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Original article

Evaluation of Cold Pressed Walnut Oil (*Junglas Regia*) Adulteration with Refined Sunflower Oil Using Differential Scanning Calaorimetry Technique

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Abstract

This paper presents the potential of differential scanning calorimetry (DSC) method to be applied in adulteration of cold pressed walnut oil (Junglas Regia). Two brands of cold pressed walnut oil were adulterated with 5% and 10% of refined sunflower oil. Thermal curves profile of oil samples was correlated with the level of oils oxidation determined by OxiTest and the lipids profile was determined by gas-chromatography/mass spectrometry (GC/MS). An increase in the lipid oxidation values was recorded for one brand of cold pressed walnut oil. Based on the lipid profile analysis, differences between samples were observed regarding the linolenic acid which was reduced by 0.1%-0.4% in cold pressed walnut oil adulterated with 5% refined sunflower oil and 1.1% in the samples adulterated a percentage of 10%. A clear differentiation between samples was found on the thermal crystallization curves where in 2 temperatures area (-17°C - -20°C and -37°C - -48°C), the thermal energy transferred indicated different degrees of freedom of the TAGs compositions. Also, it was observed that a temperature area (-52°C- -59°C) where the crystallization temperature (Tc) of the dilutions is very close to the Tc of the adulterated oil. The DSC method used in this study highlighted the adulteration of cold pressed walnut oil on the crystallization thermal curves.

Keywords: Cold Pressed Walnut Oils, DSC, Authenticity, Food Control.

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INTRODUCTION

Determining the authenticity of vegetable oils and fats from foods had generated an intense concern in developing analytical methods based on their chemical composition and physical properties (Aparicio et al., 2013). The analytical methods were oriented on two main directions of investigation and determination of foods fraud: testing for the presence / absence of a specific known adulterant (Mishra et al., 2014; Peng et al., 2017) and testing the identity, authenticity, or purity of a food ingredient (Marikkar et al., 2012; Dahimi et al., 2014; Fahimdanesh et al., 2014). High-value food oils, coming from limited or minor sources, economically motivate their fraud. An important aspect regarding the chemical composition and fatty acid content of vegetable oils refers to the specificity depending on the source and extraction technology. Differential Scanning Calorimetry (DSC) technique attracts the attention of the scientific research and it has been applied to foodstuff and to extra virgin olive oil in order to determine a thermal fingerprint able to characterize unambiguously a particular sample (Mallamace et al., 2017). The DSC technique is applied to detection of the adulterant (seed oils or refined olive oil), oil origin, and possible photo-oxidation degradation processes, before more complex and expensive procedures and analyses (Angiuli et al., 2009; Damirchi et al., 2015). The principle of the DSC method is based on submitting an oil sample to a controlled temperature program, recording a unique behaviour determined by the physical and chemical properties of the oil. The crystallization process of lipids is a spontaneous ordering of the system, given by the different molecular packing. The high complexity of the triacylglycerol molecules (TAG) allows the same set of TAGs to form crystallization units in several and relative crystalline networks. This process is greatly influenced by the cooling rate. In the case of melting, lipid polymorphism is characterized by distinct values of enthalpy and melting temperatures, values that increase from form α through β^1 to β and are greatly influenced by the heating rate.

Thermal analysis is the most valuable tool in the examination of phase transitions, especially in complex systems such as lipids, where thermal events are correlated with structural rearrangement during heating or cooling processes. From the point of view of oils authenticity, the main problem of the DSC technique is the lack of information about potential adulterants, while the main advantage of the technique refers to the speed, efficiency and precision in the fingerprinting for suspicion of adulteration.

In this study, the DSC method was used to determine the adulteration of walnut oil with 5% and 10% addition of refined sunflower oil. The thermal fingerprint of the walnut oil was evaluated in comparison with the thermal curves of the dilutions. The dilutions were considered economically advantageous for adulteration of walnut oil with an inexpensive oil.

Materials and Methods

Experimental oil samples

Vegetable oils used in the study were commercially available, consisting of:

- Cold pressed walnut oil (*Junglas Regia*), called as WO1, produced in Hungary, sold by S.C. Herbavit S.R.L., Romania, expiration date: 11.2019

- Cold pressed walnut oil (*Junglas Regia*), called as WO2, produced by TAF Presoil S.R.L., Cluj, Romania, expiration date: 10.2019

- Refined sunflower oil, called as SFO, produced by EXPUR SA, Ialomita, Romania, expiration date: 08.2019.

The cold pressed walnut oils were adulterated with refined sunflower oil in Falcon tubes of 15 mL (by volumetric measurement) by stirring and maintaining them at room temperature (20 °C ± 2 °C) for 2 h. The samples were coded as:

- P1 = WO1;

- P2 = 95% WO1 + 5% SFO;

- P3 = 90% WO1 + 10% SFO;

- P1.1 = WO2.

- P2.1 = 95% WO2 + 5% SFO;

- P3.1 = 90% WO2 + 10% SFO;

The level of oxidation of oils

The level of oxidation of oils was determined with the OxiTest FoodLab equipment (ver. 1.0 oel, produced by CDR S.R.L. Florence, Italy). The following parameters were measured: Free fatty acids with measuring range 0,01 – 26,0% oleic acid, resolution 0,01 – 0,1% and repeatability 0,02 – 0,5%; Peroxide value (PV) with measuring range 0,01 – 550,0 meqO_2/Kg, resolution 0,01 – 0,1% and repeatability 0,1 – 3%; *p*-Anisidine value with measuring range 0,5 – 100,0 AnV, resolution 0,1 AnV and repeatability 0,2 AnV. Reagent are pre-vialed, in package of 10 test, 1 year shelf life, developed and produced by the research laboratories of CDR. All determinations were performed in triplicate.

Lipid profile of oils

Fatty acids profile was determined according to PN-EN ISO 12966-1:2015-01, PN-EN ISO 12966-2:2017-05 except p. 5.3 and 5.5, PN-EN ISO 12966-4:2015-07 by JSH Hamilton, Poland.

Determination of the thermal characteristics of oils

Determination of the thermal characteristics of the samples oil was performed using a differential scanning calorimeter (DSC 8000, Perkin Elmer, USA) with power compensation. Calibration of the temperature and heat of the fusion was carried out in the temperature range of -70 °C to + 400 °C using indium (ΔHf = 28.5 J/g and Tm = 156.5 °C). Baseline is calibrated from heat flow rate r = 2 °C/min and r = 10 °C/min. From each sample, 6 and 8 mg were approximately weighed in hermetically stainless steel pans, covers and O-rings (Perkin Elmer) with help of a microbalance (Mettler Toledo, d = 0.1 μg). The pans were conditioned at 20°C for 2-3 hours. The samples were encapsulated in triplicated for each cooling/heating heat flow rate and analyzed according to method described beneath. Nitrogen 5.0 (99.999% purity) was used as purge gas at a rate of 20 mL/min. Curves were processed by the Pyris software and To, Tg, Tpeak (maxim), Tend (°C), peak area (mJ), ΔH (J/g) and Tg (°C) were calculated from crystallization and melting profiles, using the calibration curve from the heat flow rate r = 2 °Cmin^{-1}. The following method steps were employed to study the melting and crystallization of samples oil:

Step 1: Initial temperature 20 °C and isothermal for 3 min.

Step 2: Melting sample at a heat flow rate of 10 °C/min up to 50 °C to complete the melting of crystals.

Step 3: Isothermal for 10 min in order to equilibrate the sample temperature, remove polymorphic transformations and erase all memory of the crystal structure.

Step 4: Cooling sample at a heat flow rate of 10 °C/min from 50 °C to 0 °C.

Step 5: Cooling sample at a heat flow rate of 2 °C/min from 0 °C to -70 °C to format the crystalline networks in the mass of the sample.

Step 6: Isothermal for 10 min at -70 °C to balance the mass of crystals.

Step 7: Melting sample at a heat flow rate of 2 °C/min, up to 30 °C to complete melting crystals of sample.

The method assures the deletion of the thermal memory of the mixtures of TAGs by subjecting to changes from the liquid phase into the solid phase and then in the liquid phase.

Statistical analysis

All the determinations were done in triplicate. The data were expressed as mean ± SD.

Results and Discussion

The level of oxidation of oils

Lipid oxidation influences the chemical and physical characteristics of oils through the oxidized products of fatty acids and liposoluble minor compounds (vitamins, phytosterols). The evolution of

oxidative processes leads to compositional changes, with an impact on the thermal characteristics. The exo(endo) thermic curve should be correlated with the oxidation level of the oils at the time of thermal analysis. The degree of oxidation of the samples was determined initially and at 30 days by sampling from original packaging units (WO1: 10 mL, colourless glass pack and WO2: 12 mL, laminated BOPP, metallized) from the same manufacturing batch. The results obtained (Table 1) indicate that oils were with a different degree of oxidation from reduced to medium. The values obtained were reported to the values given by CODEX-STAN 210-1999 and CODEX STAN 33- 1981, Rev. 1-1989. Thus:

- Acidity represents 66% for SFO, 20% for P1 and 6.36% for P1.1 from the maximum allowable value. These values remain at approximately the same level throughout the study. During the study, for P1.1, P2.1 and P3.1 sample, the acidity increases by 32.73% from the maximum allowable value in CODEX.

- The peroxide value (PV) was about 50% lower than the maximum allowable value for SFO and about 26.6% and 55% for samples P1, P2, P3 and P1.1, P2.1, P3.1, respectively. During the study, a decrease in PV was found with about 20% in the case of samples P1.1, P2.1 and P3.1.

- AnV values were approximately 25% (for SFO), 20% (for P1 and for the samples derived from dilution) and 5% (for P1.1 and the samples derived from dilution) from the maximum allowable value in CODEX. An increase of 7.6% was determined during the study for P1.1 and the samples derived from dilution.

These values indicate a lower oxidative stability of cold pressed walnut oil WO1 compared to WO2 samples, which have a slower onset of oxidative processes. The cold pressed walnut oil samples have October and November 2019, respectively, as expiry dates.

Table 1. The level of oxidation of oils

	Acidity (%, oleic acid)	**PV** ($meqO_2/Kg$)	**Anisidine** (AnV)	**Acidity** (%, oleic acid)	**PV** ($meqO_2/Kg$)	**Anisidine** (AnV)
Samples	**initially**			**30 days**		
SFO	0.02±0.02	5.7±0.10	2.4±0.01	0.2±0.19	5.55±0.11	2.6±0.04
P1	0.71±0.04	4.0±0.02	2.5±0.03	0.75±0.01	4.0±0.04	2.65±0.12
P2	0.62±0.01	4.01±0.25	2.5±0.04	0.72±0.02	4.01±0.12	2.55±0.03
P3	0.65±0.03	4.3±0.01	2.48±0.17	0.70±0.11	4.29±0.03	2.5±0.02
P1.1	0.21±0.06	8.25±0.35	0.95±0.23	1.08±0.04	7.2±0.01	1.1±0.03
P2.1	0.16±0.04	7.91±0.04	1.01±0.02	1.02±0.03	7.31±0.06	1.83±0.15
P3.1	0.19±0.05	7.71±0.03	1.15±0.18	0.97±0.10	7.01±0.04	1.7±0.01

Lipid profile of oils

The GC/MS analysis of the lipid profile of the samples taken in this study (Table 2) indicates a reduced differentiation between cold press walnut oils (P1 and P1.1) and also between them and their dilutions with SFO. Saturated fatty acids (palmitic and stearic) are in greater quantity in SFO and come with a contribution of 4% in the walnut oil diluted with 10% SFO and an undetectable contribution in the samples diluted with 5% SFO. It is demonstrated that stearin significantly influences the peak height value at phase transitions from polymorphic mixtures with high percentage of unsaturated fatty acids as a result of crystallization temperature (Tc) of 25.9 °C (Zaliha et al., 2004) and melting temperature (Tm) of 54^0C – 72.5°C (Hidalgo and Zamora, 2005).

In the opposite direction, there is linolenic acid, which has Tc below -80 °C and Tm of -44.6 - 24.2 °C (depending on the polymorphic form), which is present in a quantity of 11% in WO1, 11.4% in WO2 and 0% in SFO. Reduction of linolenic acid content in P1 by SFO additions is of 0.1% in sample P2 and 1.1% in sample P3. In case of P2 dilution, linolenic acid content is reduced by 0.4% in sample P2.1 and by 1.1% in sample P3.1. Thermal curves are determined by the presence of oleic acid in the TAGs composition in percentage of 60.0 - 61.5%.

Table 2. Lipid profile of oils

Samples	**SFO**	**P1**	**P2**	**P3**	**P1.1**	**P2.1**	**P3.1**
Fatty acids							
C16:0, palmitic acid	6.6	6.8	6.8	6.8	7	7	7
C18:0 stearic acid	3.1	2.5	2.5	2.6	2.4	2.4	2.5
C16:1 (sum of)	0.1	0	0	0	0	0	0
C18:1 (sum of)	31.1	19	18.7	19.9	17.4	18	18.8
C18:2 (sum of)	57.8	60.8	60.6	60.0	61.5	61.4	61.3
C20:0							
C20:1 (sum of)	0.1	0	0	0.2	0.2	0.2	0
C18:3 (sum of)	0	11	10.9	9.9	11.4	11	10.3
∑SFA	10.8	9.3	9.4	9.5	9.4	9.4	9.7
∑MUFA	31.4	19	18.7	20.1	17.6	18.2	18.8
∑PUFA	57.6	71.7	71.5	69.9	72.9	72.4	71.6
∑TFA	<0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
∑Omega-3 fatty acids	< 0.1	11	10.9	9.9	11.4	11	10.3
∑Omega-6 fatty acids	57.6	60.8	60.6	60.0	61.5	61.4	61.3
∑Omega-9 fatty acids	30.4	19	18.7	20.1	16.6	17.2	17.7

Note: SFA- saturated fatty acids; MUFA- monounsaturated fatty acids; PUFA-polyunsaturated fatty acids; TFA-trans –fatty acids.

Determination of the thermal characteristics of oils

Thermal curves were recorded for both crystallization and melting. The supercooling of oil samples according to the DSC method described at point 2.3, represents the thermodynamic driving force for the supersaturation of the triacylglycerol polymorph mixture. The exothermic events were in the temperature range of 0 °C-70 °C (Figures 1a and 1b) at r = 2 °C/min. The transition between phases produces three exothermic events for the oil samples as well as for the samples diluted with SFO (Table 3).

The following conclusions were drawn from the analysis of the thermal curves at crystallization:

- first event for SFO sample is a Tg at -11.51 °C, for sample P1 a Tg at -17.94 °C, and for sample P1.1 a peak with Tg at -18.47 °C and Tc at -18.98 °C. The thermal energy transferred by the oil samples (ΔCp) is 0.4 J/g*°C for SFO and 0.365 J/g*°C for P1. P1.1 forms a peak with ΔH of -0.42 J/g.

- second event is a peak for the 3 oils studied: Tc = -40.59 °C (SFO), Tc = -41.94 ° (P1) and Tc = -42.27 °C (P1.1). The thermal energy transferred indicates different degrees of freedom of TAGs composition.

- third event is produced in the temperature area for To of -51.7- -53.04 °C and Tend of -57.88_-60.05 °C, with different Tc between the oils samples: -56.43 °C (SFO), -55.45 °C (P1) and -57.88 °C (P1.1).

In case of cold pressed walnut oils adulterated with 5% SFO, the thermal behaviour at crystallization is very close to that of the cold pressed walnut oils, thus:

- for P1 and P2 samples, a difference at Tg of 0.8 °C and Tc of 0.67 °C at peak 3 is noticed.

- for P1.1 and P2.1 samples, a difference of Tc of 0.64 °C at peak 3 is noticed.

In case of cold pressed walnut oils adulterated with 10% SFO, it was found that:

- at samples P1 and P3, peak 2 comes a Tg at sample P3,

- at samples P1.1 and P3.1, the phase transitions are produced with a Tc of approximately -1 °C for peak 1 and 3 in case of sample P3.1, for peak 2 Tc = -42.2 °C for both samples.

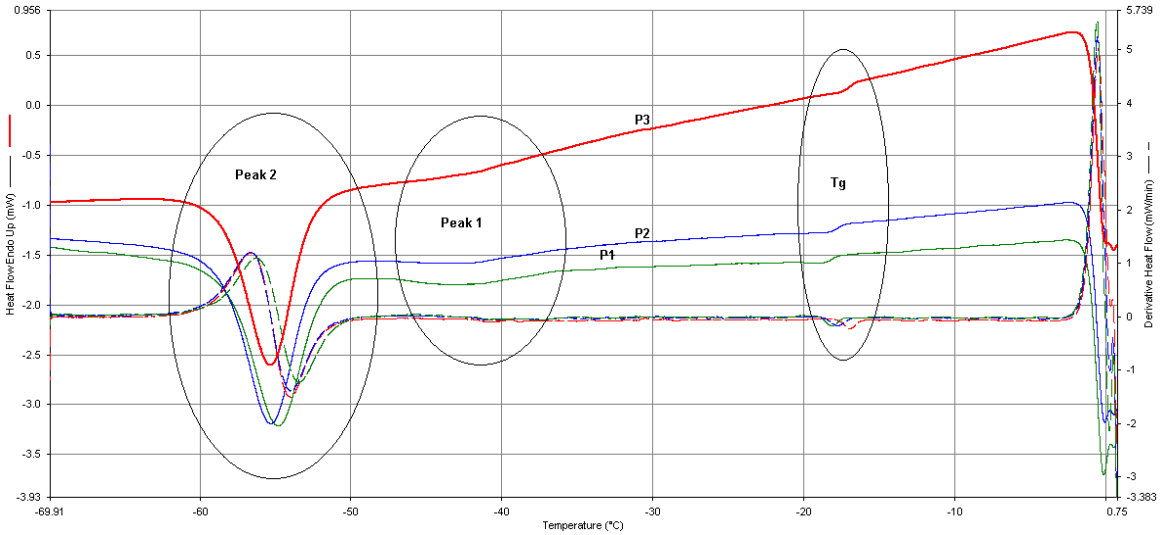

Figure 1a. Crystallization curves for samples P1, P2 and P3

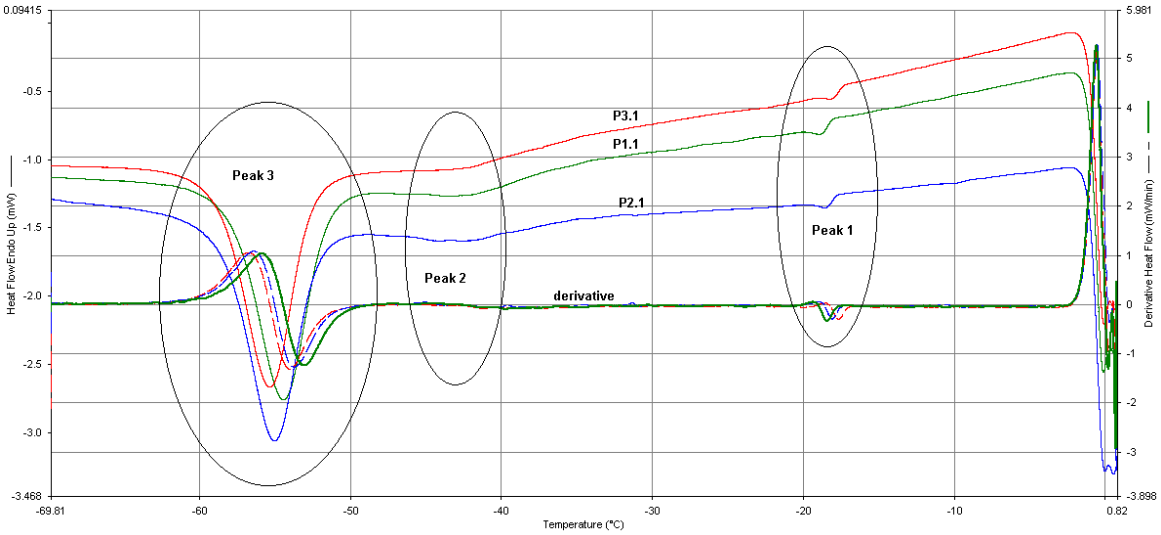

Figure 1b. Crystallization curves for sample P1.1, P2.1 and P3.1

Table 3. Thermal characteristics on the crystallization of the oil samples

CRYSTALLIZATION	**To**	**Tg**	**Tc**	**Tend**	**Area**	**ΔH**	**ΔCp**
Samples	(^{0}C)	(^{0}C)	(^{0}C)	(^{0}C)	(mJ)	(J/g)	J/g*^{0}C
SFO							
Tg	-10.87±0.13	-11.51±0.29	-	-12.11±0.00	-		0.400±0.015
Peak 2	-39.66±0.08	-40.29±0.09	-40.59±0.04	-42.16±0.20	-1.55±0.03	-0.19±0.00	
Peak 3	-53.04±0.16	-54.84±0.17	-56.43±0.07	-60.05±0.07	-264.46±0.42	-31.96±0.36	
P1 (WO1)							
Tg	-17.53±0.08	-17.94±0.05	-	-18.35±0.06	-		0.365±0.02
Peak 2	-37.74±0.08	-37.89±0.12	-41.94±0.02	-46.67±0.03	-19.37±1.32	-3.12±0.05	
Peak 3	-52.60±0.19	-54.01±0.18	-55.45±0.04	-58.79±0.42	-239.58±3.03	-30.31±0.23	
P2 (95%WO1)							
Tg	-16.69±0.12	-17.13±0.16	-	-17.51±0.23	-		0.356±0.04
Peak 2	-37.44±0.06	-37.92±0.05	-41.94±0.07	-45.62±0.15	-17.45±2.65	-2.68±0.04	
Peak 3	-53.44±0.32	-54.84±0.22	-56.12±0.02	-59.25±0.07	-202.95±3.4	-27.01±0.43	
P3 (90%WO1)							
Tg	-16.71±0.07	-17.18±0.09	-	-17.62±0.10	-		0.414±0.05
Tg	-36.93±0.01	-37.73±0.14	-	-40.07±0.55	-		1.890±0.01
Peak 3	-53.40±0.12	-54.69±0.08	-55.03±0.03	-59.01±0.11	-228.44±7.31	-30.36±0.15	
P1.1 (WO2)							
Peak 1	-18.16±0.08	-18.47±0.08	-18.98±0.02	-20.62±0.85	-3.38±0.83	-0.42±0.10	
Peak 2	-37.41±0.27	-43.48±0.58	-42.27±0.04	-47.67±0.09	-28.52±1.17	-3.61±0.14	
Peak 3	-51.70±0.03	-53.20±0.03	-54.56±0.03	-57.88±0.06	-243.24±2.27	-30.86±0.35	
P2.1 (95% WO2)							
Peak 1	-17.71±0.06	-17.97±0.12	-18.62±0.01	-19.58±0.14	-3.59±0.12	-0. 26±36.06	
Peak 2	-38.65±0.97	-40.66±0.54	-42.18±0.02	-47.95±0.10	-25.84±1.16	-3.63±0.16	
Peak 3	-52.31±0.03	-54.07±0.61	-55.20±0.02	-57.73±0.15	-205.28±0.20	-28.83±0.01	
P3.1 (90% WO2)							
Peak 1	-16.63±0.00	-17.03±0.00	-17.76±0.01	-18.13±0.56	-2.16±0.02	-0.33±0.00	
Peak 2	-40.35±0.04	-40.70±0.03	-42.19±0.01	-44.06±0.09	-17.31±0.07	-2.75±0.010	
Peak 3	-52.92±0.03	-54.09±0.01	-55.37±0.01	-58.01±0.15	-187.82±1.24	-28.87±0.11	

The thermal melting curve of SFO shows three well-defined melting peaks with Tm at -31.62 °C, -21.97 °C and -9.3 °C. The thermal curve of walnut oils as well as their samples diluted with refined sunflower oil have a well-defined peak (Table 4). At the superposition of the thermal curves of the walnut oil samples with SFO diluted samples (Figures 2a and 2b), there are differences in the shape of the thermal curve with relaxing peaks of the enthalpy probably due to polymorphic forms α, β^1 and β. In order to evaluate the differences between the samples, the peak parameters were calculated by aligning the peak to the baseline, taking the peak calculation limits from curve detachment and return it to the baseline. The results obtained are shown in Table 4. There is a difference at Tm in samples P1

and P3, P1 and P3.1 of 0.73 °C and 0.98 °C, respectively, and a difference of 0.5 °C at Tg for the same samples.

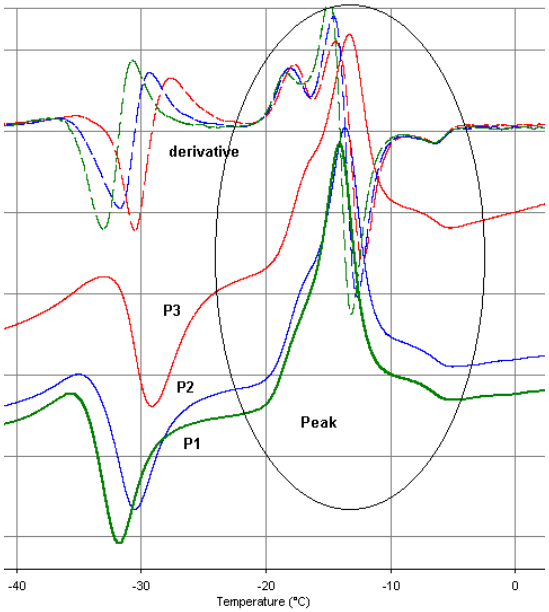

Figure 2a. Melting curves for samples P1, P2 and P3

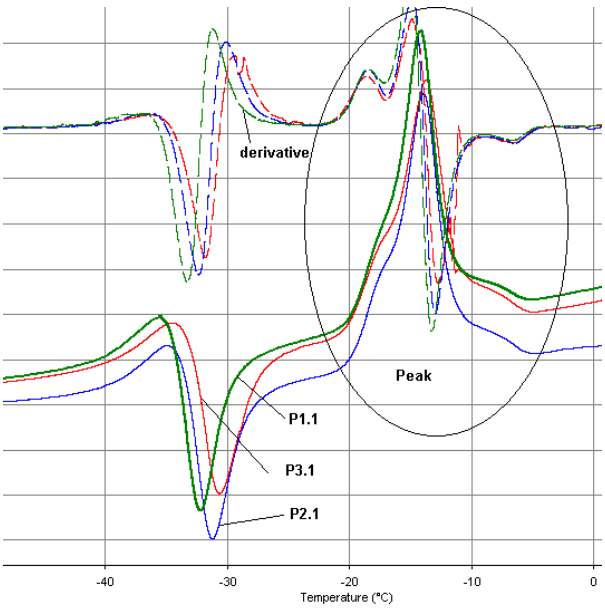

Figure 2b. Melting curves for samples P1.1, P2.1 and P3.1

Table 4. Thermal characteristics on the melting of the oil samples.

MELTING	**To**	**Tg**	**Tm**	**Tend**	**Area**	**ΔH**
Samples	(^{0}C)	(^{0}C)	(^{0}C)	(^{0}C)	(mJ)	(J/g)
SFO						
Peak 1	-35.74±0.04	-32.94±0.43	-31.62±0.02	-29.23±0.04	42.16±0.00	5.50±0.01
Peak 2	-27.72±0.05	-26.86±0.00	-25.57±0.04	-21.97±0.07	174.5±2.50	22.8±0.37
Peak 3	-11.25±0.29	-10.41±0.07	-9.30±0.04	-6.73±0.01	57.84±3.00	7.55±0.37
P1 (WO1)						
Peak	-17.30±0.13	-15.01±0.09	-14.11±0.01	-11.73±0.03	543.37±8.51	69.05±1.01
P2 (95%WO1)						
Peak	-18.51±0.04	-17.26±0.13	-13.32±0.01	-10.17±0.01	481.04±7.65	63.49±0.55
P3 (90%WO1)						
Peak	-17.06±0.05	-14.46±0.04	-13.38±0.02	-10.64±0.02	472.42±0.93	57.03±0.36
P1.1 (WO2)						
Peak	-17.28±0.10	-14.93±0.00	-14.22±0.00	-11.96±0.02	544.29±3.19	69.05±0.25
P2.1 (95% WO2)						
Peak	-17.06±0.01	-14.97±0.01	-13.94±0.09	-11.56±0.08	478.04±1.29	67.13±0.14
P3.1 (90% WO2)						
Peak	-17.40±0.14	-14.40±0.02	-13.24±0.03	-10.25±001	413.63±2.19	62.44±0.28

The melting point obtained by the DSC method was considered by many authors as To (the onset temperature) or Tm (where the heavy fraction of stearine is melted) or Tend when all crystals are considered to be melted and the system is in balance in the liquid state. The peak area calculation includes the boundary area by the tangent at the inflection points of the curve and the baseline. The delimited surfaces by To, the inflection points of the curve Tg (where there are crystalline fractions of the polymorph mixture) are not calculated. These surfaces are variable depending on the TAGs composition. The derivative highlights the steady/nonequilibrium state of the system between the points that delimit the phase transition changes. It is found that the solid-liquid system is far from the thermodynamic equilibrium on the upward side of the curve. Thus, can be distinguished areas that describe the absorption of the thermal energy with polymorphic relaxation peaks. Only in the liquid state Tm – Tend, the system is in equilibrium. The absorption of thermal energy in the To – Tg area (when the system changes its Cp) has different values for the walnut oil samples diluted with sunflower oil. It is noted that the To – Tg value is different for each sample: P2 = 1.25 °C; P3 = 2.6 °C; P2.1 = 2.09 °C; P3.1 = 3 °C. Then, it follows a relaxation peak attributed to melting of the α polymorphic shape of TAG followed by an equilibrium area for this fraction of crystals. The To – Tm area, further describes a nonequilibrium state of the polymorph system with different values for each sample: for WO1 and its dilutions, Tg – Tm is 0.9 °C (P1), 3.94 °C (P2) and 1.08 °C (P3), while for WO2 and its dilutions, the Tg – Tm value is 0.71 °C (P1.1), 1.03 °C (P2.1) and 1.16 °C (P3.1). For Tm, there is a difference of approximately 1 °C between P1 and both dilutions. In case of sample P1.1, Tm has a difference of 1 °C

at the 10% SFO addition. It is found that the solid-liquid system is far from the thermodynamic equilibrium on the upward side of the curve. Only in the liquid state Tm – Tend, the system is in equilibrium. A clearer analysis could be obtained by evaluation of the temperatures in the transition area To (the onset transition) and Tm (the end transition), considering Tg - Tg1/2, the temperature at which Cp is half the distance of the extrapolated functions of thermal capacity between solid and liquid states.

Conclusions

The analysis of the lipid profile of cold pressed walnut oil, refined sunflower oil and mixtures of them, revealed a very close composition in saturated fatty acids. The difference between samples was less than 0.5%, except for refined sunflower oil – where the difference is over 0.5% and does not contain linolenic acid. In the case of oil mixtures, differences were found between samples for linolenic acid, which was reduced by 0.1 – 0.4% in the samples of cold pressed walnut oil adulterated with 5% refined sunflower oil and 1.1% in samples adulterated with 10% refined sunflower oil. The types of oils taken into the study produced three thermal events at crystallization. On the adulterated samples, two temperature zones were recorded -17 °C – 20 °C and -37 °C – 48 °C, where the system is not in equilibrium and where the thermal energy transferred indicates different degrees of freedom of the TAGs composition and a temperature range of -52 °C – 59°C in which the lipid system produces a major exothermic event which can be attributed to a hypereutectic system.

On the melting of the oil samples, there are major differences between walnut oil and sunflower oil samples, each oil having its own thermal behaviour. The adulterated samples produce a single peak, similar to the walnut oil samples, which apparently are not significantly different. A detailed analysis of the upward part of the curve highlights the areas of phase transition which are characteristic to the polymorphic mixtures where fractions of mixed crystal produce relaxation peaks of different amplitudes. This thermal behaviour reveals different compositions of TAGs or the presence of non-TAG compounds which cause changes in the crystallization networks.

This study showed that scanning method of the lipid system using the DSC technique is a valuable tool in oils fingerprinting. Through monitoring, DSC technique can protect valuable brands against adulteration and prevent unequal competition on the market.

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