

## Article

# Application of Chromatographic and Thermal Methods to Study Fatty Acids Composition and Positional Distribution, Oxidation Kinetic Parameters and Melting Profile as Important Factors Characterizing Amaranth and Quinoa Oils

Magdalena Wirkowska-Wojdyła , Ewa Ostrowska-Ligeza , Agata Górka  and Joanna Bryś 

Department of Chemistry, Institute of Food Sciences, Warsaw University of Life Sciences, 02-787 Warsaw, Poland; ewa\_ostrowska\_ligeza@sggw.edu.pl (E.O.-L.); agata\_gorska@sggw.edu.pl (A.G.); joanna\_brys@sggw.edu.pl (J.B.)  
\* Correspondence: magdalena\_wirkowska@sggw.edu.pl; Tel.: +48-22-593-7606

**Abstract:** Amaranth and quinoa are classed as pseudocereals that do not belong to the grass family, meaning they are not technically a grain. Both of them are seeds with tremendous nutritional value; compared to other cereals, they contain much more fat. The aim of the study was to present the parameters characterizing thermal properties of amaranth and quinoa oils, such as: oxidation induction time, oxidation kinetic parameters, and melting profile. In isolated oils, the peroxide value, oxidative stability by the Rancimat test (in 120 °C) and the pressure differential scanning calorimetry (PDSC) method (at 100, 110, 120, 130, 140 °C), fatty acids composition, and their distribution between the triacylglycerol positions were determined. The kinetic parameters of the oxidation process (activation energy, pre-exponential factor, and reaction rate constants) were calculated using the Ozawa–Flynn–Wall method and the Arrhenius equation. To measure the melting profile, the differential scanning calorimetry (DSC) method was used. Both types of seeds are a good source of unsaturated fatty acids. Induction time of oxidation suggests that amaranth oil may have better resistance to oxidation than quinoa oil. The melting characteristics of the oils show the presence of low-melting triacylglycerol fractions, mainly containing unsaturated fatty acids, which means that a small amount of energy is required to melt the fats.

**Keywords:** amaranth oil; quinoa oil; oxidative stability; DSC; Rancimat



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## 1. Introduction

Amaranth (*Amaranthum*) and quinoa (*Chenopodium quinoa* Willd) are pseudocereals because their seeds resemble real cereals in terms of their composition and function. Amaranth and quinoa cultivated from tropical to subtropical regions were important food crops to Aztec, Mayan and Incan civilizations [1]. Pseudocereals are gluten-free products, which represent a significant advance towards ensuring an adequate intake of nutrients in subjects with celiac disease. Interest in quinoa and amaranth stems from their nutritional value, higher than cereal grains like corn, oats, wheat, and rice. The beneficial nutritional value of these pseudocereals is due to the high protein content, as well as dietary fibre and bioactive compounds such as polyphenolic compounds [2–4]. The quinoa seeds contain exogenous amino acids such as: lysine, arginine, histidine, and methionine [5]. These amino acids are most often found in small amounts in cereal grains and legumes [6]. Quinoa seed protein is characterized by a more balanced amino acids composition than wheat protein. Amaranth seed protein contains all the amino acids essential for the human body, surpassing soybean protein. The biological value of amaranth protein is higher than milk proteins, so amaranth can be used to produce milk replacement products for people intolerant to lactose [7].

Traditional cereals are not a rich source of fat in comparison to oilseed crop materials. On the other hand, pseudocereals like quinoa or amaranth, in comparison to other cereals,

contain much more fat, supplementing the diet with this ingredient in the daily food ration. According to Jancurova et al. [8], the fat content in quinoa seeds can range from 2 to 10%. Navruz-Varli and Sanlier [9] classify quinoa as an alternative oilseed. Although the lipid content of amaranthus seed is typically 6–9%, some species such as *A. spinosus* and *A. tenuifolius* have been reported to contain as much as 19.3% [5].

The high amount of fat in pseudocereals means that it can be susceptible to the oxidation process. Oxidation is one of the most important processes that takes place in oils during storage or heat treatment. Moreover, the oxidative stability of an oil is one of the most significant parameters from the point of view of oil safety [10].

Among several available methods to measure the lipid oxidation, differential scanning calorimetry (DSC) or pressure differential scanning calorimetry (PDSC) can be considered as the most effective. The oxidative stability of lipids is determined as oxidative induction time; in practice, the time required to begin the oxidative decomposition process of the oil sample [11,12]. Differential scanning calorimetry is an applicable tool to describe the thermal transitions of examined samples in micro-scale. It provides information about thermodynamic and kinetic characteristics dependent on the temperature of the material. In food products analysis, DSC helps in determination of the transitions resulting from the specific composition of foods because different groups of nutrients are specified by various transitions [13]. Apart from that, DSC has been suggested as a possible method for verifying quality, determining varieties, and detecting adulteration of oil. DSC is preferable to other methods because it is fast and the use of environmental damaging solvents is not required [14].

According to our knowledge, in the literature, there are no studies on the kinetics of oxidation process of oil from pseudocereals using the PDSC method. Therefore, the aim of this study was to determine the oxidative stability and kinetic parameters of oxidation of oil isolated from quinoa and amaranth seeds. The melting characteristics of these oils are also presented, as well as the analysis of fatty acid composition and their stereochemical distribution in triacylglycerols.

## 2. Materials and Methods

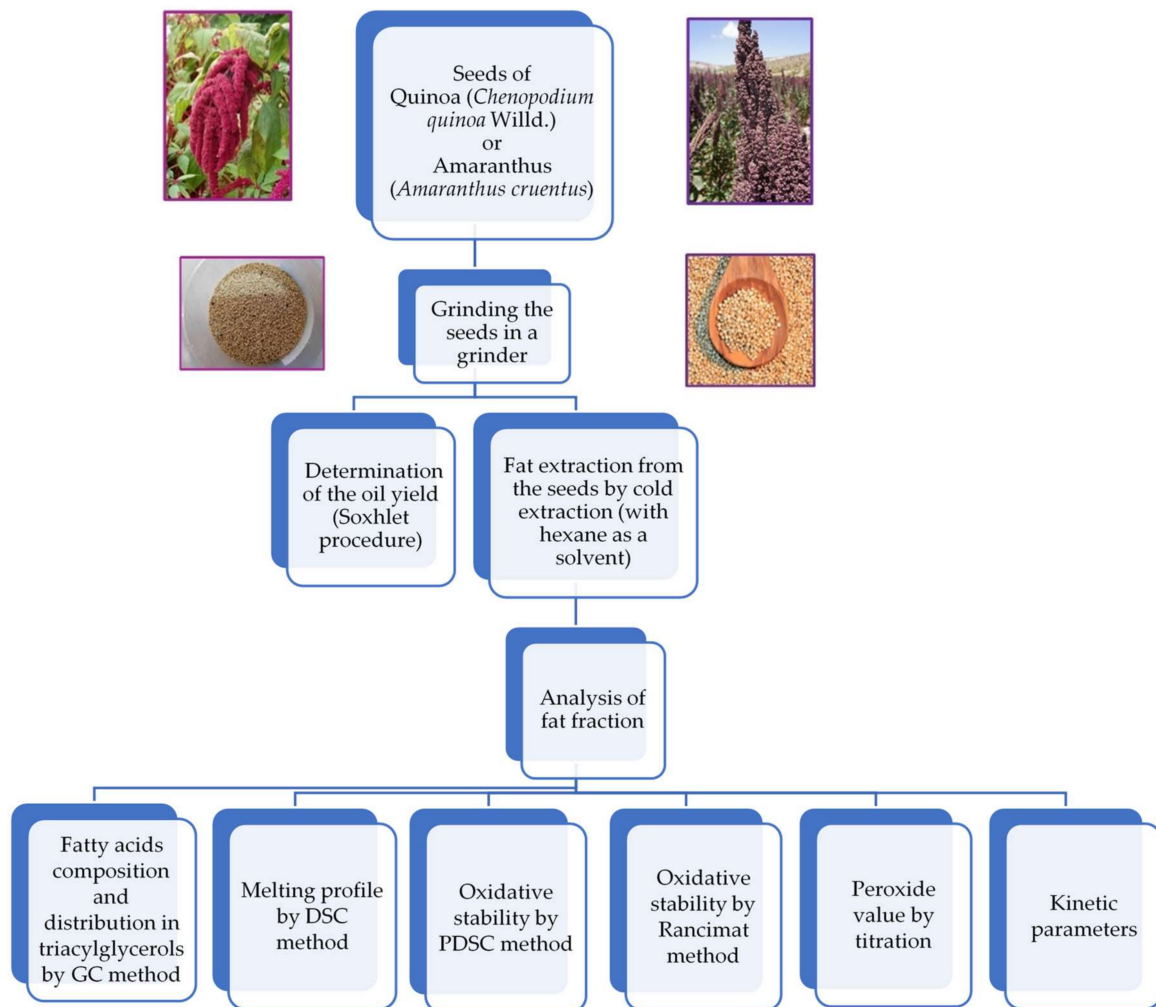
### 2.1. Materials

Two packs of quinoa (*Chenopodium quinoa* Willd) and amaranthus (*Amaranthus cruentus*) seeds were purchased in two different retail outlets in Poland in October 2019 in order to avoid the same lots of seeds. The seeds were ground in a grinder model and passed through a 60-mesh screen for the determination of the oil yield by the Soxhlet procedure according to the ISO method [15]. Oil yield was defined as the grams of oil in 100 g of dry basis. In order to perform the remaining determinations, the fat was isolated from the seeds by cold extraction (with hexane as a solvent) according to the procedure described by Bryś et al. [16]. Extraction was performed in duplicate for each part of seeds. The graphical scheme of the study approach is presented in Figure 1.

### 2.2. GC Analysis

Fatty acids composition in fats isolated from quinoa and amaranth was determined as fatty acid methyl esters by gas chromatography according to the ISO method [17]. The YL6100 (Young Lin Bldg., Anyang, Hogyedong, Korea) gas chromatograph equipped with a flame ionization detector and a BPX-70 capillary column (SGE Analytical Science, Milton Keynes, UK) was used. The procedure for analyzing fatty acid methyl esters has been described in previous studies [18].

The analysis of distribution of fatty acids between the position of triacylglycerols (TAG) was also done as the percentage content of a fatty acid in the sn-2 position, according to the procedure described by Bryś et al. [19].



**Figure 1.** Graphical scheme of study approach (GC method—gas chromatography method).

### 2.3. Melting Profile

The instrument Q200 DSC (TA Instruments, Newcastle, DE, USA) was used to record the melting profile. Procedure was described by Aguedo et al. [20] and Wirkowska-Wojdyła et al. [21].

### 2.4. Peroxide Value

Peroxide values (PV) of oils were determined by the iodometric technique in correspondence with ISO standards [22].

### 2.5. Oxidative Stability by Rancimat Method

The oxidative stability of oils was determined using a Rancimat 743 Metrohm apparatus (Herisau, Switzerland), according to the ISO method [23], at constant temperature 120 °C. The exact procedure was described by Symoniuk et al. [10].

### 2.6. Oxidative Stability by PDSC Method

Pressure differential scanning calorimeter (DSC Q20 TA Instruments, Newcastle, WA, USA) was used to determine the oxidative stability of fats. The experiment was performed at constant temperatures: 100, 110, 120, 130, 140 °C under 1400 kPa pressure of oxygen. The procedure was described in previous studies [21].

### 2.7. Kinetic Parameters

The kinetic parameters of the oxidation process (activation energy, pre-exponential factor, and reaction rate constants) were calculated using the Ozawa–Flynn–Wall method and the Arrhenius equation.

Based on the results of the induction times obtained in the PDSC test, a graph of the logarithm of the induction time ( $\tau$ ) versus the reciprocal temperature (in absolute scale) was plotted. Regression lines with correlation coefficients  $>0.99$  were determined according to the Equation (1):

$$\log \tau = a T^{-1} + b \quad (1)$$

where  $a$  and  $b$  are adjustable coefficients. Reaction of fat oxidation proceeds in an excess of oxygen and can be treated as a first-order reaction. This fact can be used to determine the activation energy using the Ozawa–Flynn–Wall (Equation (2)):

$$Ea = 2.19 \times R \times a \quad (2)$$

where  $R$  is a gas constant and  $a$  is a coefficient from Equation (1). Based on the Arrhenius equation (Equation (3)):

$$k = Z e^{-Ea/RT} \quad (3)$$

activation energy— $Ea$ , pre-exponential factor— $Z$ , and reaction rate coefficient— $k$ , for all temperatures were calculated.

### 2.8. Statistical Analysis

The Statgraphics Plus, version 5.1 (Statistical Graphics Corporation, Warrenton, VA, USA) program was used for statistical analysis of the results. Tuckey's multiple range test at a  $p$ -value of 0.05 was used to analyze significant differences.

## 3. Results and Discussion

### 3.1. Total Fat Content and Fatty Acid Composition

The quinoa seeds contained 5.43% of fat (Table 1). According to Villacrés et al. [24], yield in the oil extraction from quinoa seeds also reached about 5%. Rodriguez Gomez et al. [25], in the study of six quinoa varieties, obtained the fat content from 3.90 to 5.21 g/100 g of fresh weight. The flour from quinoa analyzed by Ascheri et al. [26], which was added to cereal products, contained 5.6% of lipids.

**Table 1.** Total fat content, peroxide value and Rancimat induction time (h) of fat extracted from quinoa and amaranth seeds.

Parameter	Quinoa	Amaranth
Fat content (g/100 g of seeds)	5.43 ± 0.51 <sup>a</sup>	7.30 ± 0.62 <sup>b</sup>
PV (meq O <sub>2</sub> /kg of fat)	8.86 ± 1.38 <sup>a</sup>	6.57 ± 0.68 <sup>b</sup>
Induction time (h)	5.10 ± 0.47 <sup>a</sup>	6.90 ± 0.38 <sup>b</sup>

Data denoted by the same letter are not statistically different ( $\alpha = 0.05$ ).

In the study, oil yield recovery from amaranth seeds reached 7.30% (Table 1). According to Caselato-Sous and Amaya-Farfán [27], the fat content in amaranth was 7%. Based on the studies conducted by Sanz-Penell et al. [28], the more than six-times higher fat content in amaranth than in wheat, i.e., about 10 g/100 g of fresh weight, affected the functionality of the flour as a stabilizing agent for the gas release during baking, which probably makes the dough elastic.

The total percentage of individual fatty acids and fatty acid groups (SFA—saturated fatty acids, MUFA—monounsaturated fatty acids, PUFA—polyunsaturated fatty acids) is shown in Table 2. The quinoa lipid fraction contained 10.98% of SFA, 30.82% of MUFA and 58.19% of PUFA. The content of fatty acid groups in amaranth seeds was: 24.94% SFA, 25.46% MUFA, 49.61% PUFA. The experiment of Ryan et al. [29] on quinoa oil showed the

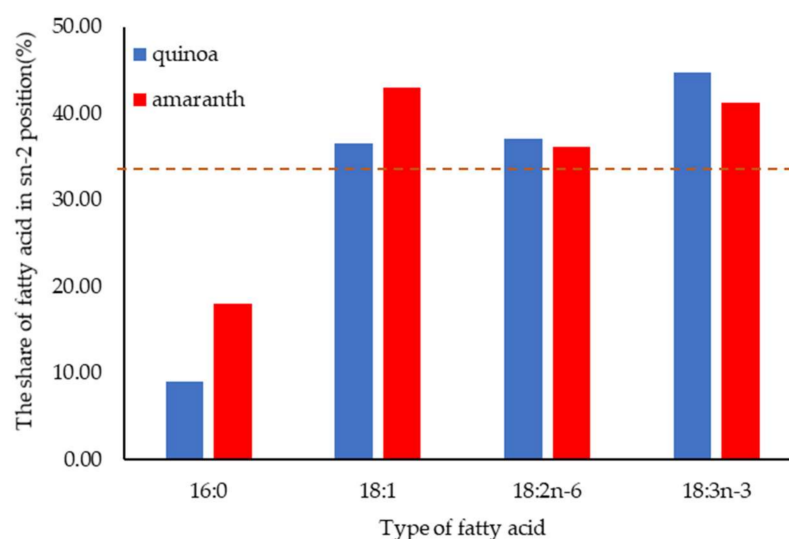
content of fatty acids at the level of: SFA 11.2%, MUFA 32.8% and PUFA 56.1%. The total content of SFA, MUFA and PUFA in the experiment conducted by Palombini et al. [30] for quinoa was 13.55%, 28.55%, 57.90%, respectively. For amaranth oil, the same researchers determined the content of SFA, MUFA, and PUFA at the levels of 25.28%, 33.82% and 40.90%. In the studies conducted by León-Camacho and García-González [31] on *Amaranthus cruentus*, the amount of SFA was 26.4%, MUFA was 34.7%, and PUFA was 38.9%. The saturated fatty acid present in the predominant amount in quinoa oil was palmitic acid, at 9.59%. Stearic acid was detected in a smaller amount, at 0.59% (Table 2). Similar amounts were obtained by Ando et al. [32]: about 10% of palmitic acid, and 0.75% of stearic acid. In amaranth fat, palmitic acid content was 18.92%, and stearic acid was 4.50% (Table 2). The experiment of Jahaniaval et al. [5] on *A. cruentus* showed the presence of palmitic acid at the level of 22.2%, and of stearic acid at the level of 3.57%. The tested quinoa oil showed a high proportion (52.59%) of C18: 2n–6 (linoleic) acid. The content of C18: 3n-3 ( $\alpha$ -linolenic) acid reached the value of 5.42% (Table 2). Tang et al. [33] experimented with white quinoa, and showed the presence of C18: 2n–6 acid at the level of 47.39%, and the content of C18: 3n-3 acid at the level of 8.44%. The total content of unsaturated fatty acids in analyzed pseudocereals can help in maintaining health, as linoleic acid reduces levels of cholesterol and LDL in serum, while oleic acid presents a neutral behavior with respect to LDL, but moderately increases the level of high-density lipoproteins (HDL) [24]. Generally, this distinctive fatty acid profile is suitable for human health as it reduces risk factors related to cardiovascular diseases [25].

**Table 2.** Fatty acids composition (%) of oil extracted from quinoa and amaranth seeds.

Type of Fatty Acids	Quinoa	Amaranth
C14:0	0.14 ± 0.08 <sup>a</sup>	0.25 ± 0.08 <sup>a</sup>
C15:0	0.05 ± 0.01 <sup>a</sup>	0.09 ± 0.02 <sup>a</sup>
C16:0	9.59 ± 1.21 <sup>b</sup>	18.92 ± 1.15 <sup>b</sup>
C16:1	0.07 ± 0.01 <sup>a</sup>	0.11 ± 0.04 <sup>a</sup>
C17:0	0.04 ± 0.01 <sup>a</sup>	0.08 ± 0.03 <sup>a</sup>
C18:0	0.59 ± 0.10 <sup>b</sup>	4.50 ± 0.59 <sup>b</sup>
C18:1 cis	28.84 ± 2.15 <sup>a</sup>	25.03 ± 1.87 <sup>a</sup>
C18:2 n-6	52.59 ± 2.67 <sup>a</sup>	48.55 ± 2.48 <sup>a</sup>
C18:3 n-3	5.42 ± 1.26 <sup>a</sup>	1.06 ± 0.36 <sup>b</sup>
C20:0	0.57 ± 0.16 <sup>a</sup>	1.10 ± 0.24 <sup>b</sup>
C20:1	1.91 ± 0.34 <sup>a</sup>	0.32 ± 0.11 <sup>b</sup>
C20:2	0.18 ± 0.08	-
SFA	10.98 ± 1.57 <sup>a</sup>	24.94 ± 2.11 <sup>b</sup>
MUFA	30.82 ± 2.50 <sup>a</sup>	25.46 ± 2.02 <sup>a</sup>
PUFA	58.19 ± 4.01 <sup>a</sup>	49.61 ± 2.84 <sup>b</sup>

Data denoted by the same letter are not statistically different ( $\alpha = 0.05$ ). SFA—saturated fatty acids, MUFA—monounsaturated fatty acids, PUFA—polyunsaturated fatty acids.

As for the distribution of fatty acids between the positions of triacylglycerols in quinoa and amaranth lipid fraction, it was typical for vegetable oils. In both quinoa and amaranth oils, unsaturated fatty acids tended to be located in the internal position sn-2 of triacylglycerols (Figure 2). The proportion of saturated fatty acids in the sn-2 position was below 33.3%, which means that saturated fatty acids were mainly located in the external sn-1,3 positions.



**Figure 2.** The percentage of palmitic, oleic, linoleic and  $\alpha$ -linolenic acids in the sn-2 position of triacylglycerols (TAG) of amaranth and quinoa oil.

In the literature, influence of the TAG structure on the oxidative stability of oils is not always consistent. Some researchers reported that TAG with unsaturated fatty acids located at the sn-2 positions were more stable than TAG with unsaturated fatty acids in external positions [34,35]. Saturated fatty acids coexisting in TAG with unsaturated fatty acids, did not affect the oxidative of fat, whereas short chain saturated fatty acids can enhance oxidative stability of unsaturated TAG. On the other hand, Martin et al. [36] discussed that location of the fatty acids in the TAG position did not seem to be conclusive of the oxidative stability of fat.

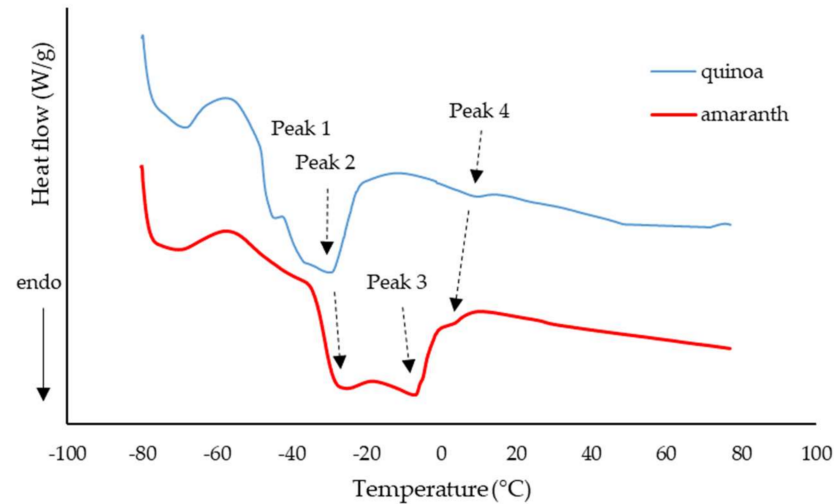
### 3.2. Melting Profile

The melting point is one of the main indicators characterizing the consistency of fats and oils, and consequently, also their possible uses. DSC melting curves of amaranth and quinoa oils are presented in Figure 3. In the quinoa oil, three endothermic peaks were observed at temperatures:  $-44.81$  °C,  $-20.34$  °C, and  $9.08$  °C. For amaranth oil, three endothermic peaks can also be observed, but in a different temperature range. The maximum of the first peak was recorded at temperature of  $-26.10$  °C, the second at  $-7.05$  °C, and the third at  $3.58$  °C. The occurrence of maximum peaks at low temperatures was attributed to the high content of low-melting triacylglycerols with a high proportion of mono- and polyunsaturated fatty acids [21]. The performed determination of the fatty acid composition of the analyzed amaranth and quinoa oils confirmed the predominant share of unsaturated fatty acids. Generally, vegetable oil with a high degree of unsaturation can remain liquid over a wide temperature range [37]. Our results are in agreement with those reported by Wirkowska et al. [21], Wirkowska et al. [38], and Rezig et al. [39], who observed that vegetable oils were characterized by the presence of peaks in the low temperature range on the melting curve, which corresponded to the presence of low-melting TAG fractions.

### 3.3. Oxidative Stability

In both oils, peroxide value did not exceed the value specified in Codex Alimentarius for refined oils ( $<10$  meq  $O_2$ /kg of fat), although in the quinoa oil, the level of peroxide value was higher. This may mean that quinoa oil was less resistant to oxidation than amaranth oil. The amount of peroxides, as the only indicator, did not clearly indicate the fat's resistance to oxidation. It is advisable to perform other tests characterizing the degree of oxidation. Oil extracted from amaranth seeds was characterized by a longer induction time measured with the Rancimat test than fat isolated from quinoa seeds (Table 1). Induction time obtained for amaranth oil (6.9 h) was consistent with the results obtained by

Szterk et al. [40] (6.14 h). In tested amaranth oils, a longer induction time was noticed than for linseed oil—0.39–0.76 h [10], rapeseed oil—4.76–5.84, and olive oil—4.79–5.26 h [41]. By contrast, quinoa oil was characterized by shorter induction time than hazelnut oil—5.19–8.94 h [41].



**Figure 3.** Melting DSC curves, determined in the temperature range  $-80$ – $80$  °C of amaranth (red line) and quinoa (blue line) oils.

The results for oxidative stability of amaranth and quinoa oils measured in the PDSC test at five different temperatures are summarized in Table 3. As expected, the induction time of the tested oils decreased with increase in temperature. The induction time for amaranth oil ranged from 435.26 min (at 100 °C) to 32.20 min (at 140 °C), and for quinoa oil ranged from 300.15 min to 20.51 min. The oxidative stability of oils assessed by the PDSC method had only been the subject of a few studies. Irwandi et al. [42] obtained an induction time of 71.4 min in a study of the cultivar *Amarantus gangeticus*. The PDSC result in an experiment carried out by Ando et al. [32] for quinoa oil was 71 min at 120 °C. In our study, the PDSC induction time of investigated amaranth and quinoa oils was much longer than in results obtained by Symoniuk et al. [10] in a similar experiment for linseed oil: 104.20–111.19 min at 100 °C, 46.19–51.93 min at 110 °C, 21.20–24.72 min at 120 °C, 10.48–11.30 min at 130 °C, 4.33–4.97 min at 140 °C. On the other hand, studies conducted by Ciemniowska et al. [41], also in similar experiment, indicated that rapeseed oils, olive oils and hazelnut oils were characterized by a longer induction time in the temperature range of 100–130 °C.

**Table 3.** PDSC induction time (min.) in the temperature range 100–140 °C of oils extracted from quinoa and amaranth seeds.

Temperature (°C)	Induction Time (min)	
	Quinoa	Amaranth
100	300.15 ± 4.98 <sup>a</sup>	435.26 ± 6.50 <sup>b</sup>
110	169.68 ± 3.21 <sup>a</sup>	200.50 ± 4.60 <sup>b</sup>
120	82.82 ± 2.10 <sup>a</sup>	112.00 ± 3.20 <sup>b</sup>
130	47.36 ± 2.06 <sup>a</sup>	62.40 ± 2.90 <sup>b</sup>
140	20.51 ± 1.13 <sup>a</sup>	32.20 ± 2.20 <sup>b</sup>

Data denoted by the same letter are not statistically different ( $\alpha = 0.05$ ).

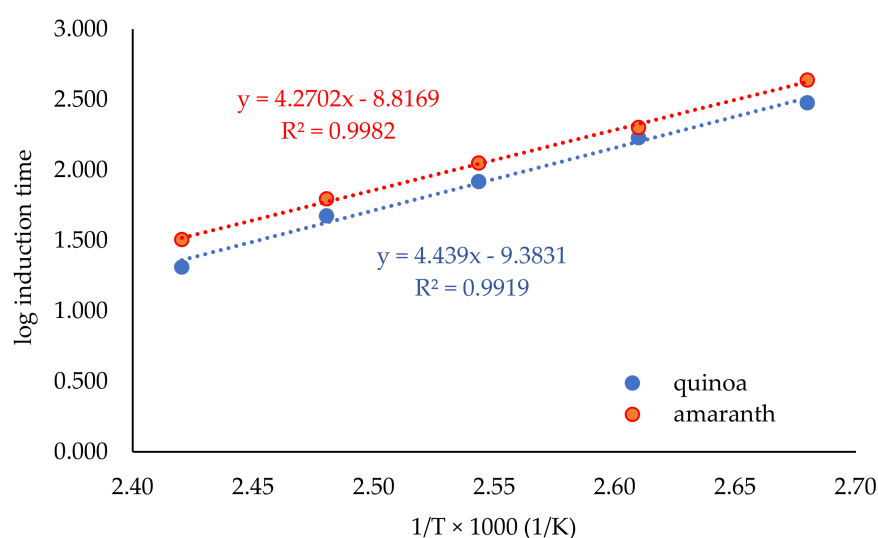
PDSC induction times in whole temperatures range (100–140 °C) were significantly longer for amaranth oil than for quinoa oil. The free fatty acids present in the oil made the fat more susceptible to oxidation. The investigated quinoa oil was characterized by a

higher level of free fatty acids (measured by acid value), which resulted in lower oxidative stability compared to amaranth oil with lower level of free fatty acids (data not presented).

If we compare the oxidative stability measured at the same temperature (120 °C) by the Rancimat and PDSC tests, it turned out that induction time values measured by PDSC were four times shorter compared to those measured by the Rancimat method. The differences could be related to the smaller sample size used in PDSC measurement (3–4 mg) in comparison to the Rancimat quantity of the sample (2.5 g) [41]. According to Tan et al. [43], higher surface-volume ratio of the PDSC oil sample also played an important role leading to the shortened analyzed time. It may also be due to the fact that the oil in the PDSC test was oxidized with pure oxygen at a pressure of 1400 kPa, while in the Rancimat test, air containing approx. 21% oxygen at a flow of 20 L/h [41] was used. Ciemniowska et al. [41] managed to obtain a statistically significant linear correlation ( $R > 0.99$ ) between PDSC and the Rancimat values for hazelnut oil. The authors recommended PDSC as an appropriate objective method for assessing the oxidative stability of oil.

### 3.4. Kinetics Analysis of Oxidation

Oxidation time measured in isothermal conditions (100–140 °C) enabled preparation of graphical dependence between the logarithm of the induction time ( $\tau$ ) and the reciprocal temperature (in absolute scale) (Figure 4).



**Figure 4.** Log PDSC induction time ( $\tau$ ) versus reciprocal temperature for oxidation of amaranth (red line) and quinoa (blue line) oil.

Due to the fact that high  $R^2$  coefficients were obtained ( $>0.99$ ), the data from the equation describing the linear relationship were the starting point for calculating the kinetic parameters (Table 4). In Table 5, the oxidation parameters of amaranth and quinoa oil (obtained in this study) with the available references data on the oxidation of other vegetable oils were presented. Obtained values of activation energy were lower than values obtained by Symoniuk et al. [10] for linseed oil (93.14–94.53 kJ), Ratusz et al. [44] for *Camelina sativa* oil (87.63–93.61 kJ), and Ciemniowska et al. [41] for hazelnut oil (89.06 kJ), olive oil (92.81 kJ), and rapeseed oil (92.68 kJ). Due to the high content of polyunsaturated fatty acids in the analyzed amaranth and quinoa oils, a small amount of energy was needed to initiate the oxidation reaction. According to Adhvaryu et al. [45], high content of MUFA and SFA would increase the activation energy, whereas the high content of PUFA would decrease the activation energy value for lipid oxidation.



**Table 4.** Kinetics parameters (*a* and *b*—adjustable coefficients, *Ea*—activation energy, *Z*—pre-exponential factor, *k*—reaction rate coefficient) of oxidation of oils extracted from quinoa and amaranth seeds.

Parameters	Quinoa	Amaranth
<i>a</i>	4.27	4.44
<i>b</i>	8.82	9.38
R <sup>2</sup>	0.9919	0.9982
<i>Ea</i> (kJ/mol)	77.75 ± 3.24 <sup>a</sup>	80.82 ± 2.87 <sup>a</sup>
<i>Z</i> (1/min)	1.44 × 10 <sup>7</sup>	5.13 × 10 <sup>7</sup>
<i>k</i> at 100 °C	1.89 × 10 <sup>-4</sup>	2.48 × 10 <sup>-4</sup>
<i>k</i> at 110 °C	3.63 × 10 <sup>-4</sup>	4.91 × 10 <sup>-4</sup>
<i>k</i> at 120 °C	6.76 × 10 <sup>-4</sup>	9.36 × 10 <sup>-4</sup>
<i>k</i> at 130 °C	1.22 × 10 <sup>-3</sup>	1.72 × 10 <sup>-3</sup>
<i>k</i> at 140 °C	2.14 × 10 <sup>-3</sup>	3.10 × 10 <sup>-3</sup>

Data denoted by the same letter are not statistically different ( $\alpha = 0.05$ ).

**Table 5.** Comparison of oxidation parameters (activation energy—*Ea*, pre-exponential factor—*Z*, and reaction rate coefficient—*k*) of pseudo-cereal oils with camelina, linseed, hazelnut, rapeseed and olive oil.

Typ of Oil	<i>Ea</i> (kJ/mol)	<i>Z</i> (1/min)	<i>k</i> range	References
quinoa seeds oil	77.75 ± 3.24	1.44 × 10 <sup>7</sup>	1.89 × 10 <sup>-4</sup> –2.14 × 10 <sup>-3</sup> (at 100–140 °C)	this study
amaranth seeds oil	80.82 ± 2.87	5.13 × 10 <sup>7</sup>	2.48 × 10 <sup>-4</sup> –3.10 × 10 <sup>-3</sup> (at 100–140 °C)	this study
camelina oil	88.37–93.61	1.40 × 10 <sup>11</sup> –4.12 × 10 <sup>11</sup>	1.17 × 10 <sup>-2</sup> –3.06 × 10 <sup>-1</sup> (at 90–130 °C)	[42]
linseed oil	93.14–94.53	3.24 × 10 <sup>11</sup> –5.38 × 10 <sup>11</sup>	1.25 × 10 <sup>-2</sup> –7.43 × 10 <sup>-1</sup> (at 90–140 °C)	[10]
hazelnut oil	89.06	2.08 × 10 <sup>10</sup>	7.10 × 10 <sup>-3</sup> –1.14 × 10 <sup>-1</sup> (at 100–140 °C)	[39]
rapeseed oil	92.68	1.02 × 10 <sup>11</sup>	1.08 × 10 <sup>-2</sup> –1.95 × 10 <sup>-1</sup> (at 100–140 °C)	[39]
olive oil	92.81	6.5 × 10 <sup>10</sup>	6.60 × 10 <sup>-3</sup> –1.19 × 10 <sup>-1</sup> (at 100–140 °C)	[39]

Taking into account the rate constant of the oxidation reaction, it can be observed that the reaction rate increased with increasing temperature, both for amaranth oil and quinoa oil. The *k* values obtained by other research [10,41,44] demonstrated the same pattern.

This study had limitations. In the present study we did not analyze the oxidative stability by the Rancimat method in wide range of temperatures (only at 120 °C), as well as in total phenolic compounds. Interest in quinoa and amaranth has markedly increased, due to their significant amount of bioactive compounds, such as phenolic compounds, flavonoids and their glycosides, betanins, and carotenoids [46]. Total phenolic compounds were positively correlated with antioxidant activities of quinoa and amaranth seeds [46,47]. Phytochemical nutrients in quinoa and amaranth may help restore the balance between oxidative stress and antioxidant defense. Diet supplemented with quinoa and amaranth seeds reduced oxidative stress in the plasma, heart, kidney, liver, spleen, lung, testis and pancreas of fructose administered rats [46]. Cisneros-Yupanqui et al. [48] reported that activity of superoxide dismutase (an enzyme that catalyzes the dissociation of the free radical in water and hydrogen peroxide) was increased when quinoa seeds were supplied to hypertension-induced rats. In addition, the free phenolic and PUFA fractions of cooked quinoa showed strong antioxidant ability based on Caco-2 cell-based antioxidant activity assay. In addition, the phenolics and unsaturated fatty acids exhibited protective effects on H<sub>2</sub>O<sub>2</sub>-induced Caco-2 cell oxidative injury [46].

#### 4. Conclusions

Our results showed that quinoa oil contained more polyunsaturated fatty acids and less saturated fatty acids than amaranth oil. Both oils were a very good source of unsaturated fatty acids. The distribution of fatty acids between the triacylglycerol positions in amaranth and quinoa oil was typical for vegetable oils. Saturated fatty acids were found mainly in the external positions, while unsaturated fatty acids were located in the internal position. The PDSC test was a very useful method for determining the oxidative stability of oils due to the short time of the analysis, the small amount of sample required, and the fact that it did not require chemical reagents for the test. PDSC has the potential to be used as an alternative method for evaluation of the stability of edible oils. Induction time of oxidation of quinoa and amaranth oils suggested that amaranth oil may present better resistance to oxidation, while activation energy values indicate that a small amount of energy should be supplied to initiate oxidation of both amaranth and quinoa oils. The obtained results of the kinetics of the oxidation reaction allowed prediction of the oxidation process under various conditions and may be useful for the assessment of the oxidation rate of oils from other pseudocereals.

The presented paper contains the preliminary study, and further investigations are needed in order to confirm the suitability of the DSC method to determine the thermal properties of pseudocereal oils.

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