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Thermal properties of expanded amaranth seed oil

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Abstract: The study presents the results of analysed amaranth oil. The aim of the research was to determine the physicochemical properties of the oil, in particular its thermal properties. The oil obtained from expanded amaranth seeds was tested. The obtained results proved the good oil resistance to oxidation. Three peaks present on the DSC melting curves of amaranth oil, were connected with the presence of low-melting triacyloglicerols with polyunsaturated fatty acids (first peak) and medium-melting fraction rich in triacyloglicerols with monounsaturated and saturated fatty acids (second and third peaks). The composition of fatty acids in the studied amaranth oil showed a high content of essential fatty acids.

Keywords: amaranth; amaranth oil; thermal properties

1. Introduction

Amaranth was present both in the culture and in the cuisine of the peoples of South America already in pre-Columbian times [1]. This pseudocereal is valued for its high content of vitamins, calcium and iron. It is used to produce bread and other bakery products, which are mainly intended for people suffering from celiac disease. The fat content of amaranth seeds is about 6-8%. The most abundant fatty acids are: stearic, palmitic, oleic and linoleic acids. These seeds are also a very good source of tocopherols, squalene and phytosterols. The oil obtained from amaranth, due to its health properties, is recommended for the elderly, pregnant women, as well as people with skeletal diseases [2].

Thermal analysis is a term describing a set of research methods used to determine changes in the physical properties of a sample under the influence of temperature [3]. The basic parameters determined by these techniques are: melting temperature, decomposition temperature, crystallization temperature, temperature of polymorphic transformations and specific heat [4]. Differential Scanning Calorimetry (DSC) consists in measuring the difference in the rate of heat flow to or from the sample and the reference. Both the sample and reference are subjected to controlled temperature changes [5]. Isothermal tests and polythermal tests can be used [6]. Differential scanning calorimetry is used in the case of: testing the degradation of fat as a result of oxidation, determining the fat solid phase index [4]. In pressure differential scanning calorimetry (PDSC), the experiment is conducted under increased pressure of gases such as air or oxygen. In the isothermal mode, the sample is heated from room temperature to the desired temperature, and then maintained at a given temperature and pressure until an exothermic reaction occurs [7].

Thermal properties of oils are a very important distinguishing feature of their quality and stability.

The aim of the study was to analyse the properties of fat extracted from extruded amaranth seeds by thermal methods.

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2. Materials and Methods

The raw material was NaturAvena expanded amaranth, manufacturer: NaturAvena Sp. z o.o., net weight: 110g. The studied material was oil extracted from amaranth.

2.1. *Extraction using the Soxhlet apparatus*

10 g of amaranth were weighed, wrapped in a filter paper thimble, and then placed in a Soxhlet apparatus. 150 ml of hexane was used as the solvent. After cooling the extracted oil, about 3 g of a drying agent, ($MgSO_4$) was added to the flask. The sample was additionally dried with nitrogen. The weight of the oil obtained from the tested sample was converted to fat content in 100 g of the product [8].

2.2. Determination of oil melting characteristics

The analysis was performed using a TA DSC Q200 differential scanning calorimeter. Before the test, the sample was stored in refrigerated conditions. 3-4 mg of oil were weighed and sealed in hermetic aluminum vessels. The samples were cooled to -80°C and then heated to 80 °C at heating rate of 5 °C/min. The determination was performed in three repetitions [9].

2.3. *Determination of oil oxidation time*

The analysis was performed using a TA PDSC Q20 pressure differential scanning calorimeter. Prior to testing, the sample was stored under refrigeration conditions. The oil was weighed in the amount of 3-4 mg into an open aluminum vessel. The samples were then heated from room temperature to 120 °C, 130 °C and 140 °C. The stated temperatures were maintained until an exothermic reaction occurred. For each temperature, the analysis was performed in three repetitions [10].

2.4. *Determination of oil crystallization temperature*

The analysis was performed using a TA DSC Q200 differential scanning calorimeter. Prior to the analysis, the sample was stored under refrigeration conditions. 3-4mg of oil were weighed and sealed in hermetic aluminum vessels. The samples were cooled from 20 °C to -80 °C at heating rate of 2°C/min. The experiment was performed in three repetitions [11].

2.5. Determination of fatty acid composition

2g of oil was mixed with 2ml of hexane and 2 ml of methanol solution of potassium hydroxide. The mixture was then stored in a thermostat at 40°C for 20 minutes. After this time, the sample was analysed. The analysis was performed using a gas chromatograph type YL6100 GC. To determine the composition of fatty acids, a BPX-70 capillary column with an internal diameter of 0.22 mm, a film thickness of 0.25 μm and a length of 60 m was used. The chromatograph was equipped with a flame-ionization detector FID. The initial temperature of 60 °C was maintained for 5 min and then it was increased by 10 °C min−1 to 180 °C; by 3 °C min−1 from 180 to 230 °C and then kept at 230 °C for 15 min. The result of the analysis was retention time compared with the standard [12]. The assay was performed in duplicate

3. Results and Discussion

3.1. *Melting profile*

Figure 1. shows the melting characteristics of amaranth oil.

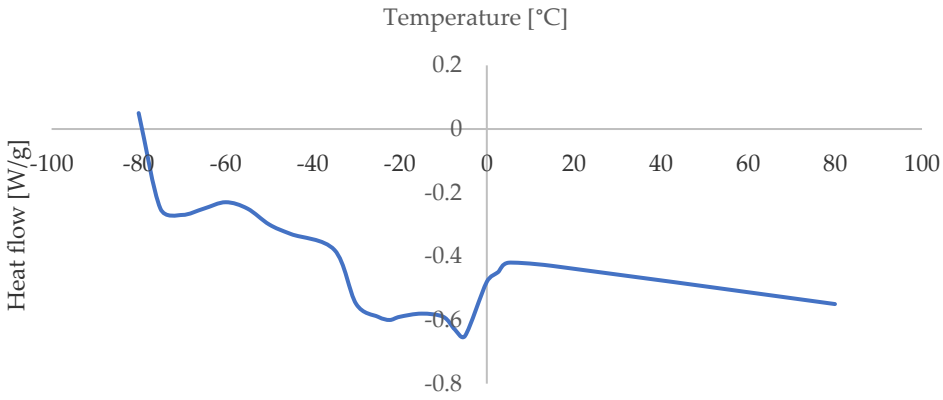

Figure 1. Melting characteristics of amaranth oil.

Based on the melting profile, it can be seen, that in the case of amaranth oil endothermic transformations occured. In the curve course three characteristic peaks can be observed (Fig.1). The peak at -22.32°C was characteristic for low-melting triacylglycerols, the so-called oleins. This value of melting temperature coresponds to the presence of polyunsaturated fatty acids, such as for example linoleic fatty acid, which was detected in the amount of 34.65% (Tab.1). Low-melting fractions require much longer cooling time than high-melting fractions to solidify [13]. The low-melting triacylglycerols contain short-chain and medium-chain fatty acids, which are responsible for the temperature of fat melting. At -7.34°C, a peak characterizing monounsaturated fatty acids occurred. In amaranth seed oil, this peak was mainly characterized by the presence of oleic acid. The oleic fat content in amaranth oil was about 18.05% (Tab. 1). The peak at 2.57°C was the result of the saturated fatty acids presence in the oil. In amaranth oil, the most abundant saturated acids were: stearic acid and palmitic acid (Tab. 1). Comparing obtained results with studies of other fats, it can be stated, that the characteristic melting temperature of cocoa butter is much higher and amounts to about 20.49°C [11]. In the case of palm oil melting, peaks can be observed at the following temperatures: 3.46°, 7.57°C and 25.23°C [6]. The differences in melting characteristics of various oils and fats are mainly due to their individual fatty acids profiles.

3.2. *Oil oxidation time at different temperature*

Figure 2 shows the curve of amaranth oil oxidation at temperature 120; 130 and 140°C.

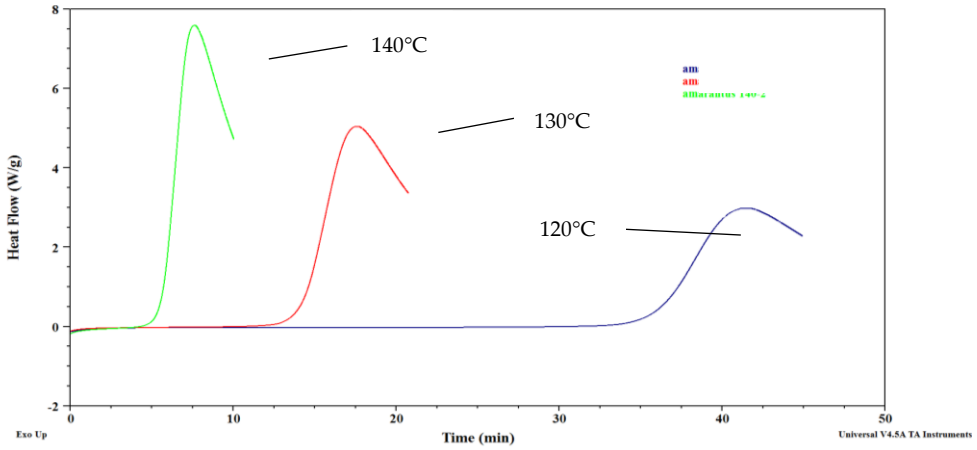

Figure 2. The curve of amaranth oil oxidation at temperature 120; 130 and 140°C.

Based on the curve course, it can be observed, that an exothermic reaction took place in amaranth oil at 120°C. The oil was oxidized after 42.70 minutes (Fig. 2). Comparing this result with data available in the literature, it can be concluded that this oil was more resistant to oxidation than many other cold-pressed oils. Linseed oil analyzed under the same conditions oxidized after about 17.82 minutes due to its high linolenic acid C18:3 content, which makes it prone to oxidation [14], hemp oil - after 18.91 minutes, and poppy seed oil - after 22.86 minutes. In the case of rapeseed oil, the oxidation time was 60.62 minutes. In the case of pumpkin oil, the oxidation induction time was much longer and amounted to 71.01 minutes [15]. The analysis carried out at the temperature of 130°C (Fig. 2) showed an increase in the rate of the oil oxidation process. Taking the average value of the oxidation time at 120°C as 42.70 minutes and the average value of the oxidation time at 130°C as 17.53 minutes, it appears that the time of oil oxidation increased by 58.9%. According to the Van't Hoff rule, an increase in the reaction temperature by 10°C results in a 2-4 times faster reaction [16].

The analysis carried out at 140°C (Fig. 2) showed an increase in the rate of the oxidation process. The mean value of the three repetitions was 7.44 minutes. Oil oxidation time at 140°C decreased by 57.6% compared to the process carried out at 130°C and by 82.6% compared to the analysis carried out at 120°C. Also in this case, the Van't Hoff rule was preserved [16]. In the case of testing the oxidation time of amaranth oil, the oxidation time at 130°C increased 2.5 times compared to the analysis at 120°C. The oxidation time tested at 130°C increased 2.4 times compared to the oxidation time at 140°C.

3.3. *Oil crystallization temperature*

Figure 3 shows the DSC curve of amaranth oil crystallization.

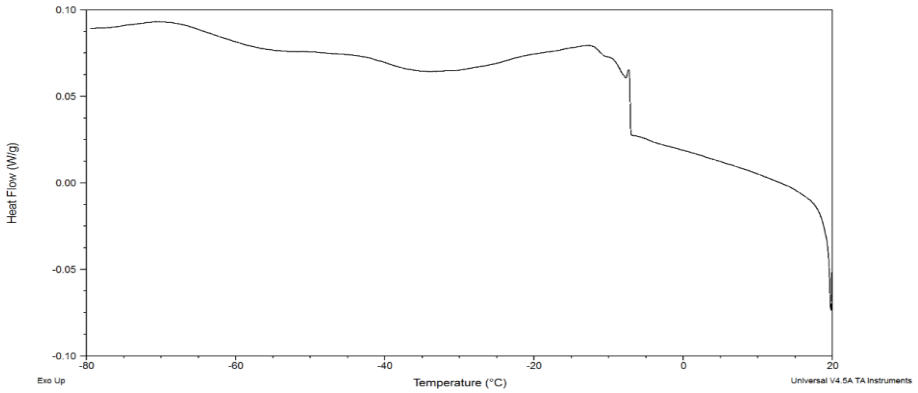

Figure 3. DSC curve of amaranth oil crystallization.

The length of the fatty acid chain and the presence of double bonds directly affect the behavior of the fat during crystallization. In the crystallization diagram of amaranth seed oil two characteristic peaks can be observed (Fig. 3). They correspond to the exothermic reactions of low-melting and high-melting fatty acids [11]. The peak at an average temperature of -12.87°C corresponded to the crystallization reaction of the low-melting fraction. This fraction consisted of short-chain, medium-chain and monounsaturated fatty acids, such as for example oleic fatty acid (Tab. 1). At average temperature of -7.24°C, a peak was present, characterizing the crystallization of the high-melting fraction. It consists mainly of saturated fatty acids [17]. The low-melting fraction of amaranth oil includes oleic acid. The high-melting fraction, on the other hand, contains such acids as palmitic acid and stearic acid [18].

3.3. *Fatty acid composition*

Table 1. Fatty acid composition of expanded amaranth seed oil.

Fatty acid	Precentage (%)
Linoleic C18:2 n-6c	34.65 ± 0.07
Oleic C18:1 n-9c	18.05 ± 0.07
Palmitic C16:0	15.05 ± 0.21
Docozadiene C22:2 n-6	8.85 ± 0.07
Stearic C18:0	3.10 ± 0.0
Others	20.20 ± 0.14

Values represent means ± standard deviations.

The fatty acid that occurred in the largest amount in amaranth oil was linoleic acid (Table 1). The obtained results were consistent with the literature, according to which the most abundant fatty acids in amaranth seeds are: linoleic, stearic, palmitic and oleic fatty acids [2]. According to Ratusz and Wirkowska [18], the content of linoleic acid in amaranth oil was 49.7%, oleic acid 25.9%, and palmitic acid 16.1%.

4. Conclusions

On the DSC melting curves of amaranth oil, 3 peaks occurred, corresponding to: fatty acids of the low-melting fraction, monounsaturated fatty acids and saturated fatty acids. PDSC analysis of the oil showed its good resistance to oxidation compared to poppy seed oil or hemp oil. However, the oxidation time was definitely shorter than that of rapeseed oil or pumpkin seed oil. Two peaks were visible on the curve obtained as a result of crystallization temperature analysis: the first characterized the low-melting fraction of the oil, the second - the high-melting fraction. The low-melting fraction consisted of short-chain, medium-chain and monounsaturated fatty acids. The high-melting fraction included mainly saturated fatty acids.

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