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# THE INFLUENCE OF FROZEN STORAGE ON FATTY ACIDS COMPOSITION FOR ALIMENTARY ANIMAL FATS

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**ABSTRACT.** The purpose of this research was to monitor the storage stability of 2 types of alimentary animal fats (poultry fat and fish oil) during frozen storage (-15...-18$^{o}$C) by fatty acids profile determination in order to follow the variation in saturated and unsaturated fatty acids proportion. Determination of chemical composition of animal fats is important in establishing physicochemical and organoleptic parameters, nature and proportion of fatty acids conferring specific characteristics to them. In the case of fresh poultry fat, in the largest proportion were determined oleic, linoleic and palmitic acids.

Fatty acids variation was correlated with hydrolysis process when fatty acids were released from triglycerides structure and with oxidation process when the degree of unsaturation decreased, due to unsaturated fatty acids oxidation.

***Keywords:*** *fatty acids, alimentary animal fats, frozen storage, oxidation*

## INTRODUCTION

Lipids entered in the composition of living matter from the very beginnings of the life on Earth. Lipids, a heterogeneous class of natural compounds, esters of alcohols with fatty acids are strictly indispensable components in human nutrition, performing many functions in the body [1]. Storage of animal fats even in frozen conditions affects in time the physicochemical, sensory and nutritional properties determining lipolytic or oxidative rancidity and may result in reduction of their validity.

Fatty acids represent the variable structure of lipids, the characteristics of the fats being conferred by the nature and proportion of fatty acids that enters into their composition [2]. From unsaturated fatty acids, linoleic, linolenic and arachidonic acids have a particularly importance, they are also called essential fatty acids because they can not be synthesized by the body and they must be brought by food intake [3].

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Lipolytic alteration occurs due to hydrolytic degradation of lipids from fat composition. Hydrolysis process is catalyzed by lipases that release fatty acids from triglycerides structure [3, 4].

Oxidative rancidity involves the oxidation of unsaturated fatty acids, especially polyunsaturated fatty acids (PUFA) and generates compounds that affect food quality by altering of color, flavour, texture, nutritional value and food safety [4, 5].

The photosensitised route is an alternative oxidative pathway that involves the direct reaction of excited singlet oxygen ($^1O_2$) to unsaturated lipids in the presence of sensitisers [7]. In the peroxidation of unsaturated fatty acids, lipid hydroperoxides form during the propagation phase. These compounds are unstable and decompose rapidly, giving rise to a range of new free radicals and other non-radical compounds, including alkoxyl and alkyls radicals, aldehydes, ketones, as well as a variety of carboxyl compounds that form a complex mixture of secondary lipid oxidation products. Volatiles such as hexanal and pentanal have been associated with the development of undesirable flavours and have been proposed as potential markers of fresh product quality [8, 9].

The purpose of the research was to study if there are significant changes in fatty acids composition for alimentary animal fats during frozen storage, when advanced hydrolysis and oxidation processes were installed, whitch represents the original part of the work, Samet-Bali et al., Sağdiç et al. reported variations in fatty acids composition for cow milk fat and butter produced from goat's milk during storage [10, 11].

## RESULTS AND DISCUSSION

The study of changes in chemical composition for poultry fat and fish oil after 6 months of storage during freezing when hydrolysis and oxidative processes were installed represents one of the original aspect of the work, fatty acids variation in time is an indicator of their stability regarding alterative processes.

Chemical composition of fresh poultry fat was the following: 30.56% SFA, 42.38% MUFA and 27.49% PUFA and presented a soft consistency. In the largest proportion were determined oleic (37.33%), linoleic (25.63%) and palmitic (23.36%) acids. For fresh poultry fat was determined a SFA : MUFA : PUFA = 1.11 : 1.54 : 1 ratio, and essential fatty acids : non-essential fatty acids = 1 : 1.54.

Figure 1 illustrates sample chromatogram for fresh poultry fat in witch fatty acids are recorded in the form of peaks separated from each other by increasing the chain length.

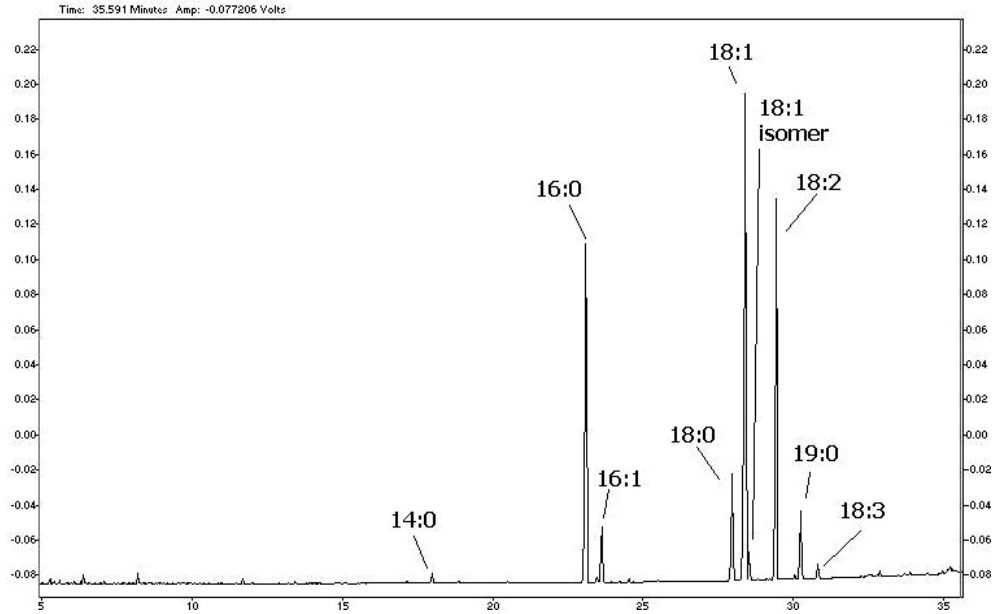


**Figure 1.** Gas chromatogram of fresh poultry fat

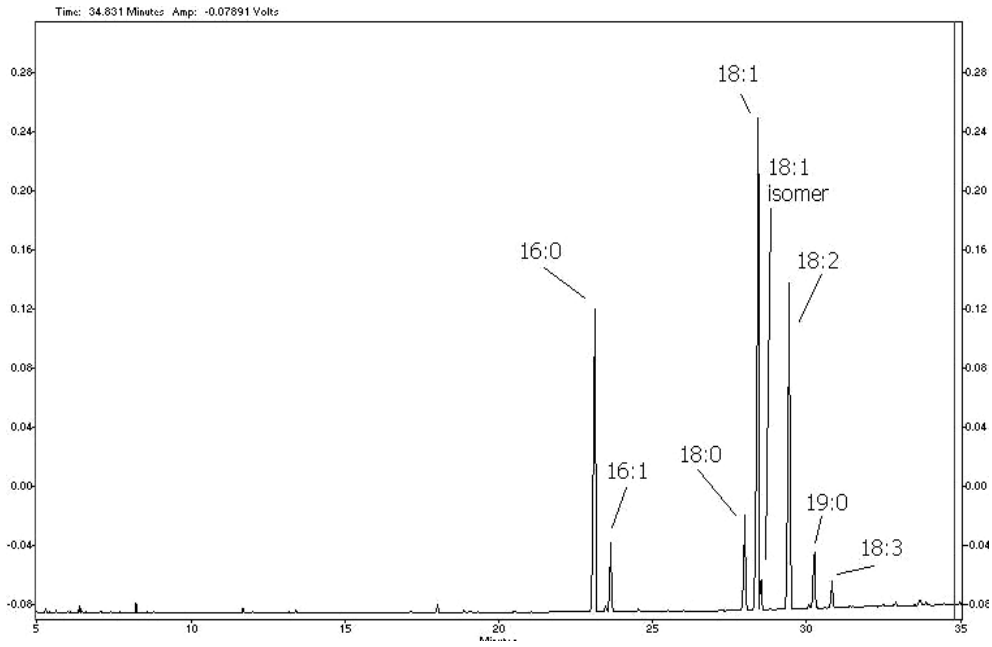


**Figure 2.** Gas chromatogram of poultry fat to 6 months under frozen storage

Poultry fat after 6 months under frozen storage presented an increase in SFA from 30.56% to 30.98% and a decrease in MUFA from 42.38% to 41.79%, and for PUFA a decrease from 27.49% to 26.22%, PUFA showed the significant variations. In the case of oxidized poultry fat, palmitic and stearic acids showed an increase, miristic acid was not detected, and palmitoleic, oleic, vaccenic, linoleic and alfalinolenic acids showed a decrease compared to fresh fat, but linoleic acid showed the greatest variability (fig. 2). For oxidized poultry fat was found a SFA : MUFA : PUFA = 1.27 : 1.60 : 1 ratio, and essential fatty acids : nonessential fatty acids = 1 : 1.60.

It was concluded that the increase of saturated fatty acids content is due to the installation of hydrolysis leading to the release of acids from triglycerides structure, which translates also through the increase of titrable acidity, and the decrease of MUFA and PUFA is due to unsaturated fatty acids oxidation at the same time with the decrease of iodine value.

Fresh fish oil presented the following chemical composition: 20.39% SFA, 44.56% MUFA and 35.05% PUFA. The main determined fatty acids were: oleic (17.14%), *cis*-5,8,11,14,17 eicosapentaenoic (17.05%), *cis*-11-eicosenoic (10.81%), palmitoleic (10.12%), palmitic (17.90%) and arachidonic (9.81%) acids. Docosahexaenoic acid (DHA) has not been detected probably due to its oxidation during the extraction process. The most valuable fatty acid from fish lipids composition is considered to be ω-3 eicosapentaenoic acid (C20:5-EPA) due to its positive influence on the health. Figure 3 illustrates sample chromatogram for fresh fish oil.

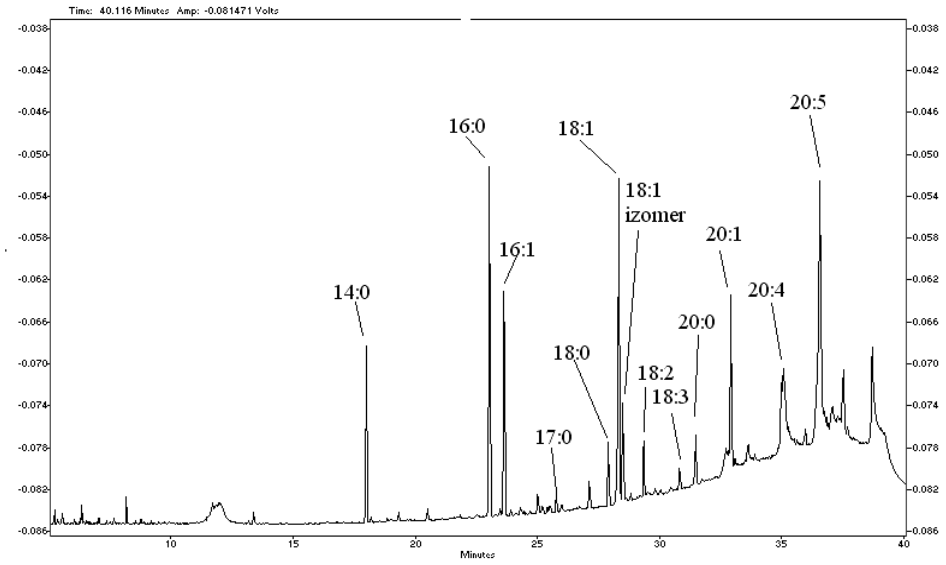


**Figure 3.** Gas chromatogram of fresh fish oil

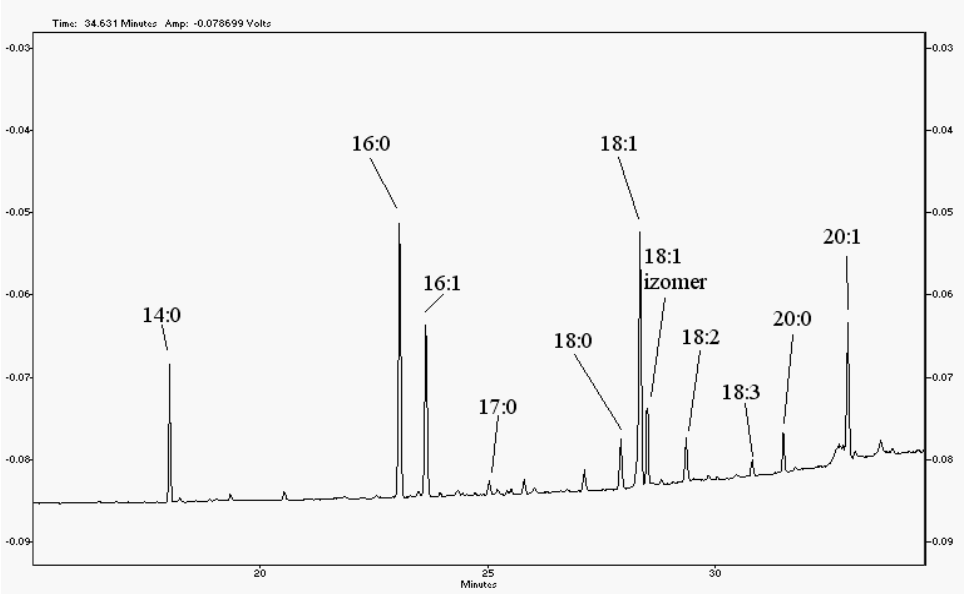


**Figure 4.** Gas chromatogram of fish oil to 6 months under frozen storage

In fish oil sample after 6 months freezing, SFA content increased from 20.39% to 21.58%, MUFA content decreased from 44.56% to 43.80%, and PUFA content decreased from 35.05% to 33.37%, PUFA showed the significant variations (fig. 4).

Arachidonic and *cis*-5,8,11,14,17 eicosapentaenoic acids were not detected, which also highlights the early installation of oxidation in the case of fish oil. For oxidized fish oil was found a SFA : MUFA : PUFA = 1 : 2.09 : 1.60 ratio, and essential fatty acids : nonessential fatty acids = 1 : 1.30.

It should be noted that in the case of poultry fat after 6 months congelation, mono and polyunsaturated fatty acids content was not so pronounced as in the case of fish oil, but the increase of saturated fatty acids content was more pronounced.

Variations in fatty acids content with a more significant decrease for unsaturated fatty acids were found in the case of milk powder storage at ambient temperature and at 15$^{o}$C [12].

Manat et al., observed changes in fatty acid profile during frozen storage of sardines. Fresh sardines had a content of 45.9% SFA, 16.7% MUFA and 35.7% PUFA, from PUFA, DHA was the most abundant followed by EPA. The authors found a reduction in PUFA content during storage, especially of EPA which decreased from 6.14% to 5.33% in the 6th day and to 4.96% in the 15th day, and a decrease in DHA from 19.7% to 18.6% in

the 6th day and to 18.5% in the 15th day. The study showed a decrease in PUFA in the 15th day storage by 8.1%, in MUFA by 9.7% and an increase in SFA by 2.3% [13].

Fátima Aparecida Ferreira de Castro et al., reported that oleic acid was found in the highest proportion in carp fillet, followed by linoleic and palmitic acid. The authors also determined an increase in arachidonic acid after 45 days of frozen storage, and a increase in DHA after 15 days under skin removal, suggesting that these acids were found in the subcutaneous layer [14].

It was concluded that the most pronounced changes in fatty acids composition toke place in fish oil, which suggests that it is more susceptible to alterative processes due to its higher content of unsaturated fatty acid. Hydrolysis and oxidation processes were installed earlier in fish oil than in poultry fat.

## CONCLUSIONS

During frozen storage there was a decrease in fatty acids content in order: PUFA>MUFA>SFA, but these variations are quite small, and storage time did not significantly affect fatty acids profile.

It was concluded that the increase of saturated fatty acids content was due to hydrolysis leading to the release of acids from triglycerides structure, and the decrease of MUFA and PUFA was due to unsaturated fatty acids oxidation. During frozen storage there are changes in fatty acids composition, that is an indicator of their stability to alterative processes.

In the case of poultry fat the changes in fatty acids composition were not so pronounced, which suggests that it can be preserved for a long period of time under freezing.

## EXPERIMENTAL SECTION

### *Samples*

Poultry fat was obtained by raw material fat melting, collected from broilers, male and female, packed in unvacuumate plastic bags, and stored under freezing. Fish oil was obtained by Soxhlet extraction from farmed carp fillets, packaged in brown glass tubes, airtight, was stored under freezing (-15...-18$^{o}$C) and for each fat was determined the chemical composition in fresh state and after 6 months of storage under freezing, when alterative processes were instaled.

### *Physicochemical examination*

Fatty acid composition was determined using gas chromatography (GC) Shimadzu GC-17 A coupled with flame ionisation detector FID. Gas chromatography column is Alltech AT-Wax, 0.25 mm I.D., 0.25 μm thick stationary phase (polyethylene), used helium as carrier gas at a pressure of 147 kPa, temperature of the injector and detector was set to 260$^{o}$C, the oven programm was the following: 70$^{o}$C for 2 min., then the temperature was raised up to 150$^{o}$C with a gradient of 10$^{o}$C/min., a level of 3 min. and the temperature was raised up to 235$^{o}$C with a gradient of 4$^{o}$C/min.

Samples preparation for GC analysis: were weight 50 mg sample, was add 1 mL benzene, from dilution were taking 100 μL and mixed with 200 μL internal standard (nonadecanoic acid 19:0), 1 mL benzene, 2 mL methanol, 4 drops $H_2SO_4$ conc. and was heated at 80$^{o}$C for 2 hours. Then we passed to esters extraction: esterificated sample was passed into a separating funnel, were added 10 mL hexane and 2 mL distilled water, the upper was retained, filtered on cellulose filter, dried with a rotary evaporator, then was dissolved in 1 mL hexane and 1 μL sample was injected into gas chromatograph.

The method consists in transformation of fatty acids in methyl esters in the sample under analysis, followed by separation of components on a chromatography column, their identification by comparison with standard chromatograms and quantitative determination of fatty acids. By chromatography separation the sample chromatogram is obtained in which fatty acids are recorded in the form of peaks separated from each other by increasing the chain length. Results were expressed as w/w (%) of total fatty acids [15, 16].

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