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Thermal and Kinetic Properties of Brazilian Coffea Arabica Beans

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Abstract: The chemical composition of green coffee beans depends on the number of parameters, such as coffee cherry processing methods, used. The quality of roasted coffee is related to the certain substances that developed during the roasting process and that are responsible for the organoleptic properties. The main objective of this study was an investigation of the thermal behaviour and the fatty acids profile of green and roasted Brazilian Santos coffee beans. The glass transition temperature was measured using modulated differential scanning calorimetry (MDSC). The thermal behaviour of coffee samples was evaluated by means of thermogravimetry (TG) and first derivative thermogravimetry (DTG). The oxidative stability and kinetic parameters were characterized with the use of differential scanning calorimetry (DSC). According to the TG and DTG curves, coffee samples showed different behaviour of thermal degradation in the atmosphere of oxygen and nitrogen. Our research shows that the thermal properties and fatty acids profile did not change during the roasting process.

Keywords: thermal behaviour; glass transition; coffee fat; fatty acids

1. Introduction

Coffee is both one of the most popular drinks and also one of the most important food commodities in the world [1]. Coffee production increases annually, with values reaching 7 million tons in 2010, and over 9 million tons in the 2015/2016 season. The worldwide importance of coffee is mainly due to the unique properties of coffee brews. Coffee beverages are known for their stimulating and refreshing effects on humans, their antioxidant activity and unique, pleasant flavour [2].

To pull out the best characteristics of each green coffee bean, a roasting process is required. The roasting causes a broad spectrum of physicochemical changes in green coffee beans. Due to the high temperatures used in the process, the moisture present in the coffee beans rapidly expands, causing the destruction of the bean matrix. The newly formed porous structure of the roasted beans induces the release of water and aromatic compounds into the atmosphere [3]. Coffee contains thousands of chemical compounds. Due to the complex chemical composition of green coffee beans, an intricate set of concurring chemical reactions lead to the formation and decomposition of many bioactive compounds. As a result, changes in the physical and sensory properties as well as the bioactive compounds profile occur [2,4,5]. The roasting process is responsible for the degradation of polysaccharides [6] and phenolic compounds due to their low thermal stability [7], and the formation of Maillard reaction products that darken the colour of the bean and contribute to its overall antioxidant activity [8]. Both green and roasted coffee beans are also a rich source of fatty acids and triacylglycerols [9,10]. The fat extracted from coffee beans has several industrial applications, mainly in cosmetics and food [11,12].
The thermal analysis of food samples supplies reliable and comprehensive information about the nature of the material or the changes within the material that occur during the processing phases. There are many studies reporting the applications of different techniques of thermal analysis in food sciences [13–15]. These techniques can be used to evaluate a range of specific properties of the analysed samples such as rheological, thermal or structural. Modulated differential scanning calorimetry (MDSC) provides an insight into the many aspects of the thermal response of materials, especially the glass transition. MDSC, through the application of a sinusoidal cooling or heating signal to a sample, measures the reversing and non-reversing component of the heat flow response [16,17]. Thermogravimetric analysis (TGA) measures the changes in the sample’s mass as a function of temperature. The loss of mass during the analysis provides an understanding of the chemical composition of the material. It can be caused by many processes and gives information about occurring phenomena, e.g., phase transition, desorption absorption, thermal decomposition, reduction or oxidation. TGA can be used to evaluate the thermal stability of the sample. In thermally stable samples, no changes in mass are observed over time [18].

Due to this, the use of thermal analysis such as thermogravimetry or differential scanning calorimetry could be considered as a useful tool to determine the final quality of coffee beans during the roasting process but also to characterize the thermal parameters of the fat extracted from coffee beans [13].

Taking the aforementioned reasons into account, the objective of this study was to evaluate the thermal properties of coffee powders obtained from Brazilian coffee beans of different roasting degrees, which were characterized using thermogravimetry analysis at nitrogen and oxygen flow and using modulated differential scanning calorimetry (MDSC). The thermal behaviour of the fat obtained from these beans was also studied.

2. Materials and Methods

2.1. Chemicals

All the used reagents and solvents were supplied by Avantor Performance Materials Poland S.A. (Gliwice, Poland), except for fatty acids mixture standard provided by Sigma-Aldrich (Saint Louis, MO, USA).

2.2. Materials

The materials used in the study included green, light and dark roasted Coffea arabica beans from the Santos region, Brazil, purchased at the local Warsaw market. The coffee roasting process was carried out using a Toper TKM_X 30 roaster. Taking into account the characteristic crackles and colour, the raw coffee beans were roasted according to appropriate roasting temperature profiles. Light and dark roasted coffee were obtained after the first and second crack, respectively. The total time of roasting was approximately 15 min. Then, the roasted coffee beans were cooled and packed in an air atmosphere in hermetically closed aluminium foil bags with a valve. The coffee samples were stored at the room temperature for further analysis in tightly closed barrier foil-paper packages. Before the analytical determination, all coffee samples were ground in a laboratory mill W ż-1 (ZBBP, Bydgoszcz, Poland).

2.3. Fat Extraction

To obtain fat from coffee beans, extraction experiments were performed using the conventional solid–liquid method. After the milling, approximately 30 g of the coffee sample was treated with 150 mL of n-hexane in a glass Schott bottle. The extraction process was carried out at an ambient temperature in a water bath Elpin Plus type 357 (Lubawa, Poland) with agitation for 60 min. Subsequently, the samples were filtered, and 3 g of anhydrous magnesium sulphate was added as a drying agent and maintained for 30 min. Then, the solution was filtered through the filter paper and the solvent was removed using a Büchi R-215 Rotavapor rotary evaporator (Büchi Labortechnik AG, Flawil,
Switzerland). The obtained fat samples were stored in sub-zero temperatures (−20 °C) until further analysis.

2.4. Modulated Differential Scanning Calorimetry

The modulated DSC analyses were performed on a TA Instrument Q200 differential scanning calorimeter (New Castle, DE, USA). At a defined water activity, the glass transition temperature of the samples was analysed. Measurements were made according to the procedure described by Jakubczyk et al. [19] and Rahman et al. [20].

2.5. Thermogravimetric Analysis

A thermogravimetric analyser Discovery TGA (TA Instruments) was used. The gases, oxygen and nitrogen, at a flow rate of 25 mL min$^{-1}$ were used to perform the analysis. Approximately 7–8 mg of the sample were loaded to the thermobalance in a platinum container. Measurements were carried out from 50 to 700 °C with a heating rate of 10 °C per min. TG curves were obtained for temperature dependence on mass loss, and first-derivative data (DTG) were calculated [21,22]. All analyses were completed in triplicate.

2.6. DSC Measurements

A differential scanning calorimeter (DSC Q20 TA) coupled with a high-pressure cell (PDSC) was used. Into an open aluminium pan, 3–4 mg of fat were weighed and then placed in the heating chamber of the calorimeter next to the reference sample. The determination was carried out at a temperature of 120 °C and an oxygen pressure of approximately 1400 kPa. The obtained diagrams were analysed using TA Universal Analysis 2000 software. The maximum PDSC oxidation time was determined based on the maximum rate of heat flow.

Additionally, the thermokinetic parameters characterizing the thermal-oxidative decomposition of fat samples were evaluated according to the procedure shown in the literature [23]. The reference pans and 3–4 mg of the sample were heated at the rates of 2.5, 4.0, 5.0, 7.5, 10.0 and 12.5 °C per min. The experiments were performed in an oxygen atmosphere with the gas flow at a rate of 100 mL min$^{-1}$. The onset and the maximum oxidation temperatures ($T_{on}$, °C; $T_{max}$, °C) were determined as the intersection of the extrapolated baseline and the tangent line (leading edge) on the recorded exotherm.

2.7. GC-FID Analysis of Fatty Acids Profile

The determination of fatty acids profile was carried out by the use of a YL6100 GC gas chromatograph equipped with a flame ionization detector and BPX-70 (0.22 mm ID × 30 m length × 0.25 µm film thickness) capillary column. The fat samples were derivatized with sodium methoxide according to ISO 5509:2001. The temperature oven program was as follows: 0.5 min isothermal at 70 °C, 15 °C per min to 160 °C, 1.1 °C per min to 200 °C, followed by isothermal period of 6 min at the latter temperature, finalizing with 30 °C per min to 225 °C. The injector and detector were held at 225 and 250 °C, respectively. Nitrogen was used as a carrier gas with the flow rate of 1 mL min$^{-1}$, and a 1:50 split ratio was used. The results were expressed as relative percentages of each fatty acid (percentages of the fatty acids peaks area were calculated). Fatty acids methyl esters were identified by comparing the relative retention times of FAME peaks in the samples with FAME chemical standard.

2.8. Statistical Analysis

Analyses were carried out in triplicate. The experimental data were analysed statistically with one-way ANOVA using the Statistica 10 software. The significance level chosen was 0.05. The ANOVA statistical analysis was implemented with the Tukey post hoc test.
3. Results and Discussion

3.1. Determination of Glass Transition Temperature

Modulated differential scanning calorimetry is a precise and reliable method of glass transition temperature (T_g) determination. By analysing MDSC curves, it is possible to notice the inflexion associated to a glass transition. The temperatures of glass transition for all the coffee samples, as well as their water activity, are shown in Table 1. The glass transition temperature was taken as the onset, midpoint and endpoint of the glass transition.

Table 1. Onset, midpoint and endpoint of the glass transition temperature determined in coffee samples (±) standard deviation (SD) from triplicate measurements.

| Coffee Sample | T_g onset (°C) | T_g midpoint (°C) | T_g endpoint (°C) | Water Activity a_w |
|---------------|---------------|------------------|------------------|-------------------|
| Green         | –19.99 ± 1.17 a | –11.24 ± 0.84 a | –1.69 ± 0.24 a   | 0.486 ± 0.007 c   |
| Light         | –19.89 ± 0.21 a | –11.93 ± 0.16 a | –2.49 ± 0.05 b   | 0.399 ± 0.002 b   |
| Dark          | –19.81 ± 0.28 a | –11.67 ± 0.15 a | –2.48 ± 0.01 b   | 0.388 ± 0.005 a   |

Different letters indicate that the samples are considered significantly different (α = 0.05) in terms of roasting degree.

The midpoint of glass transition varied from –11.2 to –11.9 °C, but the samples showed no significant differences in terms of roasting degree. Our results are in agreement with the results presented by Perdana et al. [24], who also observed minor changes in the T_g values in coffee samples of different roasting degrees. However, the Jambi Indonesia Arabica, Robusta and Liberica coffees, in their study, were characterized by higher values of T_g between –5.8 and –4.1 °C, which suggests that the glass transition of coffee beans depends highly on their geographic origin. According to Rivera et al. [25], polysaccharides such as sucrose are responsible for the glass transition in the coffee beans. The T_g values increased with the decrease in water activity in the samples, which indicates that water has a substantial plasticising effect on coffee beans [26].

It is known that roasted coffee beans are a complex hygroscopic matrix and can quickly take up moisture from the atmosphere when improperly stored, which causes a decrease in its overall quality [27]. The water activity of the samples decreased with the roasting degree. The significant differences in the water activity values between the green and roasted coffee samples are caused by the high temperatures applied during the roasting process [28].

3.2. Thermogravimetric Analysis

The thermogravimetric (TG) curves were evaluated and the first derivative (DTG) for all the coffee samples was calculated. In Figure 1, the TG and DTG curves of green, light and dark roasted coffee beans in an oxygen and nitrogen atmosphere with a heating rate of 10 °C per min are shown. A heating rate of 10 °C per min was used, according to the methodology of Materazzi et al. [21].

The thermal decomposition of coffee samples in oxygen occurs in four stages. The first stage ranged from 50 to 200 °C, second—from 200 to 350 °C, third—from 350 to 425 °C and fourth—from 425 to 700 °C.

On the DTG curve, two peaks were observed. In the case of the first peak maximum in DTG curves was observed at the temperature of 200 °C and the second at about 425 °C. The first region was characterized by the soft loss of material weight about 4–6% for roasted coffee samples and about 7–9% for green coffee beans. The low weight loss rate in the initial stage can be attributed to the evaporation of moisture trapped inside the coffee matrix. In the next region, coffee samples undergo a fast decomposition. A significant weight loss is caused by the alteration of some components such as saccharides decomposing as well as by a rapid release of volatiles from the sample material [25,29]. The last, fourth zone revealed a very slow weight loss rate.
Figure 1. Thermogravimetry/derivative thermogravimetry (TG/DTG) curves of Brazilian green (BZ), light roasted (BJ) and dark roasted (BC) coffee samples in oxygen (O₂) and nitrogen (N₂) atmospheres.

The profiles of the TG and DTG curves of samples analysed in nitrogen atmosphere were determined. In this case, we can only distinguish the following three phases: one from 50 to 150 °C, next from 150 to 335 °C and last from 335 to 700 °C. In the nitrogen atmosphere, the weight loss rate was slower than in the oxygen. The first mild peak
maximum was observed at 75–85 °C and the weight loss can be associated with the evaporation of moisture [30]. The second DTG peak maximum was observed at 300 °C and the third at 375 °C. The second peak shows the decomposition of saccharides and the third the decomposition of fatty acids [25,30].

Boonamnuayvitaya et al. [31] and Chaiklangmuang et al. [32], who both investigated the thermal properties of coffee residues, observed similar trends.

3.3. Oxidative Stability and Thermokinetic Parameters

The parameter that is used to determine the oxidative stability is induction time. The DSC curves presenting the oxidation induction times are shown in Figure 2.

![Figure 2](image)

**Figure 2.** The oxidation induction time of Brazilian coffee samples.

The PDSC analysis of the fats obtained from the roasted coffee samples, performed at an isothermal temperature of 120 °C, indicates that the induction time increased in comparison to the fats from green coffee beans. In this case, the fats obtained from green coffee beans are less stable compared to the fats extracted from light and dark roasted beans.

The oxidative stability of coffee fat is associated with the groups of compounds that have a major contribution to the overall activity of coffee beans, i.e., polyphenols, melanoidins and tocopherols. During the roasting process, oil-soluble Maillard reaction products (including melanoidins) are developed, which causes a great increase in antioxidant activity of the roasted coffee in comparison to green coffee beans [33]. At the same time, polyphenols and tocopherols are partially degraded and partially bound to the structures of the newly formed melanoidins [34]. The remaining phenolic compounds have a positive, non-linear relationship to the antioxidant activity of roasted coffee beans [35]. These phenomena could cause a slight decrease in antioxidant activity in the dark roasted coffee compared to light roasted beans, which influences the thermal stability of coffee fat.
To evaluate the kinetic data of the samples, experimental onset (\(T_{\text{on}}\)) and maximal (\(T_{\text{max}}\)) oxidation temperatures at six heating rates were determined and presented in Tables 2 and 3. The determined \(T_{\text{on}}\) values (°C) were recalculated to match an absolute scale (K).

**Table 2.** Onset oxidation temperatures (\(T_{\text{on}}\)) obtained for six sample heating rates during the thermo-oxidative processes. (±) standard deviation (SD) from triplicate measurements.

| Heating Rate (°C min\(^{-1}\)) | Ton (°C)           |
|-------------------------------|--------------------|
|                               | Green   | Light Roasted | Dark Roasted |
| 2.5                           | 154.57 ± 0.86     | 168.8 ± 0.79  | 164.3 ± 0.79 |
| 4.0                           | 161.74 ± 0.94     | 176.22 ± 1.33 | 170.86 ± 1.13|
| 5.0                           | 165.01 ± 0.76     | 180.81 ± 1.38 | 174.28 ± 0.96|
| 7.5                           | 172.56 ± 0.71     | 183.65 ± 0.69 | 180.91 ± 1.06|
| 10.0                          | 175.97 ± 1.23     | 191.61 ± 1.35 | 181.22 ± 1.19|
| 12.5                          | 181.07 ± 0.98     | 182.5 ± 0.98  | 190.31 ± 1.16|

**Table 3.** Maximal oxidation temperatures (\(T_{\text{max}}\)) obtained for six sample heating rates during the thermo-oxidative processes. (±) standard deviation (SD) from triplicate measurements.

| Heating Rate (°C min\(^{-1}\)) | Tmax (°C)          |
|-------------------------------|--------------------|
|                               | Green   | Light Roasted | Dark Roasted |
| 2.5                           | 168.3 ± 0.90      | 180.28 ± 0.99 | 177.08 ± 0.66|
| 4.0                           | 181.95 ± 0.36     | 191.79 ± 0.87 | 188.55 ± 0.55|
| 5.0                           | 192.9 ± 0.45      | 193.25 ± 0.40 | 228.55 ± 1.32|
| 7.5                           | 228.5 ± 0.90      | 252.19 ± 1.31 | 260.62 ± 1.53|
| 10.0                          | 246.84 ± 1.73     | 272.71 ± 1.64 | 287.91 ± 0.66|
| 12.5                          | 253.6 ± 1.84      |                |              |

Then, the absolute onset temperatures were presented as a function of a heating rate logarithm (log\(\beta\)) and fitted to a linear regression model (Equation (1)), as follows:

\[
\log \beta = a (1/T_{\text{on}}) + b
\]

(1)

where a and b are the regression coefficients and the regression constant, respectively.

For the established initiation conditions, fat oxidation reactions occurring in excess of oxygen are first-order reactions [36–38]. Assuming that the reaction degree is constant and independent of the heating rate while a DSC curve reaches its peak, the activation energy (\(E_a\)) was calculated based on the following Ozawa–Flynn–Wall method (Equation (2)):

\[
E_a = 2.19 R \frac{d \log \beta}{d(1/T)}
\]

(2)

where \(R\)—gas constant; \(\beta\)—heating rate (°C min\(^{-1}\)); \(T\)—temperature (K). Pre-exponential factor (\(Z\)) was also calculated using the Arrhenius Equation (3), as follows:

\[
Z = \frac{\beta E_a e^{\frac{E_a}{RT}}}{RT^2}
\]

(3)

The calculated values of kinetic parameters characterizing the thermal-oxidative decomposition of the coffee fat samples are summarized in Table 4. The activation energy of the samples ranged from 94 to 105 kJ mol\(^{-1}\) and 29 to 33 kJ mol\(^{-1}\) for \(T_{\text{on}}\) and \(T_{\text{max}}\), respectively. The estimated values of activation energy for the onset temperature were higher than the values for the maximal temperature. Similar regularity was also shown in the case of the pre-exponential factors. The difference between the activation energy values at the start of thermal-oxidation and maximum temperature may have resulted
from a reaction of autooxidation. In the initiation and propagation processes, the primary autooxidation products begin to form and a large energy expenditure is needed [39].

Table 4. Statistical and kinetic parameters characterizing the thermal-oxidative decomposition of coffee fat. \( E_a \)—activation energy (kJ mol\(^{-1}\)); \( Z \)—pre-exponential factor.

| Parameter               | a    | b    | \( R^2 \) | \( E_a \)   | \( Z \)     |
|-------------------------|------|------|-----------|-------------|-------------|
| Green coffee            |      |      |           |             |             |
| Value for \( T_{on} \)  | −5169.5 | 12.5 | 0.99       | 94.11       | 5.63 \( \times \) \( 10^{10} \) |
| Value for \( T_{max} \) | −1687.6 | 4.3  | 0.97       | 30.72       | 1.047 \( \times \) \( 10^{3} \) |
| Light roasted           |      |      |           |             |             |
| Value for \( T_{on} \)  | −5471.6 | 12.8 | 0.99       | 99.6        | 1.03 \( \times \) \( 10^{11} \) |
| Value for \( T_{max} \) | −1797.6 | 4.3  | 0.99       | 32.7        | 1.210 \( \times \) \( 10^{3} \) |
| Dark roasted            |      |      |           |             |             |
| Value for \( T_{on} \)  | −5779.8 | 13.6 | 0.96       | 105.2       | 7.01 \( \times \) \( 10^{11} \) |
| Value for \( T_{max} \) | −1589.8 | 3.9  | 0.99       | 28.9        | 5.36 \( \times \) \( 10^{2} \) |

3.4. Analysis of Fatty Acids Profile

The percentage contribution of six major fatty acids identified in coffee fat samples is presented in Table 5. The chromatograms of fatty acids profile in Brazilian Coffea arabica beans are given in Figure 3.

Table 5. The fatty acids profile in coffee fat sample. (±) standard deviation (SD) from triplicate measurements. Data denoted by the same letter are not statistically different (\( \alpha = 0.05 \)) in terms of roasting degree.

| Common Name     | Lipid Number | % of Fatty Acids Peaks Area |
|-----------------|--------------|----------------------------|
|                 |              | Green Coffee | Light Roast | Dark Roast |
| Palmitic acid   | 16:0         | 31.64 ± 0.14  | 31.18 ± 0.18 | 30.88 ± 0.22 |
| Stearic acid    | 18:0         | 8.71 ± 0.13   | 8.72 ± 0.02  | 8.8 ± 0.04   |
| Oleic acid      | 18:1(9)      | 9.79 ± 0.10   | 10.49 ± 0.01 | 10.69 ± 0.01 |
| Linoleic acid   | 18:2(9,12)   | 41.61 ± 0.17  | 41.71 ± 0.02 | 41.94 ± 0.07 |
| \( \alpha \)-Linolenic acid | 18:3(9,12,15) | 1.54 ± 0.04 | 1.69 ± 0.02 | 1.71 ± 0.01 |
| Arachidic acid  | 20:0         | 3.38 ± 0.03   | 3.31 ± 0.07  | 3.24 ± 0.05  |

In total, these six fatty acids represent about 97% of all the fatty acids detected in the samples. The fat extracted from coffee samples contained from 9.8 to 10.7% of monounsaturated fatty acids (MUFA) and from 42.9 to 43.7% of saturated fatty acids (SFA). The predominant fatty acid present in coffee beans was linoleic acid followed by palmitic acid, with contributions ranging from 41.6 to 41.9% and 30.9 to 31.2%, respectively. Additionally, the analysed coffee fats were comprised of 43.1 to 43.6% polyunsaturated fatty acids (PUFA) including essential fatty acids from \( n-3 \) and \( n-6 \) groups as \( \alpha \)-linolenic acid and linoleic acids. These observations agree with other reported data [10,40].

From all of the identified fatty acids, the PUFA fraction is, especially, very important considering the nutritional value. Omega-3 and omega-6 fatty acids are essential fatty acids that cannot be produced in the human organism because of the lack of endogenous enzymes. Omega-6 PUFA decrease the LDL fraction of the cholesterol, while omega-3 PUFA have a variable effect on total cholesterol, LDL and HDL fractions of cholesterol and can lower triacylglycerol levels [41].

The analysed coffee fat samples contain the omega-6:omega-3 ratio on the very high level of about 27:1. Due to modern agricultural trends, Western diets contain abundant levels of omega-6 PUFA with very low levels of omega-3 PUFA. According to some authors, the omega-6:omega-3 ratio in modern diets can be as high as 20:1, while the proper ratio during human evolution was closer to 1:1. It should be pointed out that a ratio of above 10:1 in the diet can have an adverse effect on human health [42,43].
Figure 3. Typical chromatograms of fatty acids profile in Brazilian Coffea arabica beans from different roasting degrees: green (A), light roasted (B), dark roasted (C). Identified fatty acids presented on chromatograms: 1—C16:0, 2—C18:0, 3—C18:1, 4—C18:2, 5—C18:3, 6—C20:0.
The fatty acids profile of coffee fat samples was not affected by the roasting process in most cases. Only the oleic acid and α-linolenic acid contribution increased slightly during the initial phases of roasting. Our result confirms the findings presented by Martín et al. [44].

4. Conclusions

The thermal parameters can be helpful in the assessment of the stability of coffee beans after the roasting process. The glass transition temperature range indicates that roasted coffee beans do not require special storage conditions (they can be stored at room temperature). Based on the shape and the peak temperatures range of the TGA and DTG curves, it is possible to define the main chemical components present in the roasted coffee beans. The Obtained experimental data suggests that the roasting process does not have a significant influence on the fatty acids profile and the thermal properties of coffee fat. However, the induction time of the oxidation reaction indicates that the fat isolated from roasted beans is more stable than the fat extracted from green coffee beans. Our study provides knowledge and deeper understanding about the thermal behaviour of Brazilian coffee and coffee fat.

Author Contributions: Conceptualization, R.B. and A.G.; methodology, E.O.-L., J.B. and M.W.-W.; formal analysis, R.B. and E.O.-L.; data curation, R.B., E.O.-L. and J.B.; writing—original draft preparation, R.B., A.G. and M.W.-W.; writing—review and editing, A.G., E.O.-L. and M.W.-W. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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