99	36.17	31.60	39.86	38.39	34.20	30.70
T.di.	16.84	5.42	6.55	6.96	14.57	14.31	7.87	13.21	3.23	17.01
T.tri.	0.18	0.40	0.21	0.27	-	0.51	0.38	0.35	10.93	0.54
T.tet r.	2.45	0.76	4.83	1.00	3.18	4.93	2.57	2.19	2.70	0.27
T.pent.	7.41	7.22	0.55	-	7.27	6.51	1.61	7.56	6.28	4.33
Ellex.	6.49.	3.54	ı	1	6.45	4.61	2.26	6.49	6.44	4.11
'i .poly.	33.37	17.34	12.14	8.23	31.47	30.87	14.69	29.80	29.58	26.26
Ks	2.24	1.66	1.31	0.67	2.09	1.66	1.20	2.14	1.76	1.32

= Total saturated f tty acids. = Total di-unsatura ed fatty acids. T.di.

T.pent. = Total pent-unsaturated fatty acids.

Ks = T.unsat | Tsai.

T.t nsnt. = Total unsatura rd fatty arid .

T.tri. = Total tri-unsaturated fatty a id = Total tri-unsaturated fatty a ids. Theo. = Total hesa-unsaturated fatty acids T.mono. =Total mono-unsaturated fatty acids
T.tetr. = Total tetra-uncaturated fatty acids = Total tetra-unsaturated fatly acids. = Total polyunsaturated fatty acids. T.poly

(TMUFA) results, it could be summarized that the percent of TMUFA nearly increased after storage for only 2 months (compared with fresh fish) then decreased till the end of frozen storage for all the samples either control or treatmen s of bolti and bouri fish (With very little exception for FGT of uri at the 6<sup>th</sup> month of frozen storage). With respect of t tal polyunsaturated fatty acids (TPUFA), in comparison wi h that of fresh fish, the TPUFA gradually decreased by increasing of storage time overall the tested samples provided that the decreasing of the TPUFA was higher in untreated samples (control) than that of treated samples (FGT and FGBHT, respectively) indicating more oxidation that occurred for controls than treatments of bolti and bouri fish. Moreover, the Ks (TUFA / TSFA) as an indicator of the unsaturated degree confirmed the previous results. The higher the Ks the lower the oxidation of fish lipids and the vice versa will be found. All the sample of bouri had higher Ks than that of bolti fish samples. Furthermore, FGBHT samples recorded higher Ks followed by FGT samples while; control samples recorded the lowest Ks and accordingly the highest oxidation of lipid.

## **E-Lipid fractions:**

The effects of glazing with tocopherol (as a natural antioxidant) or BHT (as a synthetic antioxidant) and frozen storage (-18 °C) for 6 months on the lipid fractions (as % of total lipids) of fresh bolti and bouri fish are presented in Table (38). The lipid fractions of fresh bolti and bouri fish were illustrated as mentioned above in Table (18).

Table(38): Lipid fractions (% of total lipids) of fresh bolti and bouri fish as affected by glazing with antioxidants and frozen storage (-18 "C) for 6 months.

				Tr	eatment	s and st	torage p	eriod (ir	n month	s)		
Li Tract	Tresh (R		Control			Tocop	herol			ВІ	-IT	
Lipid Fractions #	Fresh fish* (Raw)	2	4	6	0**	2	4	6	0**	2	4	6
#	*						Bolti					
1	54.40	47.48	47.04	35.43	54.10	50.16	50.15	46.39	54.31	52.89	52.62	51.16
2	28.57	19.95	17.29	7.25	27.10	23.41	21.27	21.03	26.91	24.04	22.59	22.59
3	-	2.99	4.35	9.77	-	1.90	1.91	1.95	-	1.38	1.78	1.89
4	3.11	4.37	5.29	5.62	3.15	3.65	3.88	4.00	3.13	3.47	3.60	3.85
5	4.77	9.87	7.61	20.57	4.91	6.88	7.82	11.00	4.85	6.90	6.49	6.41
6	4.36	6.18	7.88	10.30	4.38	5.83	5.91	6.19	4.36	4.80	5.44	5.85
7	2.62	2.40	2.30	-	3.90	3.50	3.25	2.45	3.60	3.52	3.38	3.25
8	2.17	6.76	8.24	11.06	2.46	4.67	5.81	6.99	2.84	3.00	4.10	5.00
							Bouri					
1	45.10	41.14	40.11	38.24	44.90	42.77	42.06	40.31	44.61	44.29	43.29	42.17
2	32.28	24.59	22.06	15.42	30.30	29.43	26.76	26.38	32.32	30.09	28.74	28.00
3	0.78	2.14	5.19	2.38	0.90	1.88	2.64	3.57	0.82	1.55	3.63	3.24
4	3.39	4.42	4.38	6.51	3.66	3.98	4.15	4.90	3.53	3.73	3.88	4.23
5	4.96	10.35	5.58	17.41	4.66	4.86	5.78	7.53	4.96	5.11	5.46	6.41
6	4.14	6.33	11.62	9.44	4.88	6.07	8.19	8.47	4.28	5.48	6.79	7.51
7	3.48	2.67	2.05	0.40	4.67	4.38	3.56	1.98	3.44	3.30	3.16	2.50
8	5.87	8.36	9.01	10.20	6.03	6.63	6.86	6.86	6.04	6.45	6.05	7.96

<sup>\*</sup> Fresh fish without any treatments (zero time of control).

 1
 =
 Triglycerides
 5
 =
 Diglycerides.

 2
 =
 Phospholipids.
 6
 =
 Free fatty acids.

 3
 =
 Monoglycerides.
 7
 =
 Tocopherol.

 4
 =
 Cholesterol.
 8
 =
 I ly drocarbons.

 $<sup>\</sup>boldsymbol{**} \ \textbf{Immediately, after glazing of fish with antioxidants.}$ 

The data of Table (38) showed that phospholipids fraction decreased during frozen storage period for control and treatments of bolti and bouri fish but, the loss of phospholipids was remarkably higher in controls than that of fish glazed with tocopherol (FGT) or fish glazed with BHT (FGBHT) of both bolti and bouri. Moreover, the loss of phospholipids was lower in FGBHT than FGT indicating that BHT as antioxidant was more effective in reducing the loss of phospholipids than tocopherol. Anyway, the loss of phospholipids fraction may be due to the phospholipids hydrolysis (destruction), as reported by **Bell** et al. (1996). For example, by the end of frozen storage (6months), the phospholipids of control, FGT and FGBHT were 7.25, 21.03 and 22.59 % for bolti corresponding values were 15.42, 26.38 and 28.00 % for bouri. On the other hand, It could be observed mono-glycerides (MG) fraction was absent in fresh bolti and immediately after glazing with antioxidants of bolti fish while appeared during storage and gradually increased with increasing of storage time till the end of storage period, the percent of MG recorded for control was higher than that of bolti treatments. All the samples of bouri fish either control or treatments recorded the same trend of MG mentioned above for control and bolti fish treatments. The results in Table (38) were also indicated that free fatty acids (FFA) fraction nearly recorded the same trend of MG fraction as, the FFA fraction increased with higher level of control compared with treatments over all the tested samples of bolti and bouri fish. Contrary to FFA, the triglycerides (TG) fraction was decreased during the frozen storage period provided that the decrement level was higher for control than treatments

either for bolti or bouri fish. Moreover, the decrement level of TG was lower for FGBHT than that of FGT either in bolti or bouri fish. With respect to diglycerides (DG) fraction, different changes at different times of frozen storage were observed for the tested samples of bolti and bouri fish. Anyway the increase of MG and FFA and the decrease of TG as well as the different changes of DG were possibly due to thee hydrolysis of lipid during storage of fish. Cholesterol and hydrocarbons fractions were nearly increased by increasing the storage period for all tested samples and almost had the same trend of the FFA. The increase of cholesterol fraction was probably due to the degradation of lipoproteins-cholesterol complex as well as the decrease of moisture during frozen storage at -18 °C for 6 months. Finally, tocopherol fraction decreased during storage of control, FGT and FGBHT to reach at the end of storage 0.00, 2.45 and 3.25 % for bolti fish versus 0.40, 1.98 and 2.50 % for bouri fish, respectively when the comparison was carried out with that of fresh bolti (2.62 %) and bouri (3.48 %) fish. Nevertheless, the increase of tocopherol was only observed immediately after glazing with tocopherol, and then decreased by storage. The decreasing of tocopherol fraction was lower for FGBHT followed by FGT then control. This maybe due to that BHT was more effective against oxidation (the latter decreases the tocopherol fraction) than tocopherol which was better than control. Similar results were given by Tsukuda (1976), Gibson and Worthington (1977), Jakobsson and Sivik (1994), Muggli (1994), Hamilton et aL (1998) and Husveth et aL (2000).

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## F-Phospholipid fractions:

The results of Table (39) show the phospholipid included phosphatidyl serine (PS), Lysophosphatidyl cholin (PC), sphingomyeline (S), phosphatidyl cholin (PC), phosphatidyl inositol (PI), phosphatidyl ethanolamine (PE), phosphatidic acid + glyceryl phosphatides (PAG), Plasmalogenes + cardio lipids (P) and glycolipids (0) of fresh bolti and bouri fish as affected by glazing with antioxidants (tocopherol and BHT) and frozen storage at -18 °C for 6 months.

Form the results, it could be noticed that the PS and LPC fractions increased during frozen storage and still increased up to the end of storage either for untreated (control) or for treated samples of bolti and bouri fish. By the end of storage, the percent of PS or LPC was higher for control than FGT and FGBHT, as well as PS was higher for FGBHT than FGT. In this concern, Marathe et al. (2001) reported that the increasing of LPC might be due to the oxidation of low-density lipoprotein (LDL). On the other hand, remarkable decrease for PC and PE fractions during frozen storage periods overall the tested samples either control or treatments of bolti or bouri fish. But, the loss of PC and PE was higher for control followed by fish glazed with tocopherol (FGT) and fish glazed with BHT (FGBHT). For example, by 1 1e end of storage, the values of PC and PE fractions for control FGT and FGBHT were 29.48 and 22.78; 37.84 and 30.94 and 39.00 and 29.86 % of bolti corresponding 22.41 and 12.38; 39.91 and 25.48 and 38.34 and 27.21 % for bouri, respectively compared to fresh fish that recorded PC and PE values of 46.86 and 33.33 for bolti and 43.36 and 38.13 % for bouri, respectively. Concerning the PI

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Table(39): Phospholipid fractions (% of total Phospholipids) of fresh bolti and bouri fish as affected by glazing with antioxidants and frozen storage (-18 °C) for 6 months.

Phos Fra	rfs		<b>a</b> :		Treatm	ents and	storage	period	(*n mon	th)		
pho			Contr	ol		Toc	pherol			1	ВНТ	
Phospholipid Fractions +	*	2	I 4	I 6	0**	12	4	6	0*	* I 2	I 4_	6
			,			,	Bol ti					
1	1.26	2.70	3.38	3.45	1.24	1.55	1.69	1.81	1.24	1.47	1.55	1.6
2	0.79	1.75	2.64	2.91	0.82	0.91	1.07	1.45	0.76	0.74	1.96	2.9
3	5.56	8.74	6.31	6.44	5.50	5.75	6.09	5.66	5.81	5.15	6.76	6.4
4	46.86	31.11	30.00	29.48	46.23	45.37	43.16	37.84	46.48	45.98	43.14	39.0
5	0.46	0.48	0.42	0.36	0.67	0.63	0.59	0.47	0.67	0.64	0.61	0.50
6	33.33	25.81	24.71	22.78	33.26	33.85	32.66	30.94	33.35	33.34	30.34	29.8
7	7.79	17.11	19.34	19.81	8.15	8.34	10.30	14.65	7.70	9.66	11.53	13.6
8	2.69	10.21	8.92	9.84	2.52	2.91	2.84	3.63	2.86	2.64	3.00	3.80
9	1.26	2.09	4.28	4.93	1.61	0.69	1.60	3.55	1.13	0.38	0.61	2.04
							Bouri		1		+ 0.01	2.04
1	0.72	5.82	6.44	8.44	0.77	1.54	1.87	2.25	1.56	1.83	1.84	2.84
2	0.88	3.55	3.63	2.42	0.93	1.13	1.23	1.76	1.45	1.88	1.54	2.30
3	7.22	9.28	6.58	8.44	6.49	7.73	7.91	7.97	5.38	5.25	6.66	8.44
4	4336	30.41	28.80	22.41	43.01	42.07	43.01	39.91	43.91	40.54	36.18	38.34
5	1.31	5.44	7.68	10.42	0.85	1.65	2.85	3.73	0.94	1.88	2.48	4.01
6	38.13	21.43	20.07	12.38	38.38	33.43	29.11	25.48	37.16	36.20	34.43	27.21
7	6.06	19.43	19.48	17.73	7.23	9.32	9.59	11.67	7.00	8.34	9.51	10.41
8	0.87	2.59	3.43	8.38	0.80	1.35	1.78	2.44	1.08	1.48	2.32	3.39
9	1.45	2.05	3.89	9.38	1.54	1.78	2.65	4.79	1.52	2.59	5.04	3.06

<sup>\*</sup> Fresh fish without any treatments (zero time of control).

\*\* Immediately, after g azing of fish with antioxidants.

I = Phosphatidyl serine

3 = Sphingomyelinc5 = phosphatidyl inositol

7 = Phosphatidic acid + glyceryl phosphatides

2 = Lysophosphatidyl choline

9 = Glycolipids

4 = Phosphatidyl cholinc

<sup>6</sup> = phosphatidyl ethanolamine

8 = Plasmalogenes + cardio lipids

fraction, it was increased immediately after glazing with antioxidants then decreased till the end of storage of bolti while, the reverse was recorded for bolti fish, since the PI fraction was decreased immediately after glazing with antioxidants then increased till the end of storage period. With respect of PAG fraction, generally, it could be noticed that the PAG fraction increased by increasing the storage period overall the tested samples of bolti and bouri fish provided that controls had higher percent of PAG followed by FGT and FGBHT which recorded mostly the lowest percent of PAG at the end of storage. This means that BHT more effective as antioxidant than tocopherol, as well as indicates that more hydrolysis of phospholipids was occurred in control samples during storage. Of S< P and G fractions, different changes at different time of storage were observed for bolti fish nevertheless, the levels of these fractions were mostly higher for control than that of treatments. Concerning the P and G fractions of bouri, it was increased during frozen storage up to the 6 th month (the end of storage) provided that the increasing level was remarkable for control than treatments. These results were confirmed by the finding of Segawa et aL (1994), Burkow et as (1995) and Nwosu (1996).

Anyway, either tocopherol or BHT, glazing with antioxidants of fish decreased the lipid and phospholipid oxidation, and the BHT was more effective than tocopherol against oxidation. Nevertheless, tocopherol should be applied instead of BHT because the predominant trend over all the world is interested in natural antioxidants (tocopherol), therefore due to

safety concerns, suggestions for its use have been intensified (Shahidi, 2000).

### <u>G\_Fat\_soluble vitamins:</u>

The effects of glazing with antioxidants- either tocopherol or BHT- and storage at -18 °C for 6 months of fresh bolti and bouri fish are indicated in Table (40). From the data, it could be noticed that glazing with tocopherol (as a natural antioxidant) or BHT (as a synthetic antioxidant) affect the fat-soluble vitamins content of treated fish compared with control (fish without any glaze additive). Immediately after glazing with antioxidants, with exception of vitamin E of fish glazed with tocopherol, slight loss of fat-soluble vitamins (FSV) was observed either for bolti or bouri fish. Vitamin E content increased (with slightly) immediately after glazing with tocopherol to reach 189.67 and 188.49 gg / g for bolti and bouri fish compared to its controls (182.68 and 165.49 gg/g), respectively. During frozen storage for 6 months, gradual loss of FSV was recorded provided that the loss rate was lower for fish glazed with BHT than that of fish glazed with tocopherol. Nevertheless, the loss rate of FSV during frozen storage was lower for fish glazed with tocopherol than that of control samples (either for bolti or bouri fish), which recorded remarked loss of FSV. This may be due to the effect of antioxidants in reducing the oxidation levels that may be occurred during storage period; in addition that water glaze provides limited protection of fish against oxygen (Chapman and Regenstein, 1997). The rate of loss was also higher for bouri than bolti glazed samples. Anyway, for example, by the end of frozen storage, the values of vitamin A, E and k of fish

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			v:)		99'1Z1	6VSZI	69 £1		187.41	68 Z9	
bA		1:			148.29	Z8'94 l	58'0Z 1		231.57		
4.4 im.		111/1	el		ort'S1	ZI.'551	Z9'8Z		srzcz	8r1.51	18T£
Vl Er	nonths)		#40		Z£'951	1r091	6t 7£		-l £'69Z	L8*£91	
o o c E	Treatments and storage period (in months)		.0		191'8	122.87	98'8		141.41	Tf 89	
-6 а	orage pe	herol	.1	!Hog	ZL'Ot1	149.80	£5'81	Bouri		.Will	
,#) 0	ts and st	Tocopherol	e'11		19'051	175.82	£9'ZZ			169,89	35•81
o 'ö 1_	reatmen		*40		irs;st	L9'681	Z9, H			61 '881	6rht
<b>bl)</b> ti O	L				9c tt	I				i	6t
Сс		Control			107.40	118.39	l£T1			Irt9	
.O n' v) '; <sup>6</sup> v':					9rtt1	132.41	1r81.			92.81	1rIt
Li C		<sub>L</sub> I-,1	<b>1 "i:</b> t,;'. x		158.84 1	897.81	19'8£		tron	6rs91	£6.9r
4.4 ea			juitmA niosle							w	2

Fresh fish without any glaze additive (zero time of control).
 Immediately, after glazing of fish with antioxidan

glazed with tocopherol and BHT were 84.61, 122.87 and 8.86 and 121.66, 125.49 and 13.69 for bolti corresponding 141.41, 73.89 and 12.55 and 187.41, 68.29 and 17.93 for bouri versus 44.36, 0.00 and 0.00 and 83.29, 0.00 and 5.29 [tg/g for control of bolti and bouri, respectively. It is clear the effect of using antioxidants through glazing of fish stored at -18 °C nevertheless, due to safety concerns, interest in natural antioxidants has intensified, therefore, tocopherol have been commercialized for keeping quality of fish. These results were in agreement with the findings of Wasson *et al.* (1991), Mitsumoto *et al.* (1991), Jakobsson and Sivik (1994), Hamilton *et al.* (1998) and Shahidi (2000).

#### **H-Statistical analysis:**

## 1- Oil constants:

Analysis of variances for oil constants of fresh bolti and bouri fish as affected by glazing with antioxidants (tocopherol and BHT) and storage at -18 °C for 6months are found in Table (41). It could be observed that the analysis of variance indicated that the differences between the fish types (bolti and bouri) were significant (r0.05) for all the oil constants. Also, the differences between the treatments (glazing with tocopherol or BHT compared to control) were significant (r0.05) for all measurements of oil constants. The same trend of the differences between fish types or between treatments was recoded for the differences of the interactions between the treatments and storage periods. The interactions between the fish species (bolti and bouri) and treatments (glazing with tocopherol or BHT

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affected by glazing with antioxidants (tocopherol and BHT) and frozen storage Table(41): Analysis of variances (P = 0.05) for oil constants of fresh bolti and bouri fish as (-18 °C) for 6 months.

Č	•			F values for oil constants••	l constants••		
source•	ı	In	AV	Vd.3	Ad	AS	NI
Replication	eN	*01'S	<u>0V9</u>	* as s	E9'\$£	ı OS,	* 017'8
⁴t		* OrZS	<u>09'EL</u>	<u>0C6S</u>		789.85 *	* OCZ111
ca	ei	Orr	. t776		13367.00 *	* SE'SII	LCS6
flxV	14	033 NS	SL'9	* 06'ZZ	* 85'98	£6,96 *	OL'IZ
Q	VI	* 667E	<u> 1r8Z1</u>	139.05 *	7653.65 *	* L5'99	16,0S
DxV	in	<u>SN L6'0</u>	* 087Z	* 96'6S	* 05't8I I —	XTI6 *	*S67
3x13	1,	<u>9111</u>	. 03'9Z	,4 9079	* 00'850Z	28.76 *	ETSZ
AxBxC	o	SN ZVI	LL't	S£11	* 98'8f	* W	* OL7
Error	<u>917</u>						
Total	E						

A = significant(P<0.05), NS = non significant(P>0.05).

C = storage period • A = fish type
B = treatments

•• RI = Refractive index.

AY = Acid value (mg KoHlgm oil).

FFA = Free fatty acids(%, as ofeic)

PW = Peroxide value(meq /kg oil )

SV = Saponification value (per gm of oil).

IN = Iodine number.

beside control), between the type of fish and storage period and between the fish type, the treatments and the storage periods were non-significant (p>0.05) for RI and significant (p<0.05) for the others oil constant.

## **ZLOcka** fractions:

Data presented in Tables (42 and 43) show the analyses of variances for lipid phospholipid fractions of fresh bolti and bouri fish (respectively) as affected by glazing with antioxidants and frozen storage for 6 months (as mentioned above). The differences due to treatments, storage periods or the interactions between treatments and storage periods were significant (p<0.05) for all lipid fractions. Also, the differences due to fish species were significant (p<0.05) for all lipid fractions but with exception for monoglycerides and tocopherol fractions (nonsignificant (p>0.05)). The interaction between the fish types and the treatments were non-significant (p<0.05) for phospholipids and hydrocarbons fractions and significant (p<0.05) for the other lipid fractions. Also, the interaction between the fish types and storage periods were only non-significant (p>0.05) for tocopherol fractions among all lipid fractions. Concerning the interactions between fish types, treatments and storage periods, the differences were non-significant (p>0.05) for hydrocarbons, tocopherol and cholesterol fractions while were significant (p<0.05) for triglycerides, free fatty acids, diglycerides and monoglycerides fractions. On the other hand, data presented in Table (43) show the analysis of variances for phospholipid fractions of fresh bolti and bouri as affected by the same conditions mentioned in Tables (41 and 42). From the data of

	7				F values for lipid fractions•	pid fractions	•		
aarnos	Ä		eu	М	er	kn	a°	N	00
<b>I</b> Replication	N	SN 8r1	SN STO	sn9ro	1.15 NS	1.15 NS 0.58 NS	SN ISO	SN 611	SN SIT
•ļ!		* 6C8OSZ	* OWSEI I	SN 9CI	* ZCLZ	* 86'tIZ	* SE19Z	STASM 020	sra
00	N	332.75 *	533.60*	<u>.6WILt</u>	*ZO'001	17.74 *	* <u>Sr99E</u>	* 69'911	38.24*
fixV	N	72.58*	1.85 NS	* St'S6Z	* 19'17	* LrZ801	* SZ'6	* 86,	O 77 NS
U	VI	<u>. 6WtZt</u>	.06'985	*178•968	* OVOZI	* OrIE	764.73 *	* I£1ZI	* 16'9Z
χV	fn	* EI'19	*ACS	138.79*	. 9V6	* 66TZt	50'8L	<u>SN 991</u>	. EWL
DM"	o	8I'IL	* 011tI	* EI'901	* 6r91 * 51.85 *	* 6r9I	* L61 8	PLLI	* IC9
[ DxfixV	o	* <b>Zr6Z</b>	* 08't	* 01'861	3.42 NS	* IZ' <u>IZZ</u>	* 9WOE	2.46 NS	0.42 NS
917	917								
I Total	IL								

Phospholipids
Monoglycerides

RESULTS AND DISCUSSION ----

	j			H	values for	F values for phospholipid fractions•	id fractions	•		
.3 31nos	5		e.1	м	et	If)		~	00	O's
Replication	1-1	* 661	SN EVE	2.44 NS	<u>SN</u> ICI	* cr /.	*96T	sN 86'1	3.41 NS	28.23 *
et	-		89'651	8!T61	675.52 *	2344.50 *	15'81.	£6'917	2533.40 * I 10 1,9 t	,4 6'J 01 I
0:1	1-1	3172.00 *	* 111 69	ZST9		3902.20 *	3902.20 * 2539.10 *	915.83 *	01'998Z	* 8919
OxV	e.II		29.73 *	6I'9Z	* L6'09	60.9T * 4660.90 * I 268.01 *	I 268.01 *	* LteZI	* P6TIS	* Z6'9
()	f	* 09'LLII	* IC9E5	* 09'9P	1775.80 *	1775.80 * 2675.90 *		541.32 *	* OrSLOI	1449.00 *
DxV	e.1	* 9614£	*£E111	* RE'S'	*9L'L	* OL'986Z	473.36 *	Z9'Or	. 61'EPI	*11171
ax*[]	•Co	* 89'Ltt	* 68'5P1	*	432.79 *	487.83 *	* 6rLOE * 88.784	134.23 *	* PITLE	It'LZ
jx\$xV	'.o	. 50'1171	*11'55	.95'5	*1 6'n	* 851LP	08*Z5	691.	05'8E1	* 06'51
Error	91?									
Total	П									
= Phosphatidyl serine = Sphingomyeline = phosphatidyl inositol z = Phosphatidic acid+gl	l serine ine inositol acid+glyce	Phosphatidyl serine Sphingomyeline phosphatidyl inositol Phosphatidic acid+ glyceryl phosphatides	I    (4 of O	Lysophosphatidyl choline Phosphatidyl choline phosphatidyl ethanolamine Plasmalogenes + cardio lipids	tidyl choline choline ethanolamin es + cardio li	spic		A= fish type B= treatments C= storage period	ŏ	* = significant(P<0.05) NS = non significant(P

A= fish type \* = significant(P<0.05).
B= treatments NS = non significant(P>0.05).
C= storage period

g = Sphingomyeline

= phosphatidyl inositol

z = Phosphatidic acid+ glyceryl phosphatides

G = Glycolipids

