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Qualitative Characteristics of Fat Fraction of Oats Based Products †

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Abstract: Oats based products are characterized by a high fat content with a favorable fatty acid composition. It is of great importance to control the quality of fat fraction as an important indicator of food products safety. The aim of this study was the analysis of fat isolated from whole grain oatmeal, mountain oatmeal and instant oatmeal. The composition of fatty acids by gas chromatography and distribution of fatty acids in triacylglycerol positions were determined. The oxidative stability of the tested fat was evaluated using pressure differential scanning calorimetry. Melting profiles were determined by differential scanning calorimetry. It was found that fat isolated from oat products is a rich source of unsaturated fatty acids. In *sn-2* position of triacylglycerols, the highest share of oleic acid was found. The fat was characterized by the highest proportion of linoleic acid in the *sn-1,3* positions of the triacylglycerols. It was observed that induction time of oxidation process of fat reached the values of 28.79 min—39.07 min in the test conducted at 120 °C and 5.84 min—7.37 at 140 °C. The analyzed melting profiles showed the presence of peaks indicating the presence of low-melting triacylglycerols containing mainly unsaturated fatty acids.

Keywords: oat products; fat; fatty acid composition; fatty acid distribution; oxidative stability; melting profiles

1. Introduction

Cereal products are an important part of the human diet. Oatmeal products are often chosen by people leading a healthy lifestyle for their health-promoting properties [1–3]. The chemical composition of oats and the health-promoting nutrients present in it contribute to the increasing use of this grain in food production [4]. Oats and products made from it are characterized by a higher content of fat with a favorable fatty acid composition compared to other cereals. They contain essential fatty acids that are not synthesized in the human body and should be supplied with food. Fat both in products containing large amounts of this ingredient and in products characterized by a low level of lipids, undergoes many changes in natural conditions and during technological processes. These transformations can be considered as desired or undesirable. The first are all kinds of modifications. The second one causes unfavorable changes in fats, which worsen the nutritional value of the product. These transformations include hydrolysis and autooxidation. Hydrolysis of fats is associated with the breakdown of ester bonds in triacylglycerol molecules under the influence of water. This process leads to the formation of diacylglycerols, monoacylglycerols and free fatty acids, and in extreme cases—glycerol. The acids released as a result of hydrolysis may undergo further

secondary changes of oxidative nature. This seems to be an important problem and should be monitored, as such processes often limit or even prevent the use and further storage of food products. Taking the above into consideration, the purpose of the study was qualitative characteristics of fat fraction isolated from oats products, such as whole grain oatmeal, mountain oatmeal and instant oatmeal.

2. Materials and Methods

2.1. Materials

The research material consisted of fat samples isolated from oats based products, such as: whole grain oatmeal, mountain oatmeal and instant oatmeal, which were purchased at a local store. The studied oats products did not contain any additional ingredients and were within the expiry date. The best before date was: 25.11.2020 in the case of whole grain oatmeal; 15.12.2020 in the case of mountain oatmeal and 02.01.2021—for instant oatmeal.

2.2. Methods

2.2.1. Extraction of Fat from Oats Based Products

Fat was extracted from silverskin according to the procedure described by Reder et al. [5]. The samples were ground and extracted with hexane by shaking for 30 min. Then, the mixture was filtered and dried with magnesium sulfate. After filtering off the drying agent, the solvent was removed by the rotary evaporator at 40 °C. The sample was additionally dried under nitrogen atmosphere to remove residual hexane.

2.2.2. Gas Chromatography

Gas chromatography was used to determine the composition of fatty acids in fat samples. Fatty acids were converted into volatile methyl esters using a methanolic KOH solution according to PN-EN ISO 5509:2001. YL6100 GC gas chromatograph apparatus, equipped with a flame ionization detector and a 30 m long BPX 70 capillary column filled with stationary phase, with an inner diameter of 0.22 mm and a film thickness of 0.25 μm was used. The carrier gas was nitrogen. Fatty acids were identified based on the retention time compared to the standard. For the quantitative analysis of fatty acids, the area of the peak in the chromatogram was determined and the percentage of a given fatty acid was calculated.

2.2.3. Enzymatic Hydrolysis of Triacylglycerols

The sample of fat was mixed with 1 cm^3 of TRIS-HCl solution with a concentration of 1 mol/dm^3 and pH = 8; 0.1 cm^3 $CaCl_2$ and 0.25 cm^3 aqueous solution of bile salts (0.05%). After 30 s of mixing, 20 mg of pancreatic lipase was added. The samples were placed in water bath for 3 min at 40 °C. After incubation, the reaction was stopped by the addition of 1 mL of 6 M hydrochloric acid and 4 mL of diethyl ether. The products were separated by preparative thin layer chromatography. The isolated *sn-2* monoacylglycerols were removed from the plate with silica gel. The fatty acid composition of the *sn-2* monoacylglycerol molecules was determined using gas chromatography, according to the procedure described above for fatty acids composition.

2.2.4. Pressure Differential Scanning Calorimetry

PDSC experiments were carried out using a DSC Q20 TA Instruments. Fat samples of 3–4 mg were weighted into an aluminium pan and placed in the sample chamber under oxygen atmosphere with an initial pressure of 1400 kPa. The maximum PDSC oxidation time (induction time) was determined based on the maximum rate of oxidation (maximum rate of heat flow). The isothermal temperature for each sample was 120 °C and 140 °C.

2.2.5. Differential Scanning Calorimetry

DSC measurements of melting characteristics were carried out with a Q200 DSC (TA Instruments, New Castle, DE, USA). Samples of 3–4 mg were placed into aluminium pans with a lid and were non-hermetically sealed. An empty sealed aluminium pan was used as a reference and the experiments were performed under a nitrogen flow rate of 50 mL/min at normal pressure. Melted samples were heated to 80 °C and held for 10 min., then cooled to −80 °C at 10 °C/min and maintained at −80 °C for 30 min. Then the melting profiles were obtained by heating the samples to 80 °C at a heating rate of 15 °C/min. The temperature measurements were performed using the functions of the Universal Analysis Software (TA Instruments).

2.2.6. Statistical Analysis

Each measurement was triplicate. The data were reported at the means ± standard deviation. One-way ANOVA was conducted using Statgraphics Plus for Windows program, version 4.1. (Statistical Graphics Corporation, Warrenton, VA, USA). Differences were considered to be significant at a *p*-value of 0.05, according to Tukey's Multiple Range Test.

3. Results

3.1. Fatty Acids Composition and Distribution in Triacylglycerols

The results shown in Figure 1 present the content of saturated, mono- and polyunsaturated fatty acids. Fat isolated from mountain oatmeal turned out to be the richest source of unsaturated fatty acids (82,76%) with high content of mono- and polyunsaturated fatty acids. In fat extracted from instant oatmeal the highest content of saturated fatty acids (22.53%) was determined in comparison to other studied samples. The fat was also characterised by the lowest content of unsaturated fatty acids.

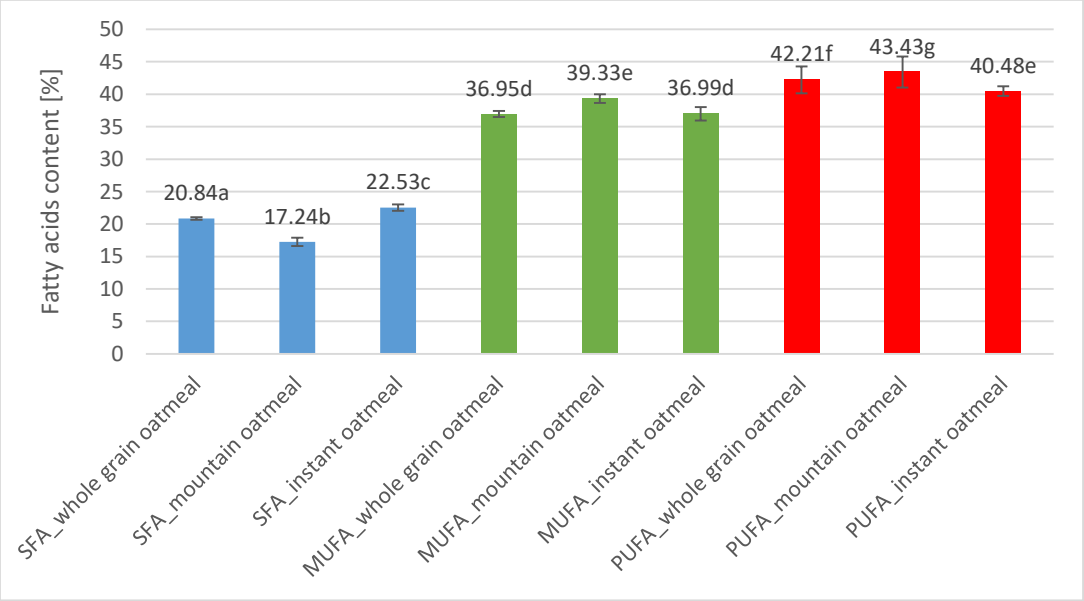

Figure 1. Content of fatty acids groups in fat isolated from oats based products (SFA—saturated fatty acids; MUFA—monounsaturated fatty acids; PUFA—polyunsaturated fatty acids).

In Tables 1–3 composition of chosen fatty acids in TAGs and their distribution in *sn-2* and *sn-1,3* positions of triacylglycerols in fat extracted from whole grain oatmeal, mountain oatmeal and instant oatmeal are presented.

Table 1. Composition of chosen fatty acids in *sn-2* and *sn-1,3* positions of triacylglycerols in fat extracted from whole grain oatmeal and a share of fatty acids in internal position.

Fatty Acid	Fatty Acid Composition in TAG [%]	Fatty Acid Composition in Positions		Fatty Acid Share in *sn-2* Position [%]
		sn-2	*sn-1,3*	
C 16:0	18.02 ± 1.09	3.41 ± 0.7	25.33 ± 2.44	6.30 ± 1.15
C 18:0	1.87 ± 0.18	0.51 ± 0.09	2.56 ± 0.53	9.00 ± 0.85
C 18:1 n-9	35.12 ± 2.75	48.59 ± 2.21	28.39 ± 1.97	46.12 ± 2.45
C 18:2 n-6	39.83 ± 1.54	44.73 ± 3.11	37.39 ± 1.65	37.44 ± 1.63
C 18:3 n-3	1.71 ± 0.28	1.66 ± 0.14	1.73 ± 0.23	32.36 ± 2.04

In Table 1 composition of selected fatty acids in internal and external positions of triacylglycerol structure of fat isolated from whole grain oatmeal is presented. Oleic acid (C 18:1 n-9) is the most abundant fatty acid in *sn-2* position with a share in this position riching 46.12%. Palmitic acid (C 16:0) was in dominant amount in external positions. It is worth mentioning that the share of palmitic acid (C 16:0) in *sn-2* position was the lowest reaching 6.30%.

The simlilar results were obtained in the case of fat isolated from mountain oatmeal, what is presented in Table 2. Oleic acid (C 18:1 n-9) is the most abundant fatty acid in *sn-2* position with the highest share in this position at a level of 42.83%. Based on the results, it can be stated that linoleic acid (C 18:2 n-6) dominated in external positions. Stearic acid (C 18:0) was found at the lowest content in *sn-2* position, but it should be noted that palmitic acid (C 16:00) is the fatty acid with the lowest share in internal position.

Table 2. Composition of chosen fatty acids in *sn-2* and *sn-1,3* positions of triacylglycerols in fat extracted from mountain oatmeal and a share of fatty acids in internal position.

Fatty Acid	Fatty Acid Composition in TAG [%]	Fatty Acid Composition in Positions		Fatty Acid Share in *sn-2* Position [%]
		sn-2	*sn-1,3*	
C 16:0	16.13 ± 1.45	4.14 ± 0.18	22.12 ± 1.74	8.56 ± 1.48
C 18:0	1.28 ± 0.07	0.67 ± 0.07	1.59 ± 0.12	17.33 ± 1.37
C 18:1 n-9	37.57 ± 2.05	48.28 ± 2.78	32.23 ± 2.06	42.83 ± 3.71
C 18:2 n-6	41.57 ± 3.14	44.08 ± 1.93	40.32 ± 3.07	35.35 ± 2.85
C 18:3 n-3	0.61 ± 0.08	1.57 ± 0.04	0.13 ± 0.05	35.51 ± 2.43

In the case of fat isolated from instant oatmeal the obtained results presented in Table 3 demonstrated that oleic acid (C 18:1 n-9), similarly to previously presented results, dominated in *sn-2* position with a highest share of 45.41% in this position. Stearic acid (C 18:0) was detected at the lowest level in *sn-2* position, whereas in the case of palmitic acid (C 16:00) the lowest share in internal position was defined.

Table 3. Composition of chosen fatty acids in *sn-2* and *sn-1,3* positions of triacylglycerols in fat extracted from instant oatmeal and a share of fatty acids in internal position.

Fatty Acid	Fatty Acid Composition in TAG [%]	Fatty Acid Composition in Positions		Fatty Acid Share in *sn-2* Position [%]
		sn-2	*sn-1,3*	
C 16:0	18.81 ± 1.75	4.45 ± 0.86	25.99 ± 2.64	7.88 ± 0.83
C 18:0	2.27 ± 0.04	0.81 ± 0.06	3.00 ± 0.06	11.85 ± 1.95
C 18:1 n-9	35.32 ± 2.04	48.11 ± 2.14	28.93 ± 1.63	45.41 ± 2.38
C 18:2 n-6	38.35 ± 2.14	43.64 ± 2.85	35.71 ± 2.36	37.94 ± 2.15

C 18:3 n-3	1.49 ± 0.05	1.46 ± 0.07	1.51 ± 0.08	32.66 ± 1.97

3.2. Oxidative Stability of Fats

Time of induction of fat oxidation is presented in Figure 2. When analysing the obtained results it can be observed that fat isolated from whole grain oatmeal is of highest stability with time of oxidation reaching 39.07 min. and 7.37 min at 120 °C and 140 °C, respectively. Fat extracted from mountain oatmeal turned out to be of lowest oxidative stability. In the case of fat from mountain oatmeal the induction time of oxidation reached the value of 28.79 min. at 120 °C and 5.84 min. at 140 °C.

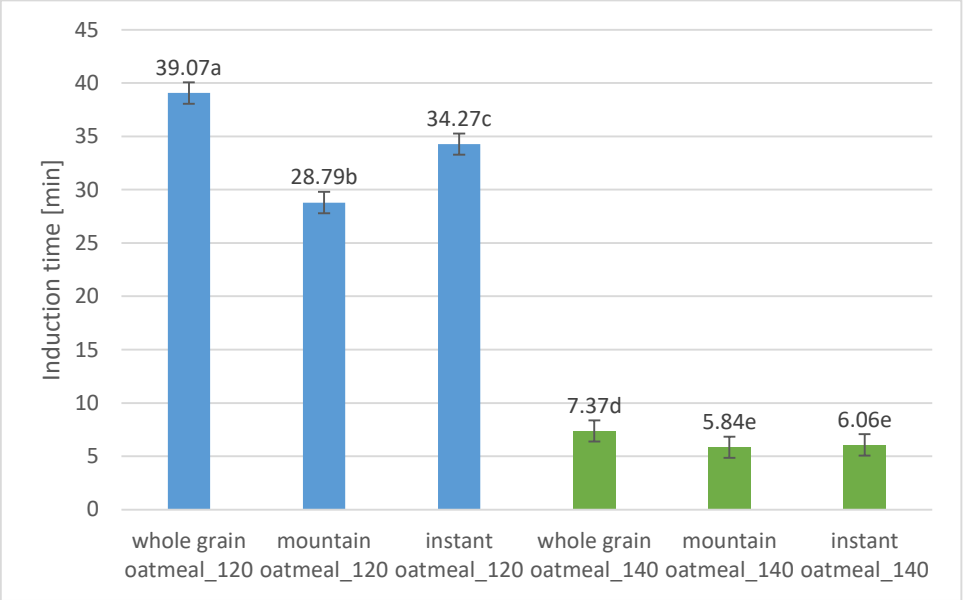

Figure 2. Induction time of oxidation [min] of fat isolated from oats based products measured at 120 °C and 140 °C.

3.3. Melting Characteristics of Fat

An example of melting curve of fat isolated from studied oatmeal products is presented in Figure 3. In the course of curve two endothermic transitions can be observed. The first mild peak was detected in the region from −70.70 °C in the case of fat isolated from whole grain oatmeal to −68.68 °C for fat from mountain oatmeal. The second intensive event can be observed at temperature reaching −19.62 °C for whole grain oatmeal, −19.77 °C for mountain oatmeal and −24.10 °C for instant oatmeal. The presence of such transitions on the course of melting curve indicates the presence of low-melting triacylglycerols containing mainly unsaturated fatty acids.

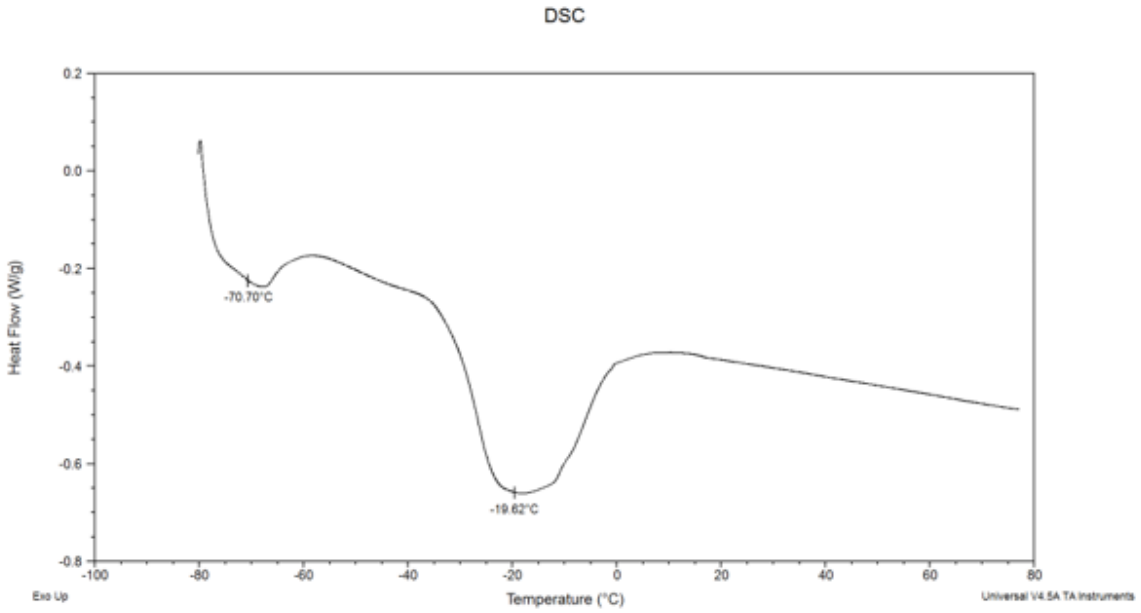

Figure 3. DSC curve of melting of fat isolated from whole grain oatmeal.

4. Discussion

Obtained results are in agreement with researches conducted by Lange et al. [6], according to which oatmeal oil is a source of unsaturated fatty acid with high content of linoleic acid reaching 26–53%, oleic acid at a level of 19–48%. It contains also α-linolenic acid at a level of 0.5–5.0%. In our study, *sn-2* position of triacylglycerole was occupied mainy by oleic acid. Oleic acid was also the fatty acid with the highest share in *sn-2* position. External positions were occupied mainly by linoleic acid. In *sn-1,3* positions also high amount of palmitic acid was found. According to Arcos et al. [7], plant oils containing common fatty acids residues are characterized by selective placement of unsaturated fatty acids in the *sn-2* position. This phenomenon can be also observed in the presented study. According to Hunter et al. [8], one of the consequences of the presence of saturated fatty acids in external positions is the formation of insoluble calcium salts, what can lead to deficiency of calcium in human body. Comparing the oxidative stability to results presented by other authors [9,10], it can be stated that fat isolated from oats based products is characterised by similar oxidative stability to extra virgin oil and huzelnut oil, but it is much less stable than rapeseed oil. Melting profiles are of typical course for products rich in unsaturated fatty acids. The results are in agreement with these presented by Knothe et al. [11]. To our best knowledge, this is the first study with detailed characteristics of fat isolated from oats products, presenting the fatty acids composition, fatty acids distribution in triacylglycerol structure, oxidative stability and melting characteristics of fat.

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