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Application of Thermal Methods to Analyze the Properties of Coffee Silverskin and Oil Extracted from the Studied Roasting By-Product

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Featured Application: Coffee silverskin is a valuable by-product of the coffee roasting process with a wide range of potential applications. Fat extracted from the studied material turned out to be a source of essential fatty acids with the recommended n-6 to n-3 ratio and could be successfully recovered and reused in other fields of industry, including, especially, the food and cosmetics industries, which fits perfectly with current trends in circular ecology. Thermal analysis can be applied to obtain quick and reliable information about the composition, phase transition and transformation kinetics of the tested sample.

Abstract: The aim of the study was to characterize the thermal properties of coffee silverskin and fat extracted from the material by using differential scanning calorimetry, modulated differential scanning calorimetry and thermogravimetry/derivative thermogravimetry. Additionally, the thermokinetic parameters, oxidative stability and fatty acid composition of the extracted oil were defined. Thermal decomposition of the studied coffee roasting by-product under oxygen occurred in three defined stages. The most significant changes in weight were observed in the region of 200–500 °C and correspond to polysaccharide decomposition. These results are in agreement with the data obtained from the differential scanning calorimetry curve. On the curve course of silverskin, two main exothermic peaks can be observed with a maximum at 265 and 340 °C. These exothermic events represent the transitions of hemicellulose and cellulose. Fat extracted from silverskin turned out to be a source of polyunsaturated fatty acids with the recommended n-6 to n-3 ratio reaching the value 4:1. The studied fat was characterized by low oxidative stability. Considering the obtained results, it can be stated that thermal analysis can provide fast and reliable data concerning the composition and properties of coffee silverskin and coffee silverskin oil.

Keywords: thermal analysis; differential scanning calorimetry; thermogravimetry; coffee silverskin; coffee silverskin oil

1. Introduction

Coffee is one of the most consumed beverages in the world and is produced in great amounts [1]. Among the many steps in coffee production, the roasting process seems to be of great importance, as under the influence of high temperature, many physicochemical changes occur. During the roasting

process, an outer layer of green coffee beans, known as coffee silverskin, is removed [2]. Generally, green coffee beans with attached tegument (silverskin) are exported to consuming countries, where the coffee beans undergo the roasting process [3]. The amount of this waste depends on the type of green beans and on the conditions of processing used, but mostly, coffee silverskin represents about 4.2% (*w*/*w*) of beans [4]. According to the International Coffee Organization (ICO) statistics [5], total production of coffee by all exporting countries is estimated at 10 million tonnes. Considering the datum presented above, the coffee industry might generated approximately 420 thousand tonnes of the studied by-product. However, this agro-industrial residue currently presents little commercial value and is mostly disposed of as industrial waste. Taking the aforementioned reasons into account, it is imperative to identify the properties and potential applications of coffee silverskin. The reuse of a waste product, such as silverskin, would fit with current trends in circular ecology [6]. In recent years, the problem of development in improving the efficiency of raw material processing has been widely discussed. There is considerably little research conducted on the topic of coffee by-products' properties. Publications mainly deal with antioxidant and prebiotics characteristics [7–10]. Results show that coffee silverskin can be reused in many industrial fields due to its functional and nutritional properties [11–13]. In the case of coffee by-products, there is still a lack of information concerning their thermal behavior, which is of great importance for defining the potential applications of this waste product. Among the thermal techniques that enable getting valuable information about tested materials are differential scanning calorimetry (DSC), modulated differential scanning calorimetry (MDSC) and thermogravimetry/derivative thermogravimetry (TG/DTG). DSC is a technique which is particularly useful in terms of food systems which undergo heating or cooling during processing. The information obtained from DSC curves can be helpful in understanding thermal transitions under certain treatment of the material [14–16]. Additional details about the studied samples can be obtained by using thermogravimetry analysis/derivative thermogravimetry. In this technique, mass loss of the material under controlled linearly varying or isothermal temperatures over time under a given atmosphere is determined. It can provide information about physical phenomena, including phase transitions and chemical changes, such as thermal decomposition [17]. Thermal techniques are widely used to obtain information about foods systems [18]. DSC is the most universal thermal analytical technique applied to detect phase and state transitions of food products containing mainly proteins and polysaccharides. MDSC is especially useful in determining glass transition temperature, which is important in determining material stability [15]. Górska et al. [19] studied the glass transition temperature of newly designed β-lactoglobulin—retinyl palmitate—disaccharide powdered systems. Based on the obtained results, the impact of the composition of the studied samples on the glass transition temperature was shown. In the case of trehalose incorporation into products, the temperature was higher than in samples containing lactose. In food systems, a higher glass transition temperature can be assumed to improve protection and stability of encapsulated substances. Calorimetry can also provide valuable information about thermal properties of proteins and, what is helpful in understanding the stability of proteins, the forces that maintain their folded structures and interactions with other macromolecules as a function of temperature [20]. Thermodynamic analysis of DSC was also applied to investigate thermal denaturation and aggregation of food proteins. It is possible to estimate the apparent denaturation enthalpy after heating protein solutions at a chosen temperature and time range. Wang et al. [21] studied the kinetics of the aggregation of α-lactoalbumin at 90 °C and found that kinetic curve of the process can be described by the first-order reaction equation with the constant rate of about 10^{-4} s^{-1}. DSC is also a valuable technique to study the influence of chemical and physical treatments used during food preservation on inactivation of bacteria. Calorimetric data provided information that can be useful in optimizing the processing conditions of food preservation, in obtaining quantitative data about bacteria inactivation process, such as thermal energy required for bacteria inactivation and kinetic parameters of inactivation [22]. Lee and Kaletunç [23] studied process of *Escherichia coli* inactivation. *E.coli* samples were preheated in the DSC to set the temperature, cooled in liquid nitrogen and rescanned to 140 °C. On the DSC scan, the thermally induced transitions' connection with the

surviving of bacterial cells could be observed. Based on the DSC curve course, apparent enthalpies of the process were calculated. Thermal analysis is also widely used in fat analysis. It gives the possibility to obtain crystallization and melting profiles obtained on cooling and heating of the sample; to monitor polymorphic forms of fats; to measure the heat of transitions; to define solid fat content in the sample; to monitor oxidation of lipids [18]. The problem of cocoa butter is often presented in the literature, as the quality of chocolate depends on the polymorphic forms of the fat. Based on thermal analysis, it can be shown that cocoa butter can be described in terms of six different polymorphic forms, with the commercially desired form V, which is not the most stable one, and form VI, which is more stable and undesirable, as responsible for fat bloom [24]. DSC studies of anhydrous milk showed that it crystallizes and melts in several steps [25]. Based on the DSC curve course, the presence of three endothermic peaks, corresponding to low melting, medium melting and high melting fractures, was observed, which differ in triacylglycerol structure. Thermal properties of fat in complex products are also the topic of scientific investigations. DSC was applied to a study of the thermal properties of fat in cheese. Lopez et al. [26] studied the crystalline structures in Emmental cheese at 4 °C and its melting characteristics during heating. They showed that the phase transition that occurred upon cooling on the DSC curve is related to fat globules' destabilization. Calorimetry is also thought to be a quick and reliable technique to determine the oxidative stability of fats. In isothermal processes, the oxidation induction time is defined, which corresponds to exothermic reaction between lipid and oxygen. Induction time can be used as primary parameter for the assessment of the resistance of tested fat to oxidative deterioration. In non-isothermal experiments, kinetic parameters can be calculated, such as activation energy of oxidation process. Brynda-Kopytowska et al. [27] studied the oxidative stability of fat extracted from newly designed spray-dried pea-protein fat preparations formulated with different types of carbohydrate components. Authors observed that after 6 months of storage, fat isolated from spray-dried products formulated with inulin and trehalose containing the mixture of palm and rapeseed oils were the most stable. Wirkowska-Wojdyła et al. [28] investigated the oxidative stability of model meat batters as affected by interesterified fat. Fats extracted from meat batters were characterized by lower resistance to oxidation than fats used in the interesterification process. It can be due to a higher content of free fatty acids and polar fraction in final products which can reduce the stability of fat against oxidation. Ciemniewska et al. [29] applied pressure differential scanning calorimetry to assess the oxidative stability of fat isolated from roasted hazelnuts. The results have shown a slight elevation in the oxidative stability as the temperature and time of roasting process increased. There are many reports confirming that DSC can provide valuable data for vegetable oil oxidation, which correlate with Rancimat and electron spin resonance spectroscopy results [30,31].

Taking the above into consideration, the main aim of the study was to analyze the thermal properties of coffee silverskin obtained as a mix of the two most common species of coffee (*Coffea arabica* and *Coffea canephora*). Additionally, fat extracted from the studied material was characterized by oxidative stability and thermokinetic parameters. Thermal characteristics of studied samples was determined by using the following techniques: differential scanning calorimetry, modulated differential scanning calorimetry and thermogravimetry/derivative thermogravimetry. The research was completed by defining fatty acid composition based on chromatographic analysis of fatty acid methyl esters.

2. Materials and Methods

2.1. Study of Coffee Silverskin

Coffee silverskin samples of the two most common species of coffee (*Coffea arabica* and *Coffea canephora*) of various geographical origins were studied. The sampling plan for the silverskin was developed on the basis of the procedure for taking samples from unpackaged batches according to PN-ISO 3534-2:1994 standard [32]. First, six times every 3 days, original silverskin samples were collected from coffee roasteries. The collected primary samples of silverskin were mixed to obtain a general sample. Representative laboratory samples used for testing were collected from the general

sample. Laboratory samples of silverskin were homogenized in a laboratory mill to form a powder and stored in polyethylene bags with a slider without light at room temperature.

2.1.1. DSC Study of Coffee Silverskin

The TA DSC Q200 differential scanning calorimeter (TA Instruments, New Castle, DE, USA) was used for DSC measurements of the samples. The cell was purged with 50 mL/min dry nitrogen and calibrated using standard pure indium. An empty sealed aluminum pan was used as a reference. Samples (12–13 mg) were hermetically sealed in aluminum pans and heated from −50 to 450 °C at a heating rate of 5 °C/min. As a result, experiment curves of heat flow (W/g) versus temperature were obtained. The thermal parameters were defined with the use of the Universal V4.5A (TA Instruments, New Castle, DE, USA) program [14].

2.1.2. MDSC Study of Coffee Silverskin

Modulated DSC analyses were performed in order to determine the glass transition temperature of the samples. Purging of the cell was performed with 50 mL/min of nitrogen. The apparatus was calibrated using pure indium standard. As the reference in each test, an empty sealed aluminum pan was used. Samples of 11–15 mg in weight were sealed hermetically in 30-µL aluminum pans. Subsequently, samples were cooled from room temperature to −50 °C at a cooling rate of 5 °C per min and then equilibrated for 5 min. After the equilibration period, samples were scanned from −50 to 200 °C at a constant heating rate of 2 °C per min with an amplitude of ±1 °C and a 60-s period of modulation. Glass transition was reported with parameters indicating its midpoint of vertical shift in the reversing transition curve. TA Instruments Universal analysis software was used to analyze the glass transition temperature. The measurement were done in three replicates for each sample [15].

2.1.3. TG/DTG Study of Coffee Silverskin

The samples were also tested using a Discovery TGA thermogravimetric analyzer (TA Instruments, New Castle, DE, USA). Measurements were performed under nitrogen and oxygen at a flow rate of 25 mL/min at a temperature range of 50–700 °C with a heating rate of 10 °C/min. Approximately 7–8 mg of the sample was placed on the thermobalance in a platinum container. TG curves were obtained for temperature dependence on mass loss, and first-derivative data (DTG) were calculated [17].

2.2. Study of Fat Extracted from Coffee Silverskin

2.2.1. Extraction of Fat from Coffee Silverskin

Fat extraction from silverskin samples was conducted according to the procedure described by Reder et al. [33]. The samples were ground and treated with hexane. After 30 min of shaking, the mixture was filtered and dried with magnesium sulfate and the solvent was evaporated from the filtrate. Additionally, the sample was dried under nitrogen atmosphere to remove residual hexane.

2.2.2. Pressure Differential Scanning Calorimetry (PDSC) Study of Coffee Silverskin Oil

PDSC experiments were carried out using a DSC Q20 TA Instrument (TA Instruments, New Castle, DE, USA). Fat samples of 3–4 mg were 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) with a 50 mL/min oxygen flow rate. The isothermal temperature for individual experiments was 100, 110 and 120 °C. Obtained diagrams were analyzed using TA Universal Analysis 2000 software. The maximum PDSC oxidation time was determined based on the maximum rate of oxidation as a peak's point of maximum deviation from a linear baseline [34].

The non-isothermal version of PDSC was also used. The samples were heated from 30 to 250 °C at the rates of 2.5, 4.0, 5.0, 7.5, 10.0 and 12.5 °C per minute. The experiments were performed in an

atmosphere of oxygen with an initial pressure of 60–70 kPa and the gas flowing at a rate of 50 mL/min. For each programmed heating rate (β, °C/min), an analysis was done at least three times. The onset oxidation temperature (t_{on}, °C) was determined as the intersection of the extrapolated baseline and the tangent line (leading edge) of the recorded exotherm. The kinetic parameters of the oxidation process (activation energy, pre-exponential factor and reaction rate constants) were calculated [34].

2.2.3. TG/DTG Study of Coffee Silverskin Oil

Samples of fats were characterized with the use of a Discovery TGA thermogravimetric analyzer. Measurements were performed using methodology described above for silverskin analysis [17].

2.2.4. GC Measurements of Coffee Silverskin Oil

Gas chromatography (GC) was used to determine the composition of fatty acids in silverskin fat samples. The fatty acids were converted into volatile methyl esters using a methanolic KOH solution according to PN-EN ISO 5509:2001 [35] and applied to the analytical column. The YL6100 GC gas chromatograph apparatus (Young Lin Bldg., Anyang, Hogye-dong, Korea) with a flame ionization detector and a 30-m long BPX 70 capillary column (SGE Analytical Science, Milton Keynes, UK) with an inner diameter of 0.22 mm and a film thickness of 0.25 µm was used. The oven temperature was programmed as follows: 60 °C for 5 min, then it was increased by 10 °C/min to 180 °C and from 180 to 230 °C at 3°C/min. The temperature was kept at 230 °C for another 15 min. The temperature of the split injector was 225 °C, with a split ratio of 1:100. The detector temperature was kept at 250 °C. Nitrogen was applied as a carrier gas, with flow at the rate of 1 mL/min. Fatty acid identification was done 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.

2.3. Statistical Analysis

Each measurement was taken in triplicate. The data are reported as 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 are considered to be significant at a *p*-value of 0.05, according to Tukey's multiple range test.

3. Results and Discussion

3.1. Study of Coffee Silverskin

3.1.1. DSC Study of Coffee Silverskin

To characterize the thermal behavior of the samples of silverskin, differential scanning calorimetry (DSC) and thermogravimetry (TG) under nitrogen and oxygen flow were performed. The DSC curve presented in Figure 1 shows the thermal transitions of the silverskin sample which occur between −60 °C and 450 °C at a heating rate of 5 °C/min under a nitrogen atmosphere.

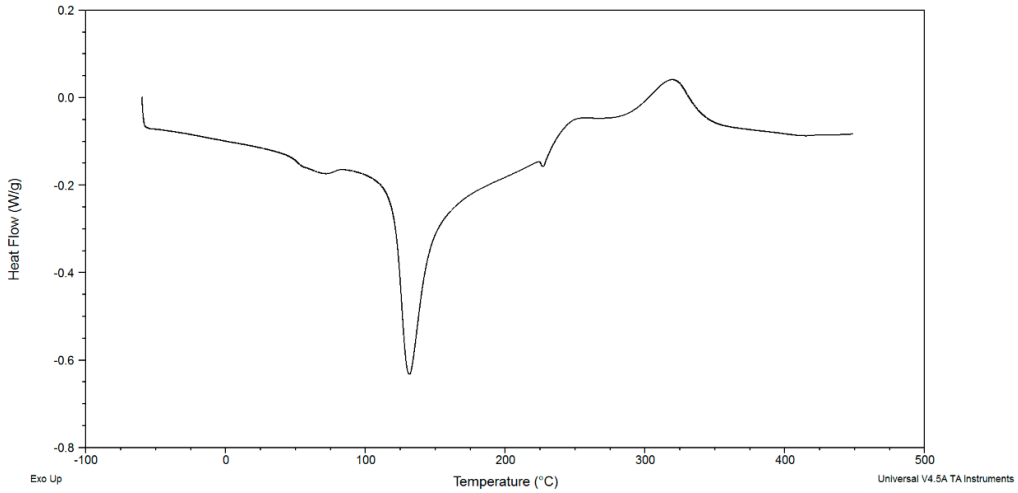

Figure 1. Differential scanning calorimetry (DSC) curve of coffee silverskin sample.

Considering the DSC curve course, three endothermic and two exothermic events can be observed. An early event observed at 70 °C is associated with water evaporation from the sample. From the DSC profile, two other transitions that occurred at higher temperatures can be observed. These thermal events present at 125 and 240 °C are related to the presence of disaccharides in the studied material. It is known that coffee silverskin is a material containing carbohydrates, with polysaccharides as the most abundant components [13]. This coffee by-product is a rich source of total fiber, including soluble dietary fiber and insoluble dietary fiber with high amounts of cellulose, hemicellulose and lignin. According to results published by Ballesteros et al. [4], cellulose and hemicellulose are present in silverskin in significant amounts of 40.45% (*w*/*w*) of the composition of a dry weight basis. Another fraction that is represented by 28.58% (*w*/*w*) is lignin. On the DSC curve course of the studied silverskin, two main exothermic peaks can be observed with a maximum at 265 and 340 °C. It can be concluded that they represent the above-mentioned components, namely hemicellulose and cellulose. The obtained results are in agreement with the experimental data presented by Bryś et al. [36] and Yang et al. [37], who observed a similar tendency in the study of hemicellulose, cellulose and lignin pyrolysis. According to data given in the literature, thermal transitions of hemicellulose and cellulose are present at temperatures range of 220–315 and 315–400 °C, with maximum of peaks found at 268 and 355 °C, respectively. According to the results obtained by Tarrio-Saavedra et al. [38], cellulose, lignin and hemicellulose decompose at temperatures ranging between 240–350, 280–500 and 200–260 °C, respectively. Based on the data obtained in this study and presented by other researchers, it can be concluded that hemicellulose is the least thermostable and lignin is the most thermostable component in studied material.

3.1.2. TG/DTG Analysis of Coffee Silverskin

The TG curve showing the changes in the mass of the silverskin sample during heating under oxygen until 700 °C is presented in Figure 2a.

The course of the TG/DTG curve shows that the thermal decomposition of the silverskin sample occurs in three defined stages. In the case of the first event at the temperature range up to 150 °C, a mass loss of 3.6% was observed. Such a low weight-loss rate in the initial stage can be attributed to evaporation of moisture from inside the studied material. This event corroborates the data obtained from the DSC curve for the first event of thermal transition, confirming a possible dehydration of the material. It is worth mentioning that mass loss in this temperature range can be also related to releasing of volatile compounds present in coffee silverskin. The second and third mass losses of 64.9% are related to the thermal decomposition of organic matter present in the studied material. The most significant changes in weight occur in the region of 200–500 °C. At this temperature, decomposition of polysaccharides and some oils, which are the components of the sample, occurs. The final region of the

TG curve allows to determine the percentage of residues. Based on the course of TG/DTG, it can be seen that the silverskin sample is not fully decomposed in the studied range of temperatures. At the temperature of 700 °C, still 31.6% of the material remains undecomposed, which can be due to the presence of inorganic compounds with high stability. The course of the TG/DTG curve obtained in the case of analysis of silverskin conducted under nitrogen is shown in Figure 2b.

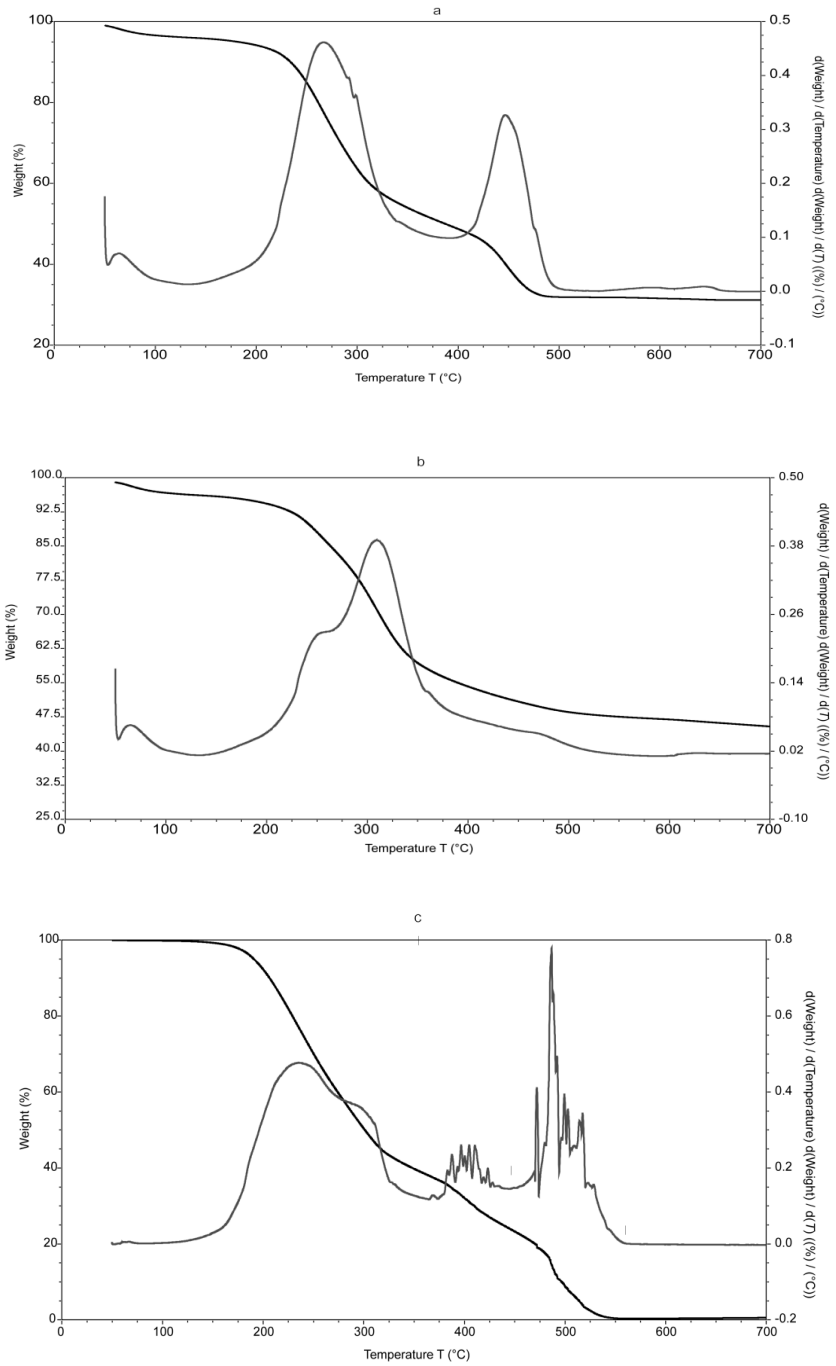

Figure 2. *Cont.*

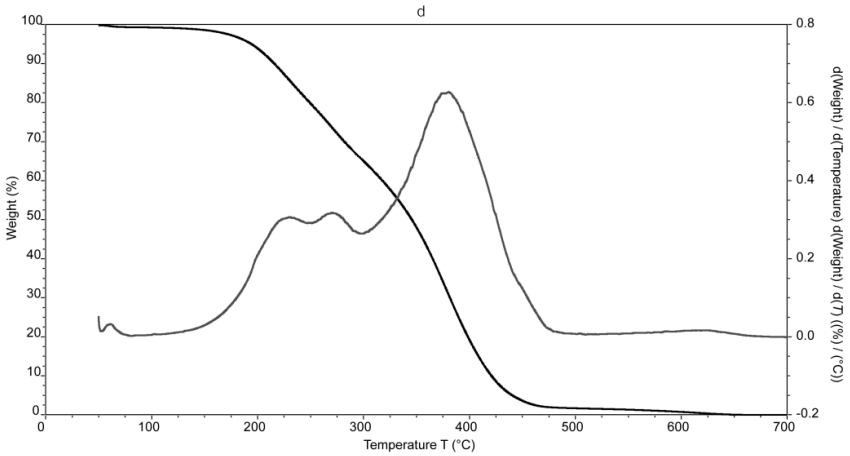

Figure 2. (**a**) Thermogravimetry/derivative thermogravimetry (TG/DTG) curves of coffee silverskin in oxygen atmosphere. (**b**) TG/DTG curves of coffee silverskin in nitrogen atmosphere. (**c**) TG/DTG curves of coffee silverskin fat samples in oxygen atmosphere. (**d**) TG/DTG curves of coffee silverskin fat samples in nitrogen atmosphere.

Similarly to the results obtained for experiments under oxygen, the first event in the temperature range up to 175 °C, with the mass loss of 3.9%, was associated with the evaporation of moisture. The second and third mass losses of 42.1% and 7.0%, respectively, were observed in the temperature range from 200 to 500 °C. Based on the curve course, it can be observed that still 47.06% of the sample remains undecomposed.

3.1.3. Glass Transition Temperature of Coffee Silverskin Sample

In the analysis of silverskin as a by-product for potential further applications, it is of great importance to determine the material's stability. Taking the above into consideration, the glass transition (T_g) temperature of the silverskin sample, which has been proven to be an effective indicator for food quality changes during storage, was determined by using MDSC method. It is worth mentioning, that the most important change in the amorphous state occurs over the glass transition temperature, which is the temperature at which polymeric materials change from an amorphous solid (glass) to an amorphous rubber [39]. In the studied material, at water activity 0.419 (as it is), two glass transition events at −26.80 and 58.96 °C were observed, which are associated with the transitions of monosaccharides and disaccharides present in the sample, respectively. In the anhydrous state, most monosaccharides, such as pentoses: arabinose, ribose and xylose and hexoses, such as rhamnose, fructose, galactose, glucose and mannose, are characterized by T_g temperature ranging from −20 to 31 °C, and most of the disaccharides (sucrose, maltose, trehalose and lactose)—from 62 to 101 °C. Analysis of the reported T_g values of anhydrous carbohydrates indicates that the higher the molecular weight of the component, the higher its T_g. Hydration of samples reduces their glass transition temperature, i.e., the higher the degree of hydration of the material is, the lower T_g value.

3.2. Study of Coffee Silverskin Oil

3.2.1. TG/DTG Analysis of Coffee Silverskin Oil

One of the components of silverskin that is worth being isolated and reused in other industrial fields due to its potential functional and nutritional properties is fat. There is no information in the literature dealing with silverskin oil characteristics. Taking the above into consideration, one of the goals of the study was fat extraction from the silverskin sample in order to define its properties by means of TG, PDSC and GC techniques. The profiles of the TG and DTG curves of fat samples

extracted from coffee silverskin, analyzed in oxygen and nitrogen atmospheres, are presented in Figure 2c,d, respectively.

The thermal decomposition of fat samples in oxygen occurs in three stages. The most significant changes in weight, associated with 60% of mass loss, are observed in the region of 150 to 350 °C and correspond to the decomposition of polyunsaturated fatty acids (PUFAs). It is thought that the initial step associated with unsaturated fatty acid decomposition is of great importance in defining the thermal stability of studied oils. The second step in the thermal decomposition of silverskin oil with 16% of mass loss is present in the temperature range from 350 to 450 °C and corresponds to the decomposition of monounsaturated fatty acids, such as oleic acid. The third event in the thermal decomposition, which occurs in a region of 450–560 °C, followed by 24% of mass loss corresponds to the thermal decomposition of saturated fatty acids, such as palmitic and stearic acids. It is worth mentioning that at the temperature of 560 °C, the decomposition of material is complete. These results are in agreement with study of Gouveia de Souza et al. [40], who determined thermal properties of sunflower oils with artificial antioxidants and without addition of artificial antioxidants. The authors observed three thermal steps in the range of 230 to 550 °C on TG/DTG curves, related to the decomposition of polyunsaturated, monounsaturated and saturated fatty acids, with no residue remaining at 800 °C. The thermal decomposition of fat samples in nitrogen atmosphere occurs in two stages ranged from 150 to 300 °C in the case of first event with 37% of loss mass to 300–520 °C for the second step, associated with 63% of loss mass.

3.2.2. PDSC Study of Coffee Silverskin Oil

Induction time is essential in the terms of fat stability and can be used as a primary parameter for the assessment of the resistance of the tested fat to its thermal oxidative decomposition. The PDSC analysis of fats was performed at isothermal conditions. The DSC curves presenting the oxidation induction times are shown in Figure 3. The time of oxidation reaction reached the values of 22, 48 and 108 min for experiments conducted at a temperature of 100, 110 and 120 °C, respectively. Comparing the obtained results with other oils, it can be stated that oil extracted from silverskin is of low stability. The oxidation induction time for rapeseed oil, hazelnut oil and extra virgin oil at 100 °C reached 200, 141 and 155 min, respectively [41,42], while in the case of silverskin oil—about 105 min. A similar tendency was observed in the case of applying higher temperatures (110 and 120 °C).

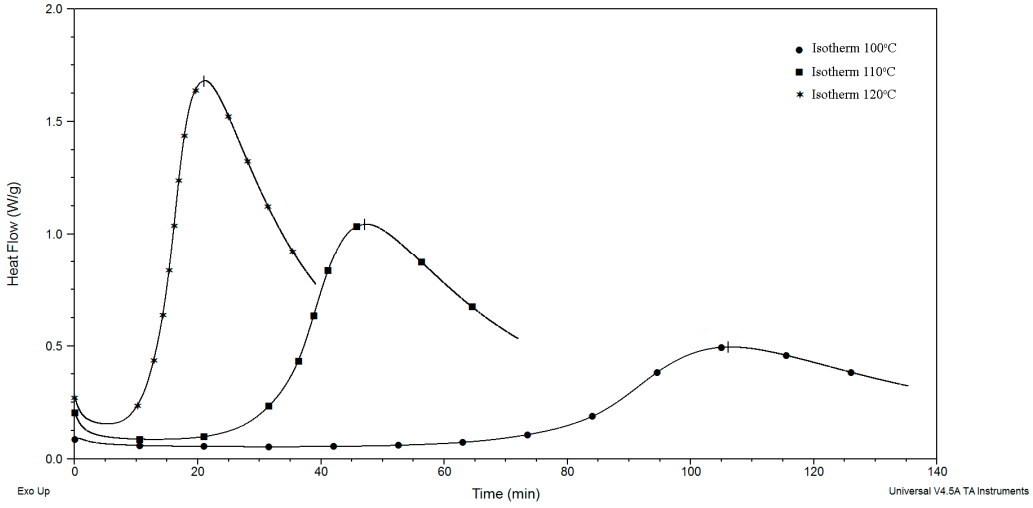

Figure 3. DSC curves of oxidation induction time of silverskin fat samples.

The DSC technique was also used in the study of thermokinetic parameters of the oxidation process. The results obtained show the effect of the sample heating rate on the T_{on} and T_{max} temperature values. With the increase in the heating rate, the temperature for initiating the oxidation process and

the temperature for the maximum of the peak increased. The temperature of the extrapolated oxidation onset temperature (T_{on}) and the oxidation temperature corresponding to the maximum peak (T_{max}) were recorded and are summarized in Table 1.

Table 1. T_{on} and T_{max} obtained for different heating rates in thermo-oxidation process of fat extracted from silverskin.

Type of Fat	Heating Rate (β) (K/min)	T_{on} (°C)	T_{max} (°C)
Fat extracted from coffee silverskin	2.5	129.46 ± 2.8	206.68 ± 2.6
	4.0	135.20 ± 3.2	213.55 ± 3.9
	5.0	138.70 ± 3.9	218.01 ± 4.4
	7.5	143.23 ± 2.4	229.72 ± 6.7
	10.0	151.08 ± 1.9	237.94 ± 3.5
	12.5	156.21 ± 3.1	241.21 ± 3.1

Based on the obtained extrapolated oxidation onset temperature (T_{on}) and the oxidation temperature corresponding to the maximum of the peak (T_{max}) and considering the heating rate, graphs of the logarithm of heating rate versus temperature for oxidation of silverskin oil were prepared and are presented in Figures 4 and 5.

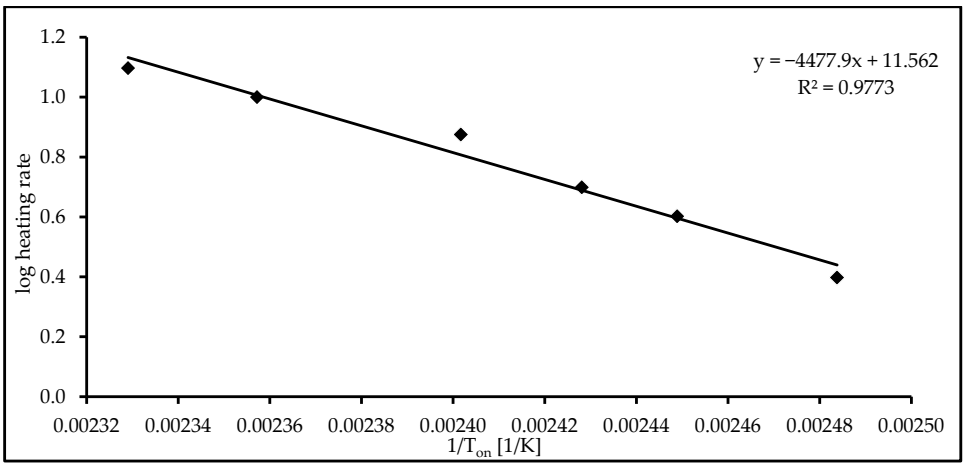

Figure 4. Temperature shift at the onset (of the oxidation process) of DSC curves depending on the logarithm of heating rate of the thermo-oxidative decomposition of silverskin fat.

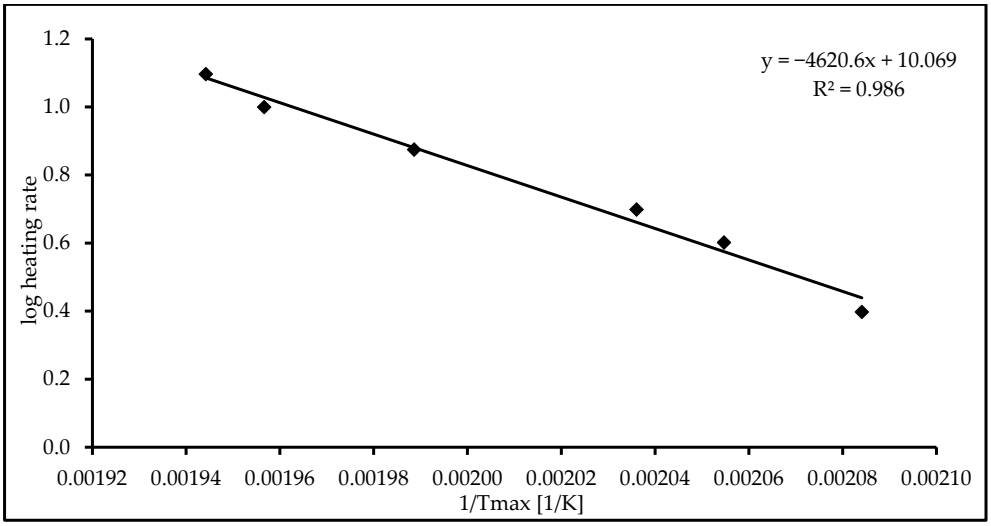

Figure 5. Temperature shift at the maximum (of the oxidation process) of DSC curves depending on the logarithm of heating rate of the thermo-oxidative decomposition of silverskin fat.

The dependencies shown in Figures 4 and 5 can be described by a regression equation:

$$\text{Log } \beta = a(1/\text{T}_{\text{on}} \text{ or } \text{T}_{\text{max}}) + b \quad (1)$$

where β is a heating rate and T is the temperature.

Activation energy (E_a) values and pre-exponential factor (Z) were calculated using Equations (2) and (3), respectively.

The activation energy values were calculated according to the Ozawa–Flynn–Wall method based on the equation:

$$\text{E}_\text{a} = -2.19\, R \cdot \frac{d \log \beta}{d(1/T)} \quad (2)$$

where R is the gas constant.

The pre-exponential factor was calculated from the dependence:

$$\text{Z} = \frac{\beta E_a e^{\frac{E_a}{RT}}}{RT^2} \quad (3)$$

Quantified regression coefficient values a, regression constant b and the determination coefficients R^2, as well as values of activation energy and pre-exponential factor, are summarized in Table 2.

Table 2. Thermokinetic parameters of oxidative process of coffee silverskin fat.

Parameter	Value Calculated for T_{on}	Value Calculated for T_{max}
a	−4477.9	−4620.6
b	11.6	10.1
R^2	0.98	0.90
E_a (kJ/mol)	81.52	84.12
Z	7.68×10^9	2.39×10^8

In the present study, E_a reached the value of 81.52 kJ/mol (calculated for T_{on}) and 84.12 kJ/mol (calculated for T_{max}). In terms of oils, the E_a value is affected mainly by the degree of unsaturation. It was previously reported that a high polyunsaturated fatty acid (PUFA) content would decreased, while high monounsaturated fatty acid (MUFA) and saturated fatty acid (SFA) content would increase, the E_a value for the lipid oxidation process [43]. When compared with other oils—hazelnut oil (E_a = 89.1 kJ/mol) and rapeseed oil (E_a = 92.69 kJ/mol)—it can be stated that silverskin oil is of low resistance to oxidation. Taking the above into consideration, the research was completed by defining fatty acids' composition, which was carried out by gas chromatographic analysis of fatty acid methyl esters.

3.2.3. GC Study of Coffee Silverskin Oil

The results obtained for the fatty acids composition of silverskin oil are reported in Table 3. A high unsaturated fatty acid content (UFA) (50.38%) was indicated, with 7.81% monounsaturated fatty acids and 42.57% polyunsaturated fatty acids. Among the unsaturated fatty acids, linoleic acid (C18:2, 32.47%) as a main acid followed by oleic acid (C18:1, 7.08%) was detected. Additionally, the obtained results showed significant amounts of gamma-linolenic acid, belonging to the n-6 family, and alpha-linolenic acid, eicosatrienoic acid and eicosapentaenoic acid of the n-3 family. Based on the obtained results, it can be stated that silverskin oil is an abundant source of PUFAs. Among the saturated fatty acids, the predominant fatty acid was palmitic acid, which accounted for 28.26% of fatty acids. Next to palmitic acid, high stearic acid (8.04%) and arachidic acid (7.41%) contents were present in the triacylglycerol structure of silverskin oil. A typical chromatogram of fatty acids' composition in the tested coffee silverskin fat is shown in Figure 6.

Table 3. Fatty acids composition (%) of coffee silverskin fat samples (SFA—saturated fatty acids, MUFA—monounsaturated fatty acids, PUFA—polyunsaturated fatty acids).

Group of Fatty Acids	Fatty Acid	Content of Individual Fatty Acid (%) *	Σ Content of the Group (%) *
SFA	C12:0	0.08 ± 0.01	46.37 ± 0.05
	C14:0	1.86 ± 0.06	
	C15:0	0.19 ± 0.01	
	C16:0	28.26 ± 0.09	
	C18:0	8.04 ± 0.05	
	C20:0	7.41 ± 0.09	
	C21:0	0.33 ± 0.04	
	C24:0	0.20 ± 0.04	
PUFA	C18:2n-6c	32.47 ± 0.09	42.58 ± 0.25
	C18:3n-6	1.62 ± 0.07	
	C18:3n-3	1.44 ± 0.04	
	C20:2	0.10 ± 0.02	
	C20:3 n-3	5.50± 0.06	
	C22:2	0.23 ± 0.04	
	C20:5 n-3	1.22 ± 0.02	
MUFA	C16:1	0.10 ± 0.01	7.81 ± 0.05
	C18:1n-9c	7.08 ± 0.04	
	C20:1 c	0.51 ± 0.02	
	C24:1	0.12 ± 0.02	
Σ identified		96.76 ± 0.20	
Σ other minor unidentified		3.24 ± 0.20	

* Data expressed as mean ± standard deviation.

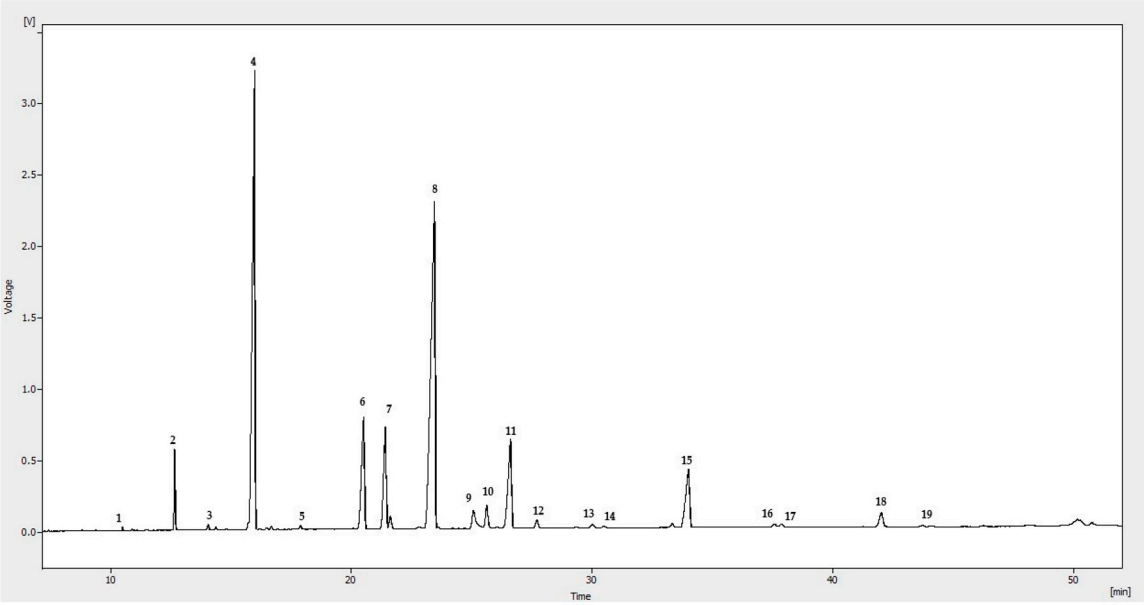

Figure 6. Typical chromatogram of fatty acids profile in coffee silverskin fat (1—C12:0; 2—C14:0; 3—C15:0; 4—C16:0; 5—C16:1; 6—C18:0; 7—C18:1; 8—C18:2; 9—C18:3 n-6; 10—C18:3 n-3; 11—C20:0; 12—C20:1; 13—C21:0; 14—C20:2; 15—C20:3; 16—C22:2; 17—C24:0; 18—C20:5; 19—C24:1).

Additionally, in the case of silverskin oil, the n-6 to n-3 fatty acids ratio was calculated. The parameter should be considered in the fat analysis as it is of high importance in the characteristics of fat from a nutritional point of view. Nowadays, the consumption of n-6 fatty acids in the diet is at a high level, which leads to an unhealthy n-6 to n-3 ratio of 20:1 or even higher, which is associated with the risk of heart disease and brain health consequences. It is worth mentioning that commonly used oils, such as sunflower, corn, soybean and cottonseed oils, contain a high amount of n-6-family fatty acids. In the present study, for silverskin oil, the n-6 to n-3 ratio value reached 4:1, which is in

agreement with recommendations and meets the trend of searching for new sources of fats which provide a beneficial balance of n-6 to n-3 fatty acids.

4. Conclusions

The obtained results contributed to better characterization of coffee silverskin as a valuable by-product of the coffee roasting process. Considering the TG/DTG curves, a well-defined step of silverskin decomposition can be observed. The most significant mass losses of 64.9% occurred in the region of –500 °C and are related to the thermal decomposition of organic matter present in the studied material. Undecomposed amounts of the sample can be related to the significant content of inorganic residue with high stability. The course of the DSC curve confirmed the observed phenomena. The DSC profile indicates the occurrence of two main exothermic peaks, which represent the main components of silverskin, hemicellulose and cellulose. In the case of isolated fat, the most significant changes in weight, associated with 60% of mass loss, correspond to the decomposition of polyunsaturated fatty acids. It has been proven that silverskin is a rich source of PUFAs, with linoleic acid as a main fatty acid followed by oleic acid. Gamma-linolenic, alpha-linolenic, eicosatrienoic and eicosapentaenoic acids were also detected in the structure of triacylglycerols. The second and third steps in the thermal decomposition of silverskin oil with 16% and 24% mass loss were associated with decomposition of monounsaturated fatty acids and saturated fatty acids, respectively. The presence of these two groups of fatty acids was confirmed by means of gas chromatography. Fat extracted from the studied coffee by-product proved to be a valuable source of essential fatty acids with the recommended n-6 to n-3 ratio and could be successfully recovered and used in other fields of industry, including, especially, the food industry, which fits perfectly with current trends in circular ecology. Based on the obtained results, it can be stated that fat isolated from silverskin can be treated as a value-added bioactive material that can be obtained from coffee roasting by-product. To the best of our knowledge, this is the first study on silverskin fat analysis.

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