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Proceeding Paper

Thermal Properties of Expanded Amaranth Seed Oil †

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Abstract: This study presents the results of an analysis of amaranth oil. The aim of this research was to determine the physicochemical properties of the oil, particularly its thermal properties. The oil obtained from expanded amaranth seeds was tested. The obtained results proved the oil's good resistance to oxidation. Three peaks present on the DSC melting curves of amaranth oil were associated with the presence of low-melting-point triacyloglicerols with polyunsaturated fatty acids (the first peak) and a medium-melting-point fraction rich in triacyloglicerols with monounsaturated and saturated fatty acids (the 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

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1. Introduction

Amaranth was already present both in the culture and cuisine of the peoples of South America 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 consumption by 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, and 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 using these techniques are melting temperature, decomposition temperature, crystallization temperature, the temperature of polymorphic transformations, and specific heat [4]. Differential scanning calorimetry (DSC) consists of measuring the difference in the rate of heat flow to or from a sample and a 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 testing the degradation of fat as a result of oxidation and determining the fat solid phase index [4]. In pressure differential scanning calorimetry (PDSC), an experiment is conducted under increased pressure of gases such as air or oxygen. In the isothermal mode, a 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].

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

The aim of this study was to analyze the properties of fat extracted from extruded amaranth seeds using thermal methods.

2. Materials and Methods

The raw material used was NaturAvena expanded amaranth manufactured by Natura Vena Sp. z o.o. (Piaseczno, Poland), with a net weight of 110 g. The studied material was oil extracted from amaranth.

2.1. Extraction Using the Soxhlet Apparatus

A total of 10 g of amaranth was weighed, wrapped in a filter paper thimble, and then placed in a Soxhlet apparatus. A total of 150 mL of hexane was used as a 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's Melting Characteristics

This analysis was performed using a TA DSC Q200 differential scanning calorimeter. Before the test, the sample was stored in refrigerated conditions. In total, 3–4 mg of oil was 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

This analysis was performed using a TA DSC Q200 differential scanning calorimeter. Prior to the analysis, the sample was stored under refrigeration conditions. A total of 3–4 mg of oil was 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

A total of 2 g of oil was mixed with 2 mL of hexane and 2 mL of methanol solution of potassium hydroxide. The mixture was then stored in a thermostat-controlled chamber at 40 °C for 20 min. After this time had elapsed, the sample was analyzed. The analysis was performed using a gas chromatograph (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). An initial temperature of 60 °C was maintained for 5 min, and then it was increased by 10 °C min^{-1} to 180 °C and 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.

Based on the melting profile, it can be seen that in the case of amaranth oil, endothermic transformations occurred. In the curve course, three characteristic peaks can be observed (Figure 1). The peak at −22.32 °C is characteristic of low-melting-point triacylglycerols, the so-called oleins. This melting temperature corresponds to the presence of polyunsaturated fatty acids, such as linoleic fatty acid, which was detected at a proportion of 34.65% (Table 1).

Low-melting-point fractions require much longer cooling times than high-melting-point fractions to solidify [13]. The low-melting-point triacylglycerols contain short-chain and medium-chain fatty acids, which are responsible for the temperature at which fat melts. 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% (Table 1). The peak at 2.57 °C was the result of the presence of saturated fatty acids in the oil. In amaranth oil, the most abundant saturated acids were stearic acid and palmitic acid (Table 1). Comparing the obtained results with findings from 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 the melting of palm oil, peaks can be observed at the following temperatures: 3.46°C, 7.57 °C, and 25.23 °C [6]. The differences in the melting characteristics of various oils and fats are mainly due to their individual fatty acid profiles.

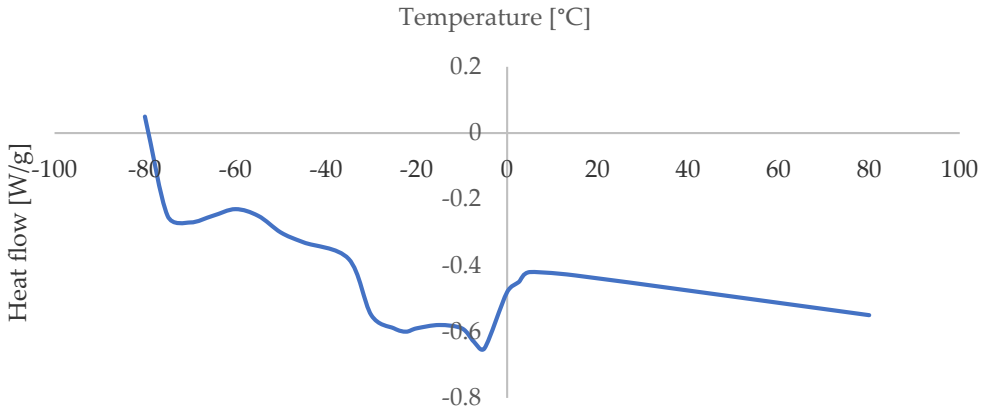

Figure 1. Melting characteristics of amaranth oil.

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

Fatty Acid	Percentage (%)
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.

3.2. Oil Oxidation Time at Different Temperatures

Figure 2 shows the curves of amaranth oil oxidation at temperatures of 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 min (Figure 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 min due to its high linolenic acid C18:3 content, which makes it prone to oxidation [14]; hemp oil oxidized after 18.91 min; and poppy seed oil oxidized after 22.86 min. In the case of rapeseed oil, the oxidation time was 60.62 min. In the case of pumpkin oil, the oxidation induction time was much longer and amounted to 71.01 min [15]. The analysis carried out at a temperature of 130 °C (Figure 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 min and the average value of the oxidation time at 130 °C as 17.53 min, it appears that the time for 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-fold faster reaction [16].

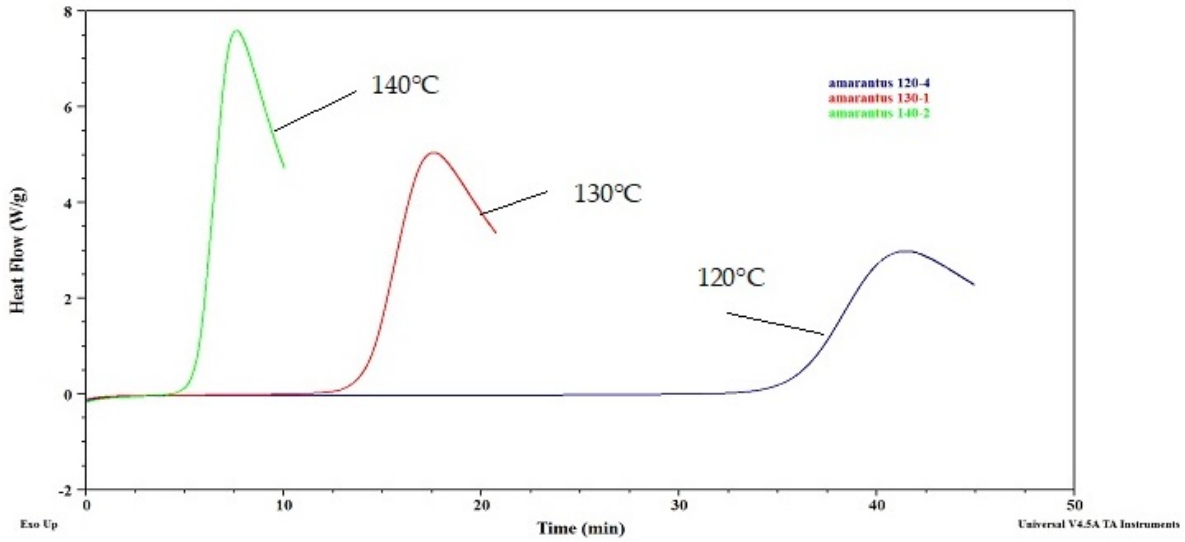

Figure 2. The curve of amaranth oil oxidation at temperature 120; 130 and 140 °C.

The analysis carried out at 140 °C (Figure 2) showed an increase in the rate of the oxidation process. The mean value of the three repetitions was 7.44 min. The 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 upheld [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's crystallization.

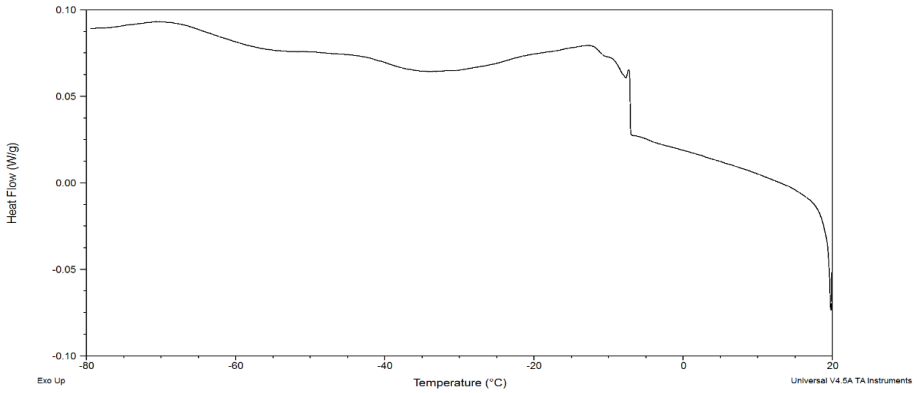

Figure 3. DSC curve of amaranth oil crystallization.

The length of the fatty acid chain and the presence of double bonds directly affect the behavior of fat during crystallization. In the crystallization diagram of amaranth seed oil, two characteristic peaks can be observed (Figure 3). They correspond to the exothermic reactions of low-melting-point and high-melting-point fatty acids [11]. The peak at an average temperature of −12.87 °C corresponded to the crystallization reaction of the low-melting-point fraction. This fraction consisted of short-chain, medium-chain,

and monounsaturated fatty acids, such as oleic acid (Table 1). At an average temperature of −7.24 °C, a peak was present, characteristic of the crystallization of the high-melting-point fraction. This fraction consists mainly of saturated fatty acids [17]. The low-melting-point fraction of amaranth oil includes oleic acid. The high-melting-point fraction, on the other hand, contains such acids as palmitic acid and stearic acid [18].

3.4. Fatty Acid Composition

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 acid [2]. According to Ratusz and Wirkowska [18], the share of linoleic acid, oleic acid, and palmitic acid in amaranth oil are 49.7%, 25.9%, and 16.1%, respectively.

4. Conclusions

On the DSC melting curves of amaranth oil, three peaks occurred, corresponding to fatty acids of the low-melting-point 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-point fraction of the oil, while the second characterized the high-melting-point fraction. The low-melting-point fraction consisted of short-chain, medium-chain, and monounsaturated fatty acids. The high-melting-point fraction mainly included saturated fatty acids.

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