SUMMARY

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Due to the importance of fish as a source of healthy oil, fish and its products should be characterized with high quality to obtain and consume fish oil with high quality. Processing, cooking method and storage condition may be affecting the quality of fish oil because of the high content of unsaturated fatty acids in its structure. Therefore, this study was conducted to evaluate the effects of some different processing, cooking methods and storage conditions on the different quality attributes of fish oil. The results of this study could be summarized as follows:

I- Smoking offish:

A-Chemical properties:

The frozen herring fish used for processing of smoked herring recorded 70.69 %, 10.71 % and 0.45 mg malonaldehyde/kg for moisture, fat and thiobarbituric acid (TBA) value, respectively (on wet weight). Meanwhile, immediately after smoking of herring (zero time), the moisture content of all the smoked herring decreased (54.72-57.55 %, according to smoking method) than that of raw frozen herring (70.69 %). Cold-smoked herring recorded the lowest (54.72 %) moisture content followed by hot-smoked herring (56.62 %) and liquid-smoked herring that recorded the highest (57.55 %) moisture content.

Due to storage either at room temperature 25 °C or at cold (4 °C), the moisture content of liquid-, cold-and hot-smoked

herring decreased with increasing of storage time provided that such loss was pronouncedly retarded when the storage temperature decreased from 25 °C to 4 °C.

The raw frozen herring contained 36.54 % of fat (on dry weight). By different smoking methods, the fat content increased (on wet weight) nevertheless, it decreased on dry weight basis where, the fat contents decreased from 36.54 in raw herring to reach 25.87, 29.11 and 25.70 % in liquid, cold and hot-smoked herring, respectively. During storage, the fat content of all the smoked samples (either at room temperature 25 °C or at cold 4 °C decreased until the end of storage periods, (on dry weigh).

Thiobarbituric acid (TBA) contents of frozen herring was 1.54 mg malonaldehyde / kg sample, but immediately after smoking (zero time), the liquid-smoked herring recorded lower TBA value (1.58) than the hot and cold-smoked herring which had values of (1.66 and 1.94 mg malonaldehyde/kg sample, respectively on dry weight basis). During storage at room temperature, the TBA values of all the smoked herring were increased by the increasing of storage time but, by the end of storage, the hot-smoked herring had lower (4.6 malonaldehyde/kg sample, more oxidation) TBA values dry than cold (6.43 malonaldehyde/kg) and liquid-smoked (8.05 malonaldehyde) herring on dry weight basis. TBA 'values of smoked herring stored at 4 °C were lower than those stored at room temperature.

Total phenols were not detected in raw frozen herring fish. By smoking with different methods, the cold-smoking herring had the higher content of phenols than liquid and hot-

smoked herring. Phenols content was decreased to reach to 33.82, 17.77 and 9.16 mg/100g sample at the end of storage for 30 days at room temperature for cold, liquid and hot-smoked herring respectively (on dry weight basis). The values by the end of storage at 4 °C for 90 days were 52.46, 40.07 and 29.07 mg/100 g samples, respectively.

B- Oil constants:

Refractive index (RI), acid value (AV), free fatty acid (FFA, as oleic acid), peroxide value (PV), saponification value (SV) and iodine number (IN) of oil extracted from raw frozen herring fish, were 1.4702, 1.64, 0.83, 4.32, 203.13 and 135.75, respectively. Immediately after smoking (zero time), the results showed that RI, PH and IN decreased while, AV, FFA, PV and S.V increased for all smoked herring samples liquid, cold or hot-smoked herring. By the end of storage either at 25 °C or 4 °C, the cold-smoked herring oil was more stable when compared with liquid and hot-smoked herring oils, respectively. Nevertheless, the quality attributes of oil extracted from liquid-smoked samples were the nearest to that recorded for cold-smoked samples (the best) during storage and by the end of storage either at 25 °C or 4 °C. Storage of smoked herring at 4 °C for 90 days may be better than storage at 25 °C for 30 days. For more safety and to consume smoked fish with high quality, storage of smoked herring should not exceed 20 days at room temperature and 60 days at cold storage under the conditions of this study.

C- Fatty acids composition and fraction:

It could be noticed that the predominant saturated fatty acids was the palmitic acid (C16-0) in raw frozen herring while,

the predominant unsaturated fatty acids were oleic ($C18_{,1}$), docosahexaenoic (C22:6), eicosapentaenoic ($C_{20:5}$) and linoleic ($C18_{,2}$) respectively. The total polyunsaturated fatty acids showed 34.01 % of total fatty acids for raw frozen herring. All smoking methods affect the essential fatty acids content, nevertheless, the liquid-smoked herring was the best followed by cold and hot-smoked herring. Immediately after smoking, lipid oxidation was occurred as the total saturated fatty acids were increased and the total unsaturated fatty acids (TUFAs) were decreased but, oxidation level was lower of liquid followed by cold-and hot-smoked fish. During storage either at 25 °C or 4 °C, the cold-smoked fish showed lower oxidation than liquid smoked one while hot-smoked fish indicated more oxidation at the same time nevertheless, oxidation levels were higher at 25 °C then 4 °C.

D- Lipid fractions:

By using thin layer chromatography, the results indicated that the raw frozen herring revealed eight fractions oI lipids as follow: 1) phospholipids (PL), 2) monoglycerides (MG), 3) cholesterol (CL), 4) diglycerides (DG), 5) free fatty acids (FFA), 6) tocopherol (TO), 7) triglycerides (TG) and hydrocarbons (HC). Immediately after smoking process the percent of MG, HC, FFA, and CL fraction, were increased by using the different smoking methods either liquid, cold or hot smoking while at the same time, the TG was decreased. During storage of smoked herring, it could be noticed that the PL and TG decreased by increasing the storage period either at 25 °C or 4 °C, for all the smoked samples included liquid, cold and hot smoked herring.

SUMMARY ---

E- Phospholipids fractions:

The results indicated that the greatest phospholipid fraction was phosphatidyl choline (PC, 35.57 %) followed by phosphatidyl ethanolamine (PE, 27.61 %). Immediately after smoking, the results summarized that PS, LPC, PAG, P and G fractions were increased while S, PC and PE fractions were decreased over all the different methods including liquid, cold and hot smoking. On the whole, the results indicated that the smoked-samples stored at 4 °C recorded mere stable phospholipids than that stored at room temperature.

F- Fat soluble vitamins:

The frozen herring contained 840.64, 159.71 and 46.34 pg/g of 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 in hot-smoked herring than that of liquid-and cold-smoked products. By storage (either at room temperature or at 4 °C) of smoked herring samples, the results indicated a gradual decreasing of vitamins. However, the decreasing rate was much higher for smoked samples stored at room temperature compared to that stored at cold storage.

G- Statistical analysis:

1- Oil constants:

The results of analysis showed that the differences between the smoking methods and the differences of the interaction between the smoking methods and the storage periods were significant for all the oil constants with exception of the refractive index (RI) at room temperature and the acid value

(AV) and free fatty acid (FFA) at 4 °C, which recorded non-sigaint differences.

2- Lipid and phospholipid fractions:

The analysis indicated that after smoking and during storage (either at room temperature or at 4 °C), the differences between all the factors were significant for all lipid fractions with exception for phospholipids of the interaction between smoking methods and storage periods at room temperature and at 4 °C, as well as, for diglycerides fraction during storage periods at 4 °C. On the other hand, nearly, the differences between all the factors were significant for all phospholipid fractions.

II- Cooking offish:

A- Chemical properties:

The results indicated that the fresh Nile bolti, aquaculture bolti and marine bouri fish recorded 79.30, 80.61 and 77.57 % moisture; 1.85, 2.85 and 5.41 fat; 0.13, 0.15 and 0.12 TBA as mg malonaldehyde / kg sample and 6.30, 6.21 and 6.15 for pH, respectively. The different cooking methods including frying, grilling and roasting decreased the moisture contents' of cooked fish provided that the roasted and grilled fish showed higher moisture contents than that of fried fish. Frying increased the fat content while grilling and roasting for all the cooked fish decreased it.

Concerning the TBA values (mg MA/kg sample), it was increased by all the different cooking methods but roasted fish recorded lower (0.21-0.33) TBA values followed by grilled (0.41-0.59) and fried (0.53-0.73) fish.

B - *Oil constants:*

Data of present work indicated that the fresh Nile bolti, aquaculture bolti and marine bouri fish had 1.4677, 1.58, 0.79, 4.72, 186.72 and 128.76; 1.4651, 1.72, 0.85, 5.73, 188.26 and 121.43 and 1.4681, 1.44, 0.74, 3.79, 184.64and 133.24 for refractive index (RI), acid value (AV), free fatty acid (FFA), peroxide value (PV), saponification value (SV) and iodine number (IN), respectively.

On the other hand, all the different cooking methods affected the oil constants of the three species of fish whereas the RI and IN decreased while the AV, FFA, PV and SV increased possibly due to oxidation. However, the levels of the lipid oxidation and / or hydrolysis were lower for the roasted fish samples than the grilled one then came the fried fish samples, which recorded the highest level of oxidation and hydrolysis.

C- Fatty acids composition and fraction:

The results indicated that the abundant fatty acids in lipid of Nile bolti were palmitoleic (C 16:1), palmitic (C16:o) and linoleic (C18:2) fatty acids while the oleic (C18:1), linoleic (C18:2), palmitoleic (C 16:1), myristic (C14:0) and palmitic (C16:o) were the predominant fatty acids in lipids of aquaculture bolti and linoleic (C18:2), palmitoleic (C16:1), oleic (C18:1) and palmitic (C16:0) in lipid of marine bouri fish, respectively. The total essential fatty acids were higher (33.37 % of total fatty acids) in lipid of fresh marine bouri followed by that (30.43 %) of fresh Nile bolti then fresh aquaculture bolti (22.41 %), respectively.

The results indicated that the cooking methods affected the fatty acids composition as some fatty acids decreased and

others increased. All cooking methods increased the total percent of saturated fatty acids in all the cooked fish compared with the fresh fish provided that the increasing rate of the total saturated fatty acids was lower for the roasted fish followed by the grilled and fried fish. The reverse was recorded for the total unsaturated fatty acids.

According to the cooking methods evaluated, the roasting method was better in cooking of fish than grilling and frying methods, and the best product was recorded for roasted marine bouri fish over all the tested cooked fish.

Lipid fractions

predominant fraction was the triglycerides (45.10-54.40 %) followed by the phospholipids fraction (21.51-32.28 %) over all the three species of fresh fish.

By cooking with different methods, the results indicated that the fried and grilled samples recorded lower percent of phospholipid component (PL) while the roasted samples recorded the higher percent compared to the fresh fish. Free fatty acid (FFA) component increased by all the different cooking methods but, the roasted fish had the lowest percent of FFA followed by the grilled and fried fish, respectively.

E- phQsnhDliHid ractions•

The main components of phospholipids were phosphatidyl choline (PC) and phosphatidyl ethylarnine (PE) over all the three species of fresh fish. The results indicated that the phosphatidylcolinein fresh Nile bolti, aquaculture bolti and marine bouri was 46.86, 39.70 and 43.36 % PC whilf PE was 33.33, 35.46 and 38.13 %, respectively. The PC ind LPC

fractions increased with different rates depending on the different cooking methods applied in this study (frying- grilling - roasting).

F-Fat-soluble vitamins:

The fresh marine bouri fish recorded higher amounts of vitamins A, E and K than that of aquaculture and Nile bolti fish.

All the cooking methods affected the vitamins content of the cooked fish whereas it was decreased. The loss of vitamins was lower in roasted samples followed by grilled fish then fried fish that recorded the highest loss of vitamins content, which may be due to the effects of the different cooking temperatures.

G- Statistical analysis:

1-Oil constants, lipid fractions and phospholipids fractions:

The analysis indicated that the differences between the fish types as well as between the treatments (cooking methods) were significant for all the oil constants, lipid fractions and pho sphol ip id fractions.

III- *Effect of* ***dry-salting conditions during processing of fermented-salted bouri (Feseekh):***

A- Chemical *properties:*

The moisture content in all the salted samples decreased compared to the fresh fish. On dry weight basis, all the salted samples recorded lower (22.92-9.94 %) fat content when compared with fresh (24.14 %) fish. By the end of salted time, the heavy-, medium and light-salted bouri fish had 16.06, 20.86 and 9.94 % of fat respectively. The loss of fat was lower in medium-salted samples followed by heavy-salted samples then

light-salted one. By the end of salting period (120 days), salt contents and concentrations were 13.75, 21.16; 11.77, 17.5 and 5.56, 8.07 % for heavy-, medium and light-salted samples respectively (on wet weight basis). The TBA values were gradually increased with increasing the salting time provided that the higher level of TBA values was recorded for li t-followed by heavy-then medium-salted fish, which recorded the lowest TBA values. Therefore, the medium-salted bouri fish showed the lower oxidation of lipids than that of heavy and light-salted samples.

B- Oil constants:

The refractive index (RI) decreased from 1.4648, 1.4646 and 1.4661 (at 15 days) to reach 1.4617, 1.4571 and 1.4643 by the end of heavy, light and medium salting period, respectively. The light-salted samples recorded the highest valu s of acids values (AV) and free fatty acids (FFA) followed by t e medium salted samples then the heavy-salted fish that recorde the lowest values. The heavy-salted samples showed higher PV than that of the medium-salted samples. This may be due to high salt content (in heavy-salted fish) which enhanced the lipid oxidation expressed as PV. Nevertheless, light-salted fish recorded the highest PV probably due to more lipolysis occurred in these samples leading to enhancing the lipid oxidation accordingly revealed higher PV. Saponification values had the same trend of PV. With respect of iodine number (IN) as an indicator of the unsaturation degree, the medium-salted fish recorded higher level when compared with heavy-and light-salted fish.

C-fatty acids composition and fractions:

The different salting systems affected (with different levels) the fatty acids composition during salting period, as there was increment of some fatty acids and decrement of others at the same time, in additions to some fatty acids that were absent at different periods of salting. By the end of salting period (120 days), the medium-salted fish recorded the highest (11.19 % of total fatty acids) total percent of essential FA (EFA) followed by the heavy-(4.59 %) then the light-salted one which recorded the lowest (2.97 %) total percent of (EFA). According to the fatty acids composition, the medium-salted fish was the beast followed by the heavy-and the light-salted samples. The total saturated fatty acids (TSFAs) were increased by increasing of salting time nevertheless the increasing rate of TSFAs was lower for medium-salted fish than that of heavy and light-salted fish (with exception of the heavy-salted fish only at 120 days), the reverse was observed concerning the total unsaturated fatty acids (TUFA). The total loss for 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. The Ks (TUFAJTSFA) was decreased when the salting time was increased. As the higher the Ks the lower the oxidation of lipid, the medium-salted samples had higher (0.72) Ks (lower lipid oxidation) than heavy-(0.70) and light-(0.20) salted samples (at the end of salting).

E- Lipid fraction:

The results summarized that during the salting process, after 15,30 and 60 days, of heavy or medium-salting, the main lipid fractions still recorded for TG and PL, while after 90 and 120 days of heavy or medium salting . the main fra bons were the TG and DG. Concerning the light salting , the G and PL recorded the great amounts only up to the 15 th day th eater, the TG and DG became the predominant fractions till the end of salting period (120 days). The PL fraction deer sed with increasing of the salting time but, the decreasing rat of the PL was higher in light-salted fish than that of the m diem- and heavy- salting. The light-salted fish recorded higher percent (18.73) of FFA than that of the medium (12.41 %) and heavy (10.60 %) salted fish (by the end of salting period) Also, the fraction decreased by increasing the salting time, pr vided that the decreasing rate was higher for light-salted sampl s followed by heavy and medium salted sample (with very little e ception).

F- Phospholipid fractions:

With very little exception for light-salted fish, the PC and PE formed the major components of phospholipi fractions either for fresh or for all the salted bouri fish at any ime of the salting process. The PS and LPC fractions increased with increasing of salting time. Sphingomyeline (S) mponent increased only after 15 days of heavy and medium sal ng of fish while decreased at all the other periods of saltin . On the contrary, the PC and PE fractions decreased with in easing of the salting time. The phosphatidic acid recorded a p ogressive

increase in the light-salted fish followed by the heavy- and medium-salted bouri fish.

G- Fat-soluble vitamins:

The different salting processes (either heavy, medium or light salting) affected the fat-soluble vitamins content, as the total loss of fat-soluble vitamins (FSV) was lower for the medium-salted fish than that of heavy- and light-salted fish at any time of salting period.

F- Statistical analysis:

1-oil constants:

The analysis indicated that the differences between the salting styles (heavy, medium and light salting methods) were significant for all oil constants with exception for RI (non-significant differences). Also, the differences between the salting periods and the differences of the interactions between the salting styles and salting periods recorded the same trend.

2- Lipid and phospholipid fractions:

The analysis of results indicated that the differences between all the factors were significant for all the lipid and phospholipid fractions.

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

A- chemical properties:

The results indicated that 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). The moisture content was

slightly increased only immediately after glazing with tocopherol (GT) or BHT (GBHT) of bolti fish nevertheless, it was gradually decreased during frozen storage period (6 months). The moisture loss during storage was higher for untreated samples (control) than that of the treated samples either for bolti or bouri fish. By the end of frozen storage the moisture content of control, fish glazed with tocopherol (FGT) and fish glazed with BHT (FGBHT) were 77.48, 78.89 and 78.91 % for bolti c rresponding 74.23, 76.44 and 75.75 % for bouri fish, respectively

The fat content decreased during storage fo all samples provided that the decreasing rate was lower for FGB T than that for FGT, however the control samples recorded the highest loss of fat content during and by the end of frozen storage period (on dry weight basis).

The TBA values increased by increasing the time of frozen storage but, the controls recorded the higher values followed by the FGT and FGBHT, respectively. The BHT as a synthetic antioxidant was more effective against lipid oxidation than tocopherol as a natural antioxidant, however due to more safety, tocopherol should be selected.

B- **Oil constants:**

The results indicated that the RI was decreased during frozen storage period for all samples of bolti and bouri fish but, the decreasing rate of RI was higher for unglazed samples compared to the glazed samples either with tocopherol or with BHT. The oxidation rate occurred in fish glazed (FGBHT) was lower than that of FGT then came the control, which recorded the highest rate of lipid oxidation during storage period provided

that bouri fish showed higher oxidation than bolti fish. The PV and SV confirmed these results; the PV increased and recoded the same trend of the previous oxidation levels during storage. Moreover, the FFA and AV increased with increasing of storage time provided that the increasing rate was higher for bouri than bolti and for control than treated samples either FGT or FGBHT.

C:- *Fatty acids composition and fractions:*

The results indicated that glazing with antioxidants and frozen storage for 6 months affected the fatty acids composition of bolti and bouri fish as some acids were increased and others decreased, in addition some fatty acids were absent. Furthermore, some fatty acids decreased then increased during storage period.

The total saturated fatty acids (TSFAs) were increased during frozen storage of all the tested samples either controls or FGT and FGBHT of bolti and bouri samples however, the increasing rate of TSFAs was higher for controls than that of FGT then the FGBHT samples which recorded the lowest increasing rate. On contrary, the total unsaturated fatty acids (TUFAs) were decreased by increasing the frozen storage time and the controls recorded the highest decreasing rate of the TUFAs indicating more oxidation than that of samples treated with antioxidants. Furthermore, the FGBHT samples recorded higher Ks values followed by the FGT then the control samples, taking into consideration that the lowest Ks indicate the highest lipid oxidation.

E- Lipid fractions:

The phospholipids components decreased during frozen storage period for controls and glazed samples of bird and bouri fish but, the loss of phospholipids was remarkably higher for controls than that of treatments either FGT or F93HT of both bolti and bouri fish. The free fatty acid fraction increased with higher level for control compared to treatments overall the tested samples. Tocopherol fraction decreased during storage period for control, FGT and FGBHT.

F- Phospholipid fractions:

The phosphatidyl serine (PS) and LPC fractions increased during frozen storage and still increased up to the end of storage either for control or treated samples of bolti and bduri fish. By the end of storage, the percent of PS and LPC was higher for control than FGT and FGBHT. On the other hand, remarkable decrease was recorded for PC and PE fractions during storage periods overall the tested samples either treated pr untreated samples of bolti and bouri fish but, the loss of PC and PE was higher for control followed by FGT and FGBHT, respectively. Generally, the BHT was more effective against lipid oxidation than tocopherol nevertheless, tocopherol should be applied instead of BHT because the predominant trend overall the world is interested in natural antioxidants (tocopherol) for safety concerns.

G Fat soluble vitamins:

Immediately after glazing with antioxidants, (with exception of vitamin E of FGT), slight loss of **fat-soluble vitamins (FSV) was observed either for** bolti or bouri fish.

During frozen storage for 6 months, gradual loss of FSV was recorded provided that the loss rate was lower for FGBHT than that of FGT. Nevertheless, the loss rate of FSV during storage period was lower for FGT than that of control samples either of bolti or bouri fish that recorded remarked loss of FSV.

F- Statistical analysis:

1- Oil constants:

The analysis indicated that the differences between all factors (fish type - treatments with antioxidants - storage periods) regardless the interactions - were significant for all the oil constants with exception of the refractive index (RI), which recorded non-significant differences.

2- Lipid and phospholipid fractions:

The analysis showed that the differences between the treatments, between the storage periods and between the interaction of treatments and storage periods were significant for all the lipid fractions. The differences between the types of fish were significant for all lipid fractions with exception of monoglycerides and tocopherol fractions (non-significant). Significant and non-significant differences due to some interactions were observed for lipid fractions. On the other hand, the differences between all factors were significant for all phospholipid fractions.