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Chemical and Sensory Evaluation of Crude Oil Extracted from Herring Byproducts from Different Processing Operations

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Fish oils extracted from marinated herring (frozen and unfrozen) byproducts and maatjes herring byproducts were evaluated on their chemical and sensory properties. The obtained crude oils had very low content of copper (<0.1 mg/kg oil), and iron values were 0.8, 0.1, and 0.03 mg/kg oil, respectively, for oil from maatjes and frozen and fresh byproducts. For the maatjes oil, a much lower value was found for α-tocopherol compared to the other oils. Storage stability results showed that the oils behave differently. Secondary oxidation products were measured for fresh oil, while for the maatjes and frozen byproducts' oil, tertiary oxidation products were detected. Over storage time, the maatjes and frozen byproducts' oils became more intense in odor, correlating positively at the end with sensory attributes of train-oil, acidic, marine and fishy. The best correlation between sensory and chemical analyses was found for FFA and fishy off-odor ($r = 0.781$).

KEYWORDS: Byproducts; crude oil; fresh; frozen herring; maatjes; marinated production; oxidation status; sensory evaluation

INTRODUCTION

Fish and fish oils contain high concentrations of ω-3 polyunsaturated fatty acids (PUFAs) (1−4). These PUFAs receive intense interest in the scientific and industrial communities because of their positive role in human health (5−9). As awareness of their nutritional importance has risen, attention for their supply has increased. Presently, most of the fish oil available on the market is produced by pressing/heating of whole pelagic fish to release the oil mainly concentrated in the flesh of the fish (10−12). However, fish oil can also be produced from byproducts from the processing industry (13−16).

In The Netherlands the main fatty fish species that is processed for human consumption is herring (*Clupea harengus*) mostly caught at the North Sea. It is estimated that the three major Dutch fish processing companies produced an amount of about 27 000 tons/year of herring byproducts. These byproducts derived from the production of two popular products: marinated and maatjes herring. Marinating herring has traditionally been applied as a conservation method, using fresh or frozen herring as raw material. For this process, brines are added after the filleting operation; therefore, the salts do not come in contact with the byproducts itself. This is in contrast to the maatjes production, where brine is added to the whole fish, as described earlier (14). Both storage history and the presence of salt are relevant to whether it is possible to keep constant stability and quality of oils extracted from herring byproducts. Marine lipids, which contain higher quantities of ω-3 PUFAs, are susceptible to oxidation following successive degradation (17). It is known that lipid oxidation takes place in fatty fish species during processing and storage, the herring fat being susceptible to oxidation both in situ in the tissue and when extracted out from the tissue (18−20). To follow the degree of oxidation, use can be made of different chemical measurements. The oxidation products formed affect sensory properties of the oil adversely. Therefore, sensory assessment remains the most direct quality criteria for edible oil and its shelf life.

The aim of this study is to investigate the quality and stability of crude oil extracted from maatjes herring byproducts and from fresh and pre-frozen marinated herring byproducts. To follow lipid oxidation progress, primary, secondary, and tertiary oxidation products were measured. The loss of α-tocopherol and the change in the free fatty acids content were also followed over time. Sensory assessment of the oil was evaluated with six aroma attributes for freshly produced oils as well as for various storage times of the oils. Multivariate data analysis was used to distinguish chemically and sensorial changes and to identify correlations between the measured parameters.

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MATERIAL AND METHODS

Experimental Procedures. Fish oil was extracted from filleting byproducts originating from fresh and prefrozen unsalted herring (*Clupea harengus)* that was to be used for marinating herring. The herring from the frozen and fresh production were respectively caught in June and October 1999, off 60.50 N 02.50 W and 51.20 N 02.60 E, with average weight of 144 ± 1 and 138 ± 23 g, length of 26 ± 1 and 24 ± 1 cm, and maturity stage III and V (in both cases, $n = 19$). The oil produced from byproducts coming from the frozen herring used in the marinated process is referred to as "frozen byproducts' oil", whereas the oil produced from byproducts of fresh herring was called "fresh byproducts' oil". For the production of the maatjes oil, the herring was caught in May 99 and was frozen until processing. This type of oil (further referred as "maatjes byproducts' oil") was extracted from salted herring byproducts as described earlier (*14*).

Equipment. Three production runs of ∼1000 kg each of herring byproducts (heads, frames, skin, viscera, etc.) generated from the different processing and storage of herring were minced. Immediately, they were pumped to an insulated scraped-surface heat exchanger indirectly heated by steam and separated in a three phase decanter into a high solids phase (referred to as protein phase), a water phase (stickwater), and lipid phase (oil) using the same conditions and system as described earlier (*14*).

Sampling Setup. In all storage experiments, the oil was blanketed with nitrogen and kept in closed dark containers at room temperature (∼ 20 °C). Two oil samples were taken, at regular intervals, from the different oils and analyzed for levels of oxidation products, FFA formation, α-tocopherol content, and odorants. Sampling was discontinued when the oils developed a strong off-odor; therefore, different maximum storage times resulted (155, 92, and 57 days for fresh, maatjes, and frozen oil, respectively). All samples were kept at −80 °C freezer until being analyzed. Prior to the analysis, the oil samples were thawed at room temperature for 30 min. Averages of the two oil samples measurements were used for further interpretation.

Chemical Analyses. The level of free fatty acids (FFA) was determined by titration according to the AOCS (*21*) Official Method Ca 5a-40. The peroxide value (PV) was determined according to the AOCS (*21*) Official Method Cd-8b-90. Determination of the anisidine value (AV) was carried out according to the AOCS (*21*) Official Method Cd 18-90. α-Tocopherol was analyzed according to the slightly modified method of Lie et al. (*22*) as described earlier (*14*) using reversed phase HPLC and fluorescence detection. The UV absorbance at 270 nm (conjugated trienes, CT) of the oil samples were measured using flow injection analysis (FIA) as described by Undeland et al. (*23*). The results were expressed as peak area units per microgram of lipid. The repeatability of the method was 4.3% ($n = 1$, $a = 6$). Total lipid soluble fluorescent lipid oxidation products (FP) with an excitation (ex) maximum at 367 nm and an emission (em) maximum at 420 nm were measured in the oil samples using FIA as described by Undeland et al. (*23*). Results were expressed as peak area units per picogram of lipid. The repeatability was 7.0% ($n = 1$, $a = 6$). On each occasion, two oil samples ($n = 2$) have been analyzed once ($a = 1$).

Sensory Analysis. Eight assessors were selected for the panel. The assessors were trained during 17 sessions on profiling fish oil (*24*) prior to evaluation of our herring oil samples. Measuring odor rather than flavor is viewed as a sensory task less likely to fatigue panelists considering that oil samples are difficult to clear from the mouth (*25*). For each profiling of fish oil, the following attributes were evaluated: fishy, train-oil, musty, green/vegetable, acidic/sour, and marine. To liberate volatiles from the oils, prior to serving, the samples (blanketed in nitrogen) were heated in a water bath at 50 °C, for 6 min. Before each session, the panel was calibrated by presenting freshly prepared reference oil to each assessor. The reference sample contained refined menhaden oil. Fish oil (0.5 mL, dispersed in glass pearls, ⌀ 2 mm) was presented to the panelists in small opaque, glass flasks (120 mL) with a black lid. The panelists evaluated six different samples per session. Tap water was provided for oral rinsing at the beginning of the sessions and between oil samples. A complete block design and triplicate samples were used for sensory assessment. The order of presentation of samples to the panelist was balanced to minimize

Table 1. Initial Compositional Data of the Three Herring Oils Extracted from Herring (*Clupea harengus*) Byproducts Originated from Different Processing Methods

	maatjes	frozen	fresh
trace elements			
Fe (mg/kg of oil)[a]	0.8 ± 0.1	0.1 ± 0.0	0.030 ± 0.006
Cu (mg/kg of oil)[a]	< 0.1	< 0.1	< 0.1
oxidation status			
PV (meq. perox./kg of lipids)[b]	3.0 ± 0.3	3.0 ± 0.2	0.65 ± 0.17
AV [b]	8.9 ± 0.5	6.2 ± 0.3	0.36 ± 0.06
FFA (%)[b]	3.1 ± 0.4	2.0 ± 0.3	0.60 ± 0.01
fatty acids			
EPA (g/kg of lipid)[b]	99 ± 13	99 ± 5	58 ± 1
DHA (g/kg of lipid)[b]	91 ± 11	110 ± 2	65 ± 1
Σ polyunsaturated[b]	277 ± 33	271 ± 12	183 ± 5
α-tocopherol (mg/100 g lipid)[b]	2.8 ± 0.1	9.8 ± 0.0	8.1 ± 0.4

[a] $n = 2$, $a = 2$, results are given as mean value $\pm$ (max − min)/2. For each of the two samples, $a = 2$. Mean values from these two analyses were used to establish sample variation. [b] $n = 3$, $a = 1$, results are given as mean value $\pm$ std.

possible carry-over effects between the samples. The panel rated all attributes for each sample on separate 10-cm unstructured scales using the Compusense Five Program (Compusense Inc., Canada), where 0 indicated no intensity or presence and 10 a high intensity or presence of the attribute to the oil.

Fatty Acid Composition. Fatty acid methyl esters (FAMEs) of oil samples were prepared according to the AOCS (*21*) Official method Ce 1b-89 and analyzed with regard to the amount of individual fatty acids. On each occasion, $n = 3$ and $a = 1$. The different FAMEs were separated from each other with gas chromatography (GC) and identified using the conditions described previously (*14*).

Analysis of Copper (Cu). The copper content present in the oil samples was determined with a Perkin-Elmer 5100 graphite furnace atomic absorption spectrometer (AAS) with Zeeman background conditions (*26*) as described previously (*14*) ($n = 2$, $a = 2$). Results are expressed as mg/kg of oil. The limits of detection were 0.1 mg/kg. The repeatability of the method was 6.0%.

Analysis of Iron (Fe). The oil samples were diluted with xylene and immediately measured with a graphite furnace atomic absorption spectrometer (Perkin-Elmer 5100; Norwalk, CT) using a deuterium background correction (*27*) ($n = 2$, $a = 2$). Results are expressed as mg/kg of oil. The limits of detection were 0.01 mg/kg, and the repeatability of the method was 10.0%.

Internal or certified reference materials were analyzed together with the samples, except for the fatty acids analysis.

Statistical Analysis. Data from the α-tocopherol, stability measurements, and sensory analysis were subjected to multivariate data analyses. The chemical and sensory data sets were evaluated separately by principal component analysis (PCA). The differences in the sensory score levels of the different assessors and each individual attribute were first evaluated by PCA. Differences in how assessors scale sensory scores are a recognized problem in sensory assessment, and the problem occurs despite intensive training of panelists (*28*). Partial least squares (PLS) regression was performed on the data in order to relate chemical and sensory measurements: chemical data was used as X variables and sensory data as Y variables. In all analyses, all variables were weighed by 1/standard deviation, full cross validation and the Jack-knifing principle were employed.

RESULTS AND DISCUSSION

In the first part of this section, a characterization of the initial crude oils is presented. In the second part, the stability of the different oils during storage is compared and discussed.

Crude Composition. The data shown in **Table 1** indicate the properties of the different extracted crude herring oils. In all cases, the concentrations of iron were much higher than the copper concentrations (the latter below the detection limit). The

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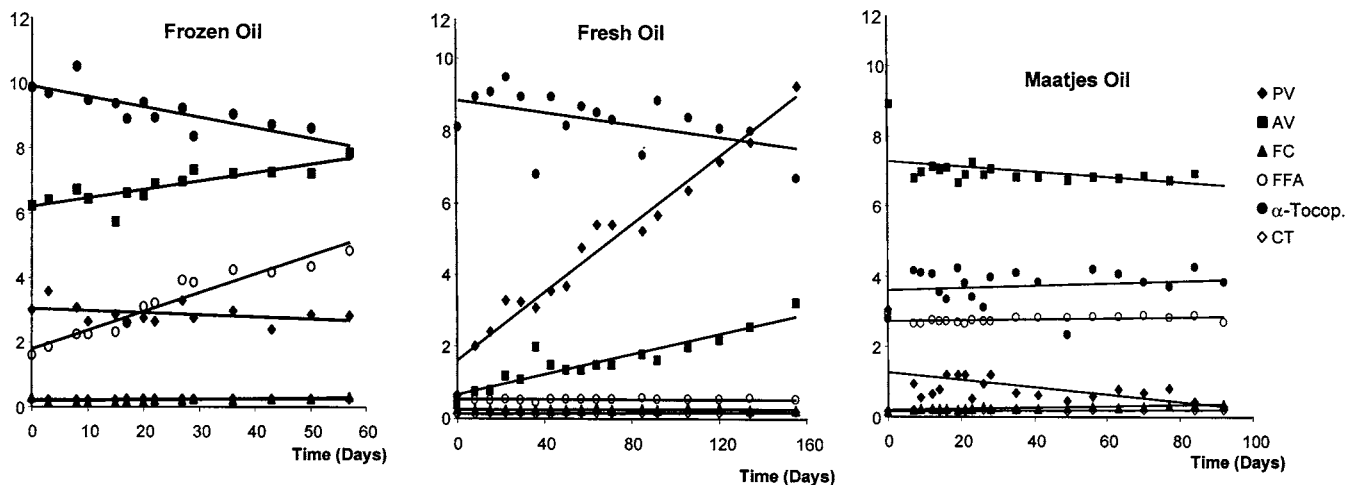
Figure 1. Trend lines and values determined for crude oil extracted from frozen, fresh, and maatjes herring byproducts, stored under nitrogen and dark condition (20 °C). α-Tocopherol is expressed as mg/100 g of lipids; PV is expressed as meq perox/kg of oil, CT is expressed as area units per nanogram of lipids, FC is expressed as area units per picogram, and FFA is expressed in percentage as oleic acid.

metal contents, in particular copper, are known to be important as a catalyst for the oxidation of oils and fats (*29*, *30*). For the iron content, it can be observed that the maatjes byproducts' oil presented a value eight and almost 27 times higher than the frozen and fresh byproducts' oil, respectively. This is in accordance with what should be expected, since for the maatjes production salt is used in the brine before the filleting operation and byproducts' collection. It is known that salt may contain inorganic substances such as copper and iron (*29*, *31*, *32*). Nevertheless, the values determined for the studied oils fulfill the quality guidelines as reported in the literature (*29*, *30*) for crude fish oils.

The maatjes byproducts' oil presented the highest initial oxidation values as well as FFA content. In contrast, fresh herring oil had the lowest values. It is worth noticing that oil produced from fresh raw material presented lower oxidation values and iron and FFA levels than the oil from frozen raw material. Frozen byproducts' oil presented lower iron and FFA levels and initial oxidation products than the maatjes byproducts' oil.

Different amounts of EPA, DHA, and total PUFAs were determined in the oils (**Table 1**). It can be observed that the fresh oil presented the lowest value in all cases. However, the differences in fatty acids content are more likely to be related to the seasonal cycle (*16*, *33*, *34*) than to the herring processing method employed or to the prior storage of the herring. **Table 1** also shows that the initial α-tocopherol content found in the maatjes oil is much lower (∼1/3) than the content of the frozen and fresh oil. Possibly, the reduced levels of this endogenous antioxidant resulted from the oxidation of the oils. That means that the consumption of α-tocopherol occurred in an early stage probably already in the raw material itself.

Oxidative Stability. For evaluation of the oxidative stability of the oils, first the chemical changes inherent in the stages that can be discerned in the oxidation process are described and assessed. Second, the sensory changes are presented and discussed. Finally, the relation between chemical and sensory data is evaluated.

Chemical Analyses. The chemical variables measured during storage of the three studied oils at ∼20 °C are shown in **Figure 1**. To evaluate what storage and process background that had the greatest effect on oxidative changes in the extracted oils, all of the data were subjected to a multivariate data analysis. **Figure 2** shows three distinct clusters (maatjes, frozen and fresh)

obtained from the PCA evaluation. The first two PCs, PC1, and PC2 described 52% of variance in *X* and 30% variance in *Y*. The bi-plot of PC1 and PC2 showed that oil produced from frozen and maatjes herring had positive values for PC1, whereas oil samples from fresh herring had negative values for PC1. This means that PC1 describes the difference between oil produced from frozen and fresh herring. On the other hand, samples produced from unsalted byproducts (frozen) had negative values for PC2, whereas oil samples with salt had positive value for PC2 (maatjes). Thus, PC2 mainly describes differences between oil samples obtained from byproducts processed with or without salt.

In the same plot (**Figure 2**), the variance of the different chemical variables is shown. During storage of the oils different behaviors were found. The variables describing AV, FFA, and CT presented a positive value of PC1, whereas FC had a positive value for PC2. The AV and FFA measured variables were close to each other and were located far to the right. Hence, these variables correlate with each other to a high degree (*r* = 0.914) and were of high significance. The correlation found between FFA measurements with lipid oxidation products such as AV is in accordance with the theory of the influence of lipid hydrolysis on lipid oxidation (*35*). AV and FFA are positively related to frozen and negatively related to fresh byproducts' oil. The frozen byproducts' oil moved from left to right with progressive storage time. Thus, frozen byproducts' oil stored for 50 days was located far to the right, indicating that this oil presented the highest levels of AV and FFA. Furthermore, CT seemed to correlate quite well with the frozen byproducts' oil. The FC increased during storage time of maatjes and frozen byproducts' oil. α-Tocopherol decreased during storage of frozen and to some extent with fresh byproducts' oil.

α-Tocopherol. It is known that antioxidants act by being oxidized in preference to the oils (*36*, *37*); therefore, the level of α-tocopherol as a whole can provide useful information on the progress of oxidation. The value is dependent on the handling and storage of the raw materials and the recovered oils as well. The α-tocopherol was consumed significantly in fresh and frozen oil, and this consumption occurs faster in the frozen than in the fresh byproducts' oil. Surprisingly, no significant change was found in the maatjes oil. The reduced amount of α-tocopherol present in this oil cannot prevent the progress of the autoxidation process. Therefore, permitting a
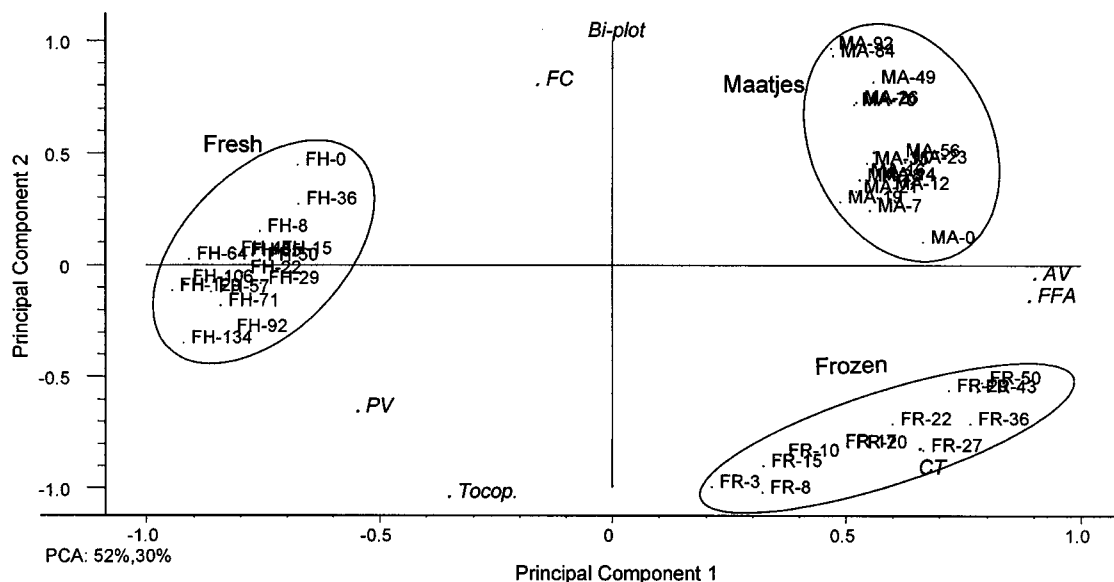
Figure 2. Scores and loading plots from principal component analysis (PCA) for the data from the chemical analyses. The number after the hyphen in the variable name refers to the storage time in days.
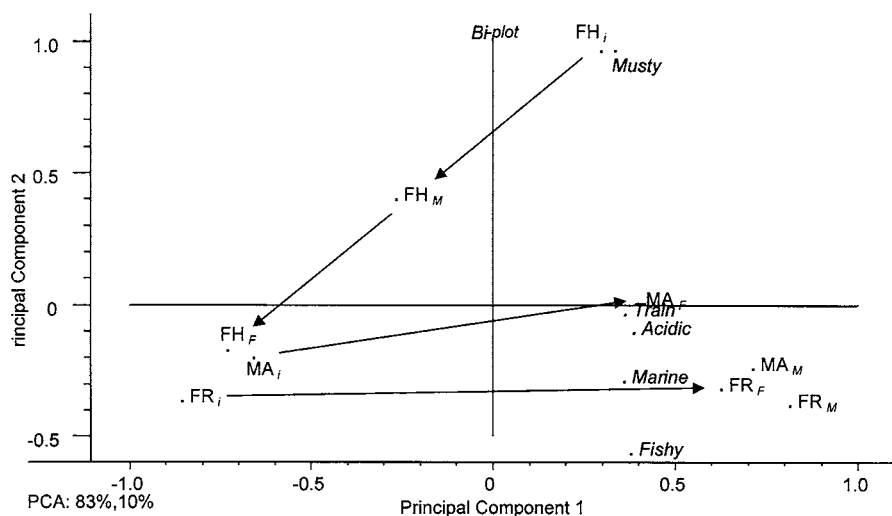

Figure 3. Scores and loading plots from PCA for the data from the sensory analysis. Abbreviations used are the following: FH, fresh oil; MA, maatjes oil; FR, frozen oil. The letters i, M, and F refers to initial, middle, and final storage time, whereas 0, 71, 155; 0, 49, 92; and 0, 27, 57 refer to days for fresh, maatjes, and frozen oil, respectively.

rapid degradation of the primary oxidation products favoring the formation of secondary and tertiary oxidation products.

FFA. The results shows that the level of FFA presented in the maatjes and fresh oil was low and remained almost constant during storage for these oils, in particular for the fresh byproducts' oil. For the frozen byproducts' oil, a significant and consistent increase in time was determined for the FFA formation. This suggests that significant hydrolysis of the oil occurred during the storage period, probably due to the iron content. Nambudiry (*38*) and Hsieh and Kinsella (*31*) showed that with an increase in the salt content, the rate of FFA production in sardine muscle tissue decreases. In addition, in crude capelin oil, Notevarp and Chahine (*39*) found a positive correlation between iron content and FFA: oils with low iron contents tend to have low FFA values. Therefore, the salt content present in the flesh and byproducts of the maatjes production and the very low initial iron content for the fresh oil would explain, as suggested previously (*14*), the nonincrease of FFA over time in contrast to the increase trend developed for the frozen oil.

Primary Oxidation Products. The primary oxidation products were measured as hydroperoxides presented by the PV and by the conjugated trienes analyses. During the autoxidation process, hydroperoxides are produced. This is shown for the fresh oil, where PV increased significantly over time, as can be seen in **Figures 1** and **2**. In contrast, for the maatjes oil, the PV remained low; in fact a significant decrease was detected. This suggests that the degradation of hydroperoxides was faster than its generation. Degradation of hydroperoxides of the maatjes oil, however, did not increase the formation of a higher level CT. However, for the fresh oil, a significant development of CT was found. It has been reported that a 270 nm not only CT hydroperoxides but also various bifunctional oxidation products, such as ethylenic diketones and oxodienes, are detected (*35*, *40*, *41*). The results confirm our previous findings that the CT measured are related to the formation of secondary oxidation products containing a conjugated triene system (*14*).

Secondary Oxidation Products. The secondary oxidation stage is characterized by the further degradation of lipids through a radical oxidation process initiated by the hydroperoxides,
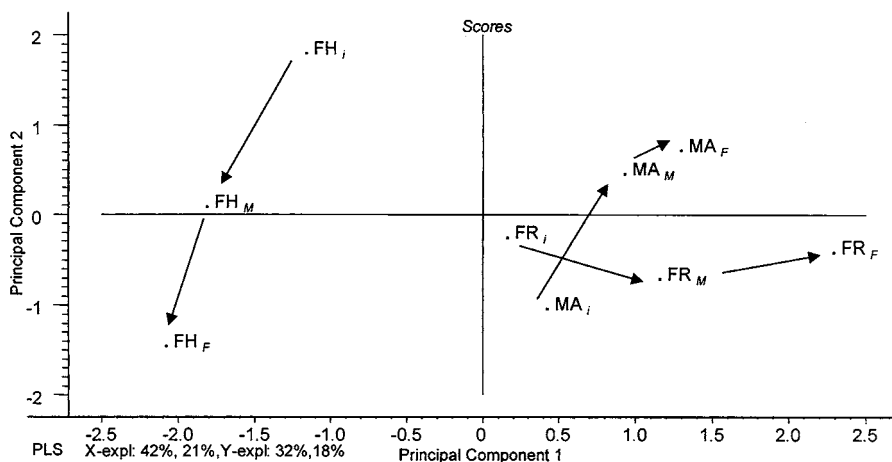
Figure 4. Correlation scores plot from the PLS regression on the studied chemical and sensory measurements of the different oils.
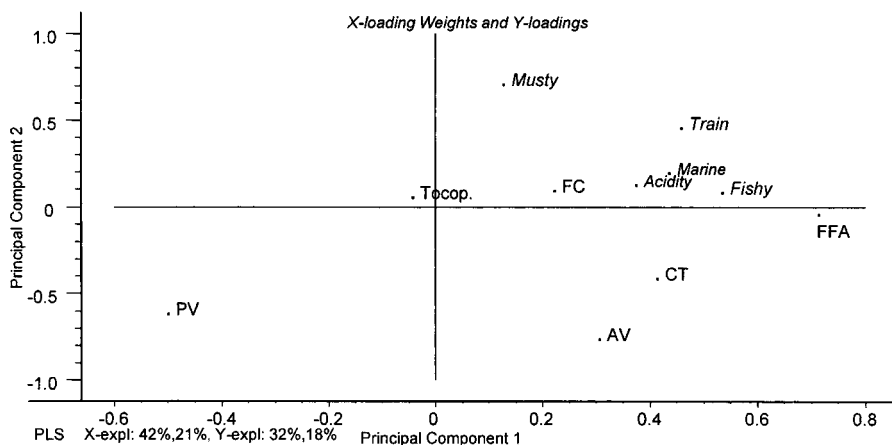

Figure 5. Correlation loading plot from the PLS regression on the studied chemical and sensory measurements of the different oils. The designed chemical variables were used as X-data, and the sensory variables were used as Y-data.

which generates the level of off-flavors and off-odors (*42*). A possible way to quantify the oxidation process is by measuring the AV. Following the same tendency as the CT formation, the AV measurements increased significantly for the frozen and fresh oils. In fact, for frozen oil, the formation of secondary oxidation products was faster than for the fresh herring. Slightly lower values were obtained for the maatjes oil.

Tertiary Oxidation Products. The measurement of FC has been successfully applied to marine oils (*14, 43−45*). As can be seen in **Figures 1** and **2**, the reaction from secondary to tertiary oxidation products clearly takes place for the maatjes and for the frozen byproducts' oils. In both cases, FC presented a significant positive increase over time. This indicates that the tertiary oxidation stage was reached. In contrast, the fresh oil presented a stable value for the FC, which showed that the formation of tertiary oxidation products was not yet important. Possibly, a termination reaction is favored above a propagation reaction, resulting in a stable value of the FC measurements.

These results suggest that the FC analysis can be successfully applied for oils in a later stage of degradation and/or produced from frozen raw material while for the fresh oil early oxidation quality parameters such as PV, CT, and AV should be employed.

Sensory Analysis. In each of the experiments, seven trained panelists sniffed fresh and stored oil samples and then rated their odor intensity of various attributes on the intensity scale. During evaluation of the data, the attribute green/vegetable was removed from further calculations because there was disagreement between the panelists in the score of this attribute. The

results were first analyzed by PCA in order to find the main quality variation among the oil samples as well as to find the relation between the attributes. Triplicate samples were used but for matter of clarity, only average values are shown in **Figure 3**. Middle and final storage times of the frozen and maatjes oils presented positive PC1 values, whereas initial frozen and maatjes oil had negative values. Therefore, it can be concluded that PC1, explaining 83% of the data variance, is related to storage time of the oil. The odor of the fresh byproducts' oil was evaluated as strongly musty when initially extracted, but surprisingly, during storage, distinct differences from musty in odor intensity were observed. It is likely that the musty attribute is associated with the natural odor of the fresh oil, which may intensify at early storage periods. This attribute diminished rapidly and was largely replaced by other type of odors. The typical sensory attributes identified at later storage times of the fresh oil were identical to the attributes for initial maatjes and frozen oil. These latter oils were negatively correlated with train-oil, acidic, marine, and fishy sensory attributes. In contrast, the odors of maatjes and frozen oils became increasingly more intense over storage period; both oils correlated positively with the train, acidic, marine, and fishy attributes. In frozen fatty fish species, the principal changes in odor resulted from alteration in lipid components (*46*). The panelists could clearly distinguish between fresh and stored frozen and maatjes oil samples, since they were placed in different quadrants. However, discrimination between middle and final storage time could not be well performed. Nevertheless,

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the final maatjes oil's samples correlated strongly with train and acidic off-odors attributes. The fresh oil samples moved from the first to the third quadrant during storage time. The samples from the initial frozen and maatjes oils appeared also in this quadrant. During storage time, the maatjes and frozen oils moved further to the fourth quadrant. Flavor and odor deterioration has been attributed mainly to the formation of secondary oxidation products from the polyunsaturated fatty acids (*42*), which make up 18−28% of the total fatty acids in herring oil. The results confirmed that because of the higher proportion and degree of unsaturation of the fatty acids (**Table 1**), the more prone the oil is to oxidation.

During storage, maatjes and frozen oils, both processed from frozen herring, were found to be less stable than fresh oil. The differences should be explained by the effects of variations found of the starting raw material quality, since the conditions during production of the oils were identical.

Chemical versus Sensory Data. Data from analyses of PV and AV did not indicate that the maatjes were oxidized further than the frozen oil samples. However, the sensory data revealed a stronger off-odor for the maatjes than for the frozen byproducts' oil.

For clear comparison between the chemical and sensory data, partial least square (PLS) regression was performed (**Figures 4** and **5**). PC1 explained 42% and PC2 21% of the variance in the *X* variables and 32 and 18% of the variance in the *Y* variables, respectively. Hence the two components explained 63% of the variance in the *X* variables and 50% of the variance in the *Y* variables. The score plots (**Figure 4**) supply information about the relationship between the objects, whereas the loadings plot (**Figure 5**) gives information over the relationship between the original variables. The fresh oil presented a negative PC1 value. In contrast, all samples from the maatjes and frozen oils presented positive PC1 values, increasing over storage time. In the loading plot, it is clear that the longer the oils were stored, the higher the FFA levels and, to a lesser extent, the development of acidity, fishy, and marine off-odors. This is in accordance with the PCA results obtained for the chemical and sensory data. Apart from the musty attribute, all the other attributes were located close to each other. This indicates a certain degree of interdependency (in all cases $r > 0.88$). The FFA measurement correlates well with fishy off-odor ($r = 0.781$). On the other hand, the PV measurement showed a negative correlation to all the sensory attributes, being stronger to the train off-odor ($r = -0.664$). Apparently, low PV's are related to the development of off-odors. This implies that the low PV's measured were not related to a low degrees of oxidation but to the reverse situation: the oxidation process progressed further toward secondary and probably tertiary oxidation products. This hypothesis is supported with the development of off-odors, CT, AV, and FC measurements over time, in particular for the maatjes byproducts' oil. Predictors projected close to the center, such as α-tocopherol, are not very well represented in the model. Although the α-tocopherol level decreased over time (**Figure 1**), this cannot be related directly to any of the off-odors studied. In other studies, the FC measurement show a high correlation with sensory measurements for salted dried sardines and herring fillets (*47*, *48*); however, in our study this was not observed. Storage promotes gradual lipid oxidation with decrease in shelf stability due to continuing chemical processes. The results suggested that FFA evaluation was the chemical method that correlated best with off-odors such as fishy, acidity, marine and train presented in the oil and therefore interesting to be followed.

CONCLUDING REMARKS

The whole organization of the supply and processing chain has a large effect on the properties of fish oil, and the way it develops over time. Using freshly caught herring yielded oil that was in the beginning of the oxidation process, since only primary and secondary oxidation products were detected, and a much lower decrease of α-tocopherol level occurred. Freezing the herring immediately after the catch caused the extracted oil to reach the secondary and tertiary oxidation stage, favoring over time the development of off-odors such as train oil, fishy, acidic and marine. FFA enhances the odor changes in the oils. When the byproducts were in contact with transition metals ions, such as from the maatjes production, oil with more oxidation products and less α-tocopherol levels was extracted. The facts suggest that the oil obtained from byproducts of fresh herring production is different from the ones produced from frozen raw material. Furthermore, within the frozen raw material, different oils are obtained depending of the prior treatment of the herring. As expected, the use of salt accelerates the oxidation process. This leads to the conclusion that the best oil is obtained when extraction is made from fresh and unsalted herring byproducts. Nevertheless, all oils present a relatively good chemical and even sensory stability over time, which suggests that it is possible to upgrade the byproducts from the different processes of the herring industry into fish oil.

ABBREVIATIONS USED

EPA, 5,8,11,14,17-eicosapentaenoic acid; DHA, 4,7,10,13,-16,19-docosahexaenoic acid; FFA, free fatty acids; PV, peroxide value; AV, anisidine value; FC, lipid soluble fluorescent oxidation products; CT, conjugated trienes; $A_{270\ nm}$, absorbance measured at 270 nm; PUFAs, polyunsaturated fatty acids; SD, standard deviation; *a*, number of analyses of each sample preparation; PCA, principal component analysis; PC, principal component; PLS, partial least-squares regression; fresh oil, oil extracted from fresh unsalted herring byproducts; maatjes oil, oil extracted from salted byproducts originated from frozen herring; frozen oil, oil extracted from unsalted byproducts originated from frozen herring.

LITERATURE CITED

(1) Ackman, R. G. Fatty acids composition of fish oils. In *Nutritional Evaluation of Long-chain Fatty Acids in Fish Oil*; Barlow, S. M., Stansby, M. E., Eds.; Academic Press: London, 1982; pp 25−88.

(2) Ackman, R. G. The Year of the fish oils. *Chem. Ind.* **1988**, 139−145.

(3) Ackman, R. G. Fatty Acids. In *Marine Biogenic Lipids*, *Fats and Oils*; Ackman, R. G., Ed.; CRC Press: Boca Raton, FL 1989; pp 103−137.

(4) Kinsella, J. E. Sources of omega-3 fatty acids in human diets. In *Omega-3 Fatty Acids in Health and Disease*; Lees, R. S., Karel, M., Eds.; Marcel Dekker Inc.: New York, 1990; pp 157−200.

(5) Glomset, J. A. Fish, fatty acids, and human health. *New Engl. J. Med.* **1985**, *312*, 1253−1254.

(6) Schmidt, E. B.; Dyerberg, J. Omega-3 Fatty Acids: Current Status in Cardiovascular Medicine. *Drugs* **1994**, *47*, 405−424.

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(7) Lanting, C. I.; Fidler, V.; Huisman, M.; Touwen, B. C. L.; Boersma, E. R. Neurological differences between 9-year-old children fed breast-milk or formula-milk as babies. *The Lancet* **1994**, *344*, 1319−1322.

(8) Uauy-Dagach, R.; Valenzuela, A. Marine oils: the health benefits of n-3 fatty acids. *Nutr. Rev.* **1996**, *54*, II S102−S108.

(9) Vidgren, H.; Ågren, J. J.; Schwab, U.; Rissanen, T.; Hänninen, O.; Uusitupa, M. Incorporation of n-3 Fatty Acids into Plasma Lipid Fractions, and Erythrocyte Membranes and Platelets During Dietary Supplementation with Fish, Fish Oil, and Docosahexaenoic Acid-Rich Oil Among Healthy Young Men. *Lipids* **1997**, *32*, 697−705.

(10) FAO. *The Production of Fish Meal and Oil*; Fishery Industries Division, Fish. Technol. Pap. 142; FAO, Rome, 1986; 63.

(11) Pigott, G. M.; Tucker, B. W. Extracting and Processing Marine Lipids. In *Seafood*: *Effects of Technology on Nutrition*; Pigott, G. M., Tucker, B. W., Eds.; Marcel Dekker: New York, 1990; pp 294−314.

(12) Pigott, G. Marine Oils. In *Bailey's Industrial Oil and Fat Products*; Hui, Y. H., Ed.; John & Wiley Sons: New York, 1996; pp 225−254.

(13) Skåra, T.; Cripps, S. Upgrading of waste from salmon slaughteries using a three phase separation process. In *Seafood From Producer to Consumer*, *Integrated Approach to Quality*; Luten, J. B., Børresen, T., Oehlenschläger, J., Eds.; Elsevier Science, B. V.: Amsterdam, 1997; pp 103−111.

(14) Aidos, I.; van der Padt, A.; Boom, R. M.; Luten, J. B. Upgrading of maatjes herring byproducts: production of crude fish oil. *J. Agric. Food Chem.* **2001**, *49*, 3697−3704.

(15) Aidos, I.; Masbernat-Martinez, S.; Luten, J. B.; Boom, R. M.; van der Padt, A. Composition and Stability of Herring Oil Recovered from Sorted Byproducts as Compared to Oil from Mixed Byproducts. *J. Agric. Food Chem.* **2002**, *50*, 2818−2824.

(16) Aidos, I.; van der Padt, A.; Luten, J. B.; Boom, R. M. Seasonal Changes in Crude and Lipid Composition o- Herring Fillets, Byproducts and Respective Produced Oils. *J. Agric. Food Chem.* **2002**, *50*, 2818−2824.

(17) Gardner, H. W. Effect of lipid hydroperoxides on food components. In *Xenobiotics in Foods and Feeds*; Finley, J. W., et al., Eds.; American Chemical Society: Washington, DC, 1983; pp 63−84.

(18) Shahidi, F.; Spurvey, S. A. Oxidative Stability of Fresh and Heated-Processed Dark and Light Muscles of Mackerel (*Scomber scombrus*). *J. Food Lipids* **1996**, *3*, 13−25.

(19) Undeland, I. Lipid Oxidation in Fatty Fish During Processing and Storage. In *Farmed Fish Quality*; Kestin, S. C., Warriss, P. D., Eds.; Fishing News Book, Blackwell Science: Bristol, U.K., 2001; pp 261−275.

(20) Undeland, I. Lipid Oxidation in Fillets of Herring (*Clupea harengus*) during Processing and Storage. Ph.D. Thesis, Chalmers University of Technology, Goteborg, Sweden, 1998.

(21) AOCS *Official Methods and Recommended Practices of the American Oil Chemists' Society*, 5th ed.; American Oil Chemists' Society: Champaign, IL, 1998.

(22) Lie, Ø.; Sandvin, A.; Waagbø, R. Transport of alpha-tocopherol in Atlantic salmon (*Salmo salar*) during vitellogenesis. *Fish Phys. Bioch.* **1994**, *13*, 241−247.

(23) Undeland, I.; Stading, M.; Lingnert, H. Influence of Skinning on lipid Oxidation in Different Horizontal Layers of Herring (*Clupea harengus*) during Frozen Storage. *J. Sci. Food Agric.* **1998**, *78*, 441−450.

(24) ISO Sensory analysis- dentification and selection of descriptors for establishing a sensory profile by a multidimensional approach. *ISO* **1994**, *11035* (*E*), 1−26.

(25) Malcolmson, L. J.; Vaisey-Genser, M.; Przybylski, R.; Eskin, N. A. M. Sensory stability of canola oil: present status of shelf life studies. *J. Am. Oil Chem. Soc.* **1994**, *71*, 435−440.

(26) Perkin-Elmer. The THGA graphite furnace: Techniques and Recommended Conditions. *Perkin-Elmer Publication B3210*; Perkin-Elmer: Ueberlingen, Germany, 1992; pp 16.

(27) Perkin-Elmer Standard conditions for iron. *Perkin-Elmer Cookbook*, *Vol. 2*; Perkin-Elmer: Norwalk, CT, 1976.

(28) Meilgaard, M. C.; Civille, G. V.; Carr, B. *Sensory Evaluation Techniques*; CRC Press: Boca Raton, FL, 1991.

(29) Young, F. V. K. The Chemical and Physical Properties of Crude Fish Oils for Refiners and Hydrogenators. *Int.l Assoc. Fish Meal Manufact.* **1986**, *Fish Oil Bulletin No.18*, 1−19.

(30) Bimbo, A. P. Guidelines for characterizing food-grade fish oil. *Int. News Fats*, *Oils Relat. Mater.* **1998**, *9*, 473−483.

(31) Hsieh, R. J.; Kinsella, J. K. Oxidation of polyunsaturated fatty acids: mechanisms, products, and inhibition with emphasis on fish. In *Advances in Food and Nutrition Research*; Kinsella, J. F., Ed.; Academic Press: New York, 1989; pp 233−341.

(32) Huss, H. H. *Quality and Quality Changes in Fresh Fish*, 348 ed.; FAO Fishery Technology Paper; FAO: Rome, 1995; p 195.

(33) Stroud, G. D. The herring. In *Torry Advisory Note, n.57*; Torry Research Station: Aberdeen, U.K., 1987; pp 1−16.

(34) Aro, T.; Tahvonen, R.; Mattila, T.; Nurmi, J.; Sivonen, T.; Kallio, H. Effects of Season and Processing on Oil Content and Fatty Acids of Baltic Herring (*Clupea harengus membras*). *J. Agric. Food Chem.* **2000**, *48*, 6085−6093.

(35) Takagi, T.; Wakasa, N.; Miyashita, K. Formation of conjugated diene and triene products in lipoxygenase oxidation of C18, C20, C22 PUFAs. *J. Am. Oil Chem. Soc.* **1987**, *64*, 1320−1323.

(36) Buettner, H. G. The pecking order of free radicals and antioxidants: lipid peroxidation, α-tocopherol and ascorbate. *Arch. Biochem. Biophys.* **1993**, *300*, 535−543.

(37) Frankel, E. N. Antioxidants. In *Lipid Oxidation*; Frankel, E. N., Ed.; The Oily Press Ltd: Glasgow, Scotland, 1998; pp 129−160.

(38) Nambudiry, D. D. Lipid Oxidation in fatty fish: the effect of salt content in the meat. *J. Food Sci. Technol.* **1980**, *17*, 176−178.

(39) Notevarp, O.; Chahine, M. H. Trace Metal Contents, Chemical Properties and Oxidative Stability of Capelin and Herring Oils Produced in Norwegian Plants. *J. Am. Oil Chem. Soc.* **1972**, *49*, 274−277.

(40) Brown, H. G.; Snyder, H. E. Conjugated Dienes of Crude Soy Oil: Detection by UV Spectrophometry and Separation by HPLC. *J. Am. Oil Chem. Soc.* **1982**, *59*, 280−283.

(41) Undeland, I.; Ekstrand, B.; Lingnert, H. Lipid Oxidation in Herring (*Clupea harengus*) Light Muscle, Dark Muscle, and Skin, Stored Separately or as Intact Fillets. *J. Am. Oil Chem. Soc.* **1998**, *75*, 581−590.

(42) St. Angelo, A. J. Lipid Oxidation in foods. *Crit. Rev. Food Sci. Nutr.* **1996**, *36*, 175−224.

(43) Aubourg, S. P. Recent advances in Assessment of Marine Lipid Oxidation by Using Fluorescence. *J. Am. Oil Chem. Soc.* **1999**, *76*, 409−419.

(44) Aubourg, S. P. Assessment of antioxidant effectiveness on thermally treated marine lipids by fluorescence detection. *Eur. Food Res. Technol.* **2000**, *211*, 310−315.

(45) Aidos, I.; Lourenço, S.; van der Padt, A.; Luten, J. B.; Boom, R. M. Stability of Crude Herring Oil Produced from Fresh Byproducts: Influence of Temperature During Storage. *J. Food Sci.*, **2002**, *67* (9), 3314−3320.

(46) Stansby, M. E. Flavors and Odors of Fish Oils. *J. Am. Oil Chem. Soc.* **1971**, *48*, 820−823.

(47) Lubis, Z.; Buckle, K. A. Rancidity and lipid oxidation of dried-salted sardines. *Int. J. Food Sci. Technol.* **1990**, *25*, 295−303.

(48) Undeland, I.; Hall, G.; Lingnert, H. Lipid oxidation in fillets of herring (*Clupea harengus*) during ice storage. *J. Agric. Food Chem.* **1999**, *47*, 524−532.