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Monovarietal Extra Virgin Olive Oils. Correlation between Thermal Properties and Chemical Composition: Heating Thermograms

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Extra virgin olive oils from drupes of three Sicilian varieties (Biancolilla, Cerasuola, and Nocellara del Belice) collected at three different harvesting periods were analyzed upon heating by means of DSC, and thermal properties were related to the chemical composition of the samples. All thermograms exhibited multiple transitions with a minor exothermic peak, followed by a major endothermic event. Cerasuola samples showed higher overall enthalpy and narrower range of transition at all harvesting periods, as compared to the other oils. A more ordered crystal structure originating from a more uniform chemical composition, with higher triolein content, in Cerasuola may be hypothesized. At different harvesting periods, thermal transitions started at lower temperatures and developed over a narrower range in all cultivars, probably due to the insertion of molecules derived from triacylglycerol lysis (diacylglycerols and free fatty acids) and lipid oxidation products into the triacylglycerol crystal lattice. All heating thermograms were deconvoluted into one exothermic and five endothermic constituent peaks, and the effect of chemical components on thermal properties of the peaks was evaluated. DSC application upon heating appears to be very promising in discriminating among oil samples from olives of different cultivars and/or harvesting periods.

KEYWORDS: Extra virgin olive oil; cultivar; DSC; heating; thermal properties; chemical composition

INTRODUCTION

EVOO is widely produced and consumed in the Mediterranean area. The quality and uniqueness of this vegetable oil are primarily determined by genetic and climatic factors, as well as by agricultural practices (*1–3*). Chemical composition of the different olive varieties and harvesting periods not only defines EVOO quality but also influences its oxidative stability and sensorial characteristics (*4–6*). The production of monovarietal EVOOs has largely increased during the past few years; characterization of these oils is needed to identify specific properties that distinguish them and increase their value with respect to other niche EVOOs, such as Protected Designation of Origin.

DSC has been proposed as a valuable tool for the characterization of oils from olive and other vegetable sources (*7, 8*). In particular, crystallization and melting profiles were found to be influenced by chemical composition (e.g., TAG and FA profiles) in several vegetable oils (*9–11*). Oxidative stability of EVOO was investigated by Vittadini et al. (*12*) and by Kanavaouras and Selke (*13*). The suitability of DSC to discriminate between commercial EVOO and other samples of known geographical origin was suggested by Angiuli and co-workers (*14*); however, no correlations with chemical parameters were considered in that work. To our knowledge, only one study evaluated the feasibility of DSC application to distinguish among monovarietal EVOOs (*15*). In this research, Jiménez Marquez and Beltrán Maza analyzed crystallization and melting profiles of EVOOs from six different Spanish cultivars, and thermal properties were correlated with major components, such as triacylglycerol and fatty acid compositions (*15*). Both crystallization and melting profiles were found to be largely influenced by oleic and linoleic acid content, as well as triacylglycerol composition.

Little information is available in the literature about how different chemical compositions may affect the thermal properties of EVOO. In addition, the effects of minor components, which are largely present in this type of vegetable oil (i.e., DAG), on thermal properties have not been studied in depth. Thermal properties of three Sicilian monovarietal EVOOs, from drupes collected at three different harvesting periods, were evaluated upon cooling and related to the chemical composition

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in a previous study (*16*). Differences in both major (e.g., TAG, FA) and minor components (e.g., FFA, DAG and lipid oxidation products), ascribable to different varieties and/or harvesting periods, were found to influence peak onset and temperature range of crystallization. In addition, the overlapping cooling transition was resolved into three constituent exothermic peaks for all samples, by deconvolution analysis of DSC thermograms. To the authors' knowledge, this is the first time that deconvolution of oil and fat transitions has been performed on DSC thermograms. Deconvoluted peaks were further interpreted and related to specific TAG species. In particular, the areas of the two lower temperature exotherms had high Pearson correlation coefficients ($R > 0.85$) with the amount of TUTAG and MSTAG present in the oils.

The aim of this work was to evaluate the influence of major and minor chemical components on heating thermogram profiles and thermal properties of EVOO samples obtained from olives of different cultivars and harvesting periods, previously analyzed upon cooling (*16*). The possibility of using DSC heating profiles to discriminate among samples was also evaluated. In addition, deconvolution analysis was applied to all thermograms to characterize the complex nature of the heating transition, in an attempt to attribute deconvoluted peaks to different TAG polymorphic forms and to better establish the influence of major and minor components.

MATERIALS AND METHODS

Sampling. Three monovarietal (Biancolilla, Cerasuola, and Nocellara del Belice) EVOOs from Palermo (Sicily, Italy) were studied. The olives used for oil production were hand-picked at three different harvesting periods [October (A), November (B), and December (C)] in 2004. EVOO samples were produced as previously described (*16*). Samples were stored in dark bottles without headspace at room temperature and analyzed after 1 year of storage. One olive oil sample per harvesting period and olive cultivar was analyzed. The crystallization process and chemical composition of EVOO samples (TAG, FA and FFA, DAG, and lipid oxidation products) can be found in Chiavaro et al. (*16*).

DSC. Samples of oil (8–10 mg) were weighed into aluminum pans and covers were sealed into place. Samples were analyzed with a DSC Q100 (TA Instruments, New Castle, DE). Indium (melting temperature = 156.6 °C, ΔH_f = 28.45 J/g) and *n*-dodecane (melting temperature = −9.65 °C, ΔH_f = 216.73 J/g) were used to calibrate the instrument, and an empty pan was used as reference. Oil samples were equilibrated at −80 °C for 3 min, after cooling from 30 to −80 °C at the rate of 2 °C/min, and then heated from −80 to 30 °C at 2 °C/min. Dry nitrogen was purged in the DSC cell at 50 cm^3/min. Thermograms were analyzed with Universal Analysis software, version 3.9A (TA Instruments), and enthalpy (J/g), T_{on} and T_{off} of the transitions (intersection of baseline and tangent at the transition) were obtained according to the method of Wunderlich (*17*). The range of the transitions was calculated as temperature difference between T_{on} and T_{off}. At least triplicate analyses were carried out for each sample.

Overlapping transitions of the melting thermograms were deconvoluted into individual constituent peaks using PeakFitTM software (Jandel Scientific, San Rafael, CA). The following parameters were considered for each deconvoluted peak: onset (T_{on}), offset (T_{off}), and peak temperatures (T_p) and percent peak area (percentage area of the total peak area).

Statistical Analysis. Means and standard deviations were calculated with SPSS (version 13.0; SPSS Inc., Chicago, IL) statistical software. SPSS was used to perform one-way analysis of variance and Tukey's honest significant difference test at a 95% confidence level ($p < 0.05$) to identify differences among groups. Pearson correlation coefficients were calculated among the measured variables at a 95% confidence level ($p < 0.05$).

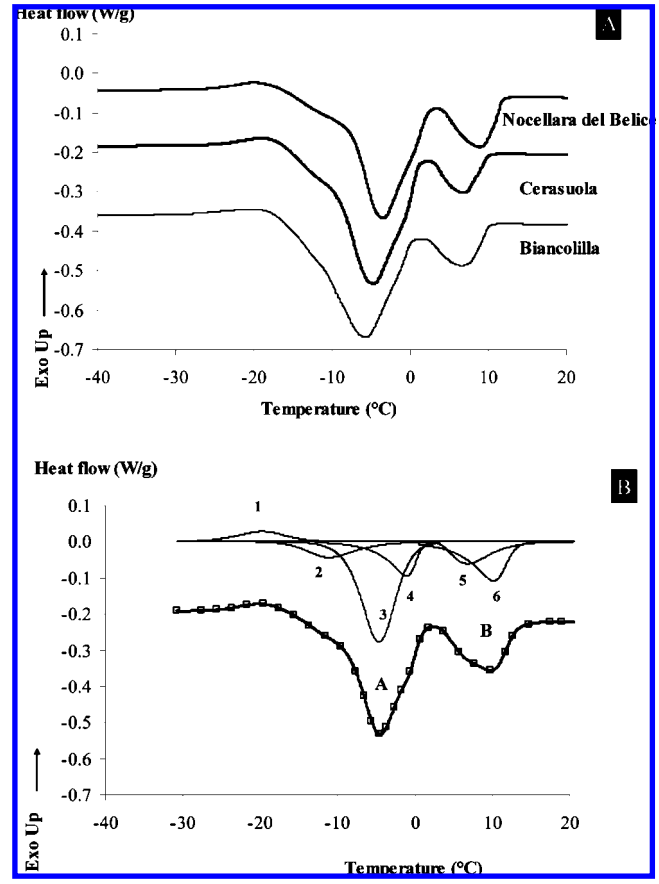

Figure 1. (**A**) Representative DSC heating thermograms of the three monovarietal extra virgin olive oils at the C harvesting period; (**B**) deconvolution of the heating thermogram of a Biancolilla sample; experimental data (□), fitted curve (bold line), and the constituent peaks are shown.

RESULTS AND DISCUSSION

Thermal Properties. Figure 1A shows representative DSC heating thermograms of the three monovarietal EVOOs. Heating curves of all samples had similar, but not identical, lineshapes and exhibited multiple transitions as the samples were heated from −80 to 30 °C. All samples showed, at first, a minor exothermic peak and, successively, a major endothermic event occurring over the −18/12 °C temperature range.

The first exothermic event originated at ∼−28 °C was possibly due to the crystallization of an oil fraction that did not solidify under the selected cooling regime and/or exothermic molecular rearrangement of TAG fractions into more stable polymorphic crystal forms, as reported for other vegetable oils (*9, 18*). Such exothermic peaks were more pronounced in the Cerasuola cultivar as compared to the other EVOOs here considered.

The endothermic peak observed at temperatures above −18 °C was attributed to the melting of crystallized lipids, and it embodied multiple overlapping contributions as shown by the complex lineshapes. Two well-defined events were distinguishable: a major endothermic event peaking at ∼−5 °C (A), previously reported in olive oil samples by Tan and Che Man (*9*), and a smaller and flattened event peaking at ∼8 °C (B). The latter peak was more asymmetric and skewed toward higher temperature in Nocellara del Belice and more symmetric in the other two cultivars. An additional endothermic event was possibly observed at lower temperatures (∼−15 °C), but it was less evident than the others and displayed itself as a shoulder

Table 1. DSC Data Obtained from the Heating Thermograms of the Monovarietal Extra Virgin Olive Oils at Three Harvesting Periods[a]

harvesting period	cultivar	ΔH (J/g)	T_{on} (°C)	range[b] (°C)
A	Biancolilla	69.4 ± 1.7 b	−27.4 ± 0.3 b	40.8 ± 0.2 a
	Cerasuola	74.1 ± 0.8 a	−26.3 ± 0.2 a	37.2 ± 0.5 c
	Nocellara del Belice	69.9 ± 1.6 b	−27.1 ± 0.2 b	39.4 ± 0.9 b
B	Biancolilla	68.8 ± 1.1 y	−27.3 ± 0.3 y	40.4 ± 0.3 x
	Cerasuola	71.9 ± 0.6 x	−26.3 ± 0.4 x	37.0 ± 0.5 y
	Nocellara del Belice	68.6 ± 0.7 y	−27.2 ± 0.4 y	40.1 ± 0.5 x
C	Biancolilla	70.6 ± 1.6 A	−28.1 ± 0.2 B	39.5 ± 0.3 A
	Cerasuola	72.8 ± 1.8 A	−26.8 ± 0.4 A	36.0 ± 0.8 C
	Nocellara del Belice	69.2 ± 1.8 A	−28.6 ± 0.4 B	37.7 ± 0.5 B

[a] Data are expressed as mean ± standard deviations of three determinations. The same letters within each column at each harvesting period do not significantly differ ($p < 0.05$). [b] Temperature difference between T_{on} and T_{off}.

in the major peak (∼−5 °C). The presence of two small shoulder peaks at both lower and higher temperatures (at −18.7 and 2.2 °C) of the major endothermic peak (−6.3 °C) were previously reported (*11*); however, they were not as clearly defined as in this work, probably due to different experimental conditions and/or instrumentation and/or nature of the oil commercial category. Multiple endothermic peaks were also observed in heating thermograms of vegetable oils (*9, 11*), and they were ascribed to both TAG composition (TAG fractions with different degree of saturation) and different fat polymorphic forms (*9*).

The characterizing overall thermal properties (enthalpy, T_{on} and temperature range) were obtained from the heating thermograms for each sample, from the onset of the exothermal to the offset of the endothermic events (**Table 1**).

The overall enthalpy was significantly higher in Cerasuola samples (**Table 1**) than in the other two varieties at both A and B harvesting periods. At harvesting period C, Cerasuola samples still had the highest overall enthalpy, but the difference with respect to the other two varieties was no longer significant. A more ordered crystal structure having TAG chains more compactly associated may be hypothesized for Cerasuola samples; this might be related to the more uniform chemical composition (higher OOO content) of Cerasuola as compared to that of the oil obtained from the other cultivars, even though no significant differences were found among the overall crystallization enthalpies (*16*).

Significant differences were found in T_{on} of the heating curves, as the Cerasuola samples underwent phase transition at higher temperatures than the other two cultivars at all harvesting periods (**Table 1**). Phase transition also occurred in a significantly narrower range of temperature for Cerasuola in comparison with Biancolilla and Nocellara del Belice at all harvesting periods (**Table 1**). Compositional data of Cerasuola cultivar indicated a higher degree of unsaturated fatty acids and triacylglycerols (MUFA, PUFA, and TUTAG) than the other two cultivars (*16*). Lower T_{on} of melting was previously associated with a higher degree of unsaturation in vegetable oils (*11*). Virgin olive oil samples from cultivars with a high PUFA content were reported to exhibit both lower T_{on} of melting and narrower range of transition (*15*). In this study, T_{on} of the thermal transition encompassed not only the endo- but also the exothermic phase transition, because these two events were not completely resolved. Ripening induced a slight decrease of overall enthalpy only in Cerasuola samples (from stage A to stage B). In addition, heating lipid transitions started at lower temperatures and developed over a narrower range in all cultivars, from A to C harvesting periods (**Table 1**). During ripening, EVOO samples showed an increase of lipid oxidation products, as well as of FFA and DAG generated by TAG lysis (*16*). These molecules were reported to be adsorbed into the crystal lattices of TAG, forming mixed crystals that melted at lower temperature and over a narrower temperature range than pure TAG crystal; this results in a heterogeneous structure that is more easily disrupted upon heating than pure TAG, as previously observed (*19–21*).

Deconvolution of Heating Thermograms. Separation of overlapping transitions was obtained by deconvolution analysis to better describe and characterize the complex nature of the phase transition process observed in the heating thermograms.

The heating thermograms of all samples were best deconvoluted using six peaks, as shown in **Figure 1B**, where experimental data, fitted curves, and constituent peaks are shown for a representative curve ($R^2 \geq 0.98$ for all fitted curves). All peaks were asymmetric double-Gaussian functions. The six peaks identified were consecutively numbered, starting from the lowest to the highest temperature, and named peaks 1, 2, 3, 4, 5, and 6, respectively. Peak 1 was an exothermic transition, whereas the other peaks were all endothermic events.

Three different events (peaks 2−4) were involved in the first major endothermic event A (−18 to 2 °C) observed in the thermograms, whereas the smaller peak shoulder B (2–12 °C) was resolved with two endothermic transitions. The main endothermic peak may, therefore, be related to the melting of three crystalline forms with different melting temperatures. These may be ascribed to different polymorphic forms of the *most* unsaturated fractions of triacylglycerols (TUTAG), especially OOO and OOL, which were the major TUTAG in all samples (*16*). Similarly, the smaller peak (2–13 °C) may be associated with the melting of two polymorphic forms of the MSTAG, in particular, OOP and POL, which were the most representative in all samples. Che Man and co-workers (*22*) reported that heating thermograms of pure TAG displayed a single peak centered at ∼3 °C for OOO and two peaks for OOP (at ∼12 and 15 °C). Jiménez Marquez and Beltrán Maza (*15*) already associated the major endothermic event of the heating thermograms with the melting of the more unsaturated fractions of TAG and the smaller peak mainly to POL. Attribution of the deconvoluted peaks to a single polymorphic form was difficult, due to the lack of literature data about the polymorphic behavior of TAG in olive oil. Hagemann, Tallent, and Kolb (*23*) observed that OOO could exhibit four polymorphic forms (β_3', β_2', β_1', and β), which melt at −12, −8, −5, and 5 °C, respectively. Heating thermograms of crude palm oil and its products (refined, bleached, and deodorized palm oil, olein and superolein), which are mainly constituted by MSTAG and DSTAG, were reported to have polymorphic forms β_2', α', and α that melt at 1.08/4.41, 4.78/8.08, and 4.05 °C (found in only refined, bleached, and deodorized palm oil), respectively (*21*). Further studies are required to characterize TAG polymorphism in olive oil by means of tandem techniques, such as DSC and X-ray diffraction, already applied to the analysis of polymorphic forms of other vegetable oils (*24*) and fat mixtures (*25*).

Figure 2 shows the percent peak areas (from deconvolution analysis) and percent TAG areas [from HPLC, (*16*)] during ripening of Biancolilla (**Figure 2a**), Cerasuola (**Figure 2b**), and Nocellara del Belice (**Figure 2c**); TAG data were reported previously (*16*). Although a limited number of samples was considered, the sum of area percentages of deconvoluted peaks

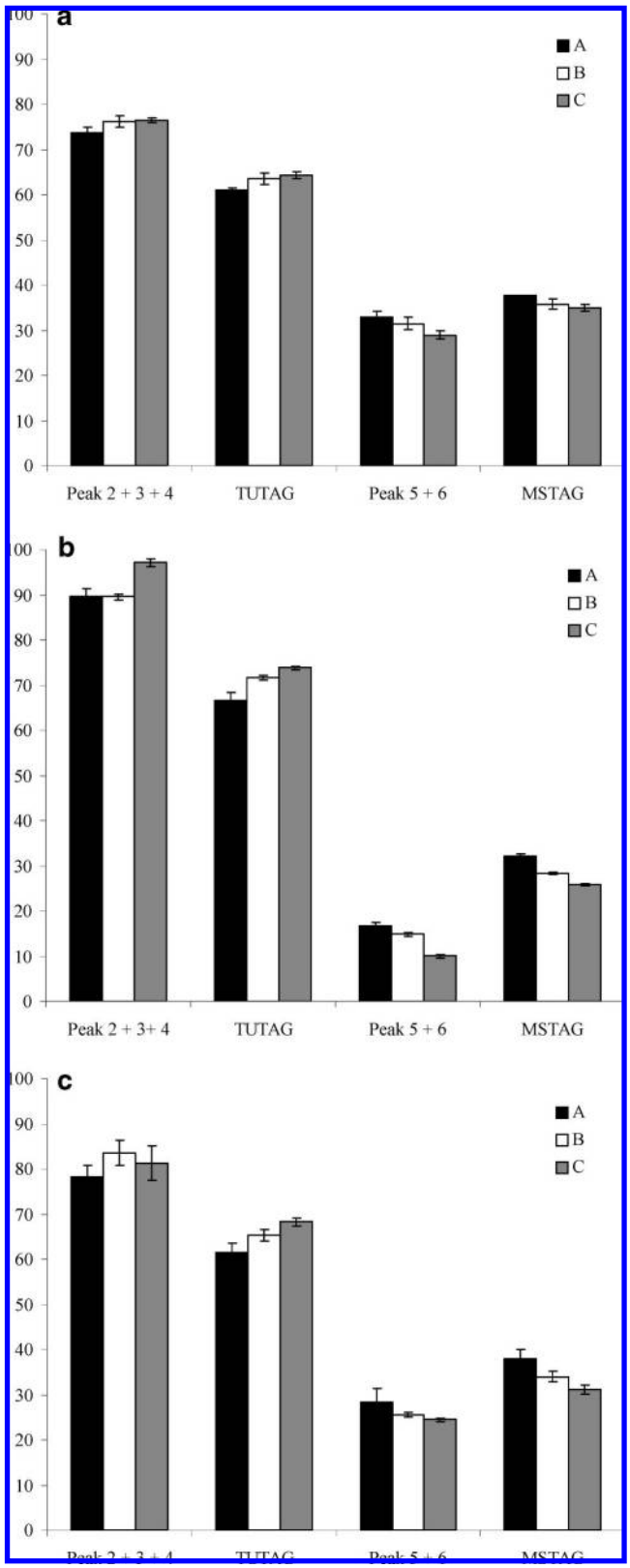

Figure 2. Comparison between percentage area of deconvoluted heating peaks and TAG composition (MSTAG, PLL + POLn + POL + OOP + SOO; TUTAG, OLL + OOL + OOO) at different harvesting periods for Biancolilla (**a**), Cerasuola (**b**), and Nocellara del Belice (**c**) cultivars. Error bars represent ±1 standard deviation ($n = 3$). TAG data are reported in ref *16*.

2−4 correlated with TUTAG ($R = 0.78$; $p < 0.01$). Similarly, total area percentages of peaks 5 and 6 correlated with MSTAG ($R = 0.90$; $p < 0.01$). DSTAG were also found in all samples at low amount (<1%), as only PPO could be separated by HPLC (*16*). Pure PPO was reported to melt at ∼25 °C (*22*), but it was not detected by DSC, as no endothermic event was observed in proximity of this temperature, probably due to its very low presence in the samples. In addition, a cooperative and simultaneous phase transition of MSTAG and DSTAG, ascribable to the formation of vicinal interacting crystals, may have occurred, especially in Cerasuola and Biancolilla, which showed a more symmetric peak profile.

Deconvoluted peaks were further characterized by means of T_{on}, T_p, and T_{off} peak temperatures, as well as temperature transition range (**Table 2**). Peak 1 of Cerasuola samples showed higher T_{on} than the other two cultivars at all harvesting periods and developed over a narrower range of temperature. A significant shift of peak 1 T_{on} toward lower temperatures was observed in all cultivars at C harvesting period. Area percentages of peak 1 were found to be ∼−8–10% for Biancolilla and Nocellara del Belice and ∼−3–4% for Cerasuola (data not shown), and they were unvaried during ripening. Peaks 2 showed lower T_{on} in Cerasuola samples at A and B harvesting periods, probably due to the higher degree of unsaturation of Cerasuola as compared to the other two cultivars. At C harvesting period, T_{on} did not significantly vary among samples, whereas TUTAG increased in all cultivars during ripening (*16*). Peak 3 also showed lower T_{on} for Cerasuola in comparison with the other two cultivars at both A and B harvesting periods. Peak 4 did not show significant differences in thermal properties among cultivars within the same harvesting period and during ripening. Peaks 5 and 6 of Cerasuola samples developed in a narrower range of transition at all harvesting periods, as compared to the other two cultivars, showing a significantly lower T_p as well. During ripening, peak 5 shifted toward lower temperatures for Biancolilla and Nocellara del Belice samples. A significant shift of T_{on} toward lower temperatures was also observed for peak 6 in all cultivars from A to C harvesting periods.

Differences in temperature range of the deconvoluted peaks among cultivars and their shift during ripening may be related to a change in chemical composition of the major components (mainly TUTAG and MSTAG), as well as to the presence of minor olive oil components (DAG, FFA, lipid oxidation products). In particular, the 1,2 isomer of DAG, which was found in all samples in larger amounts than the 1,3 form (*16*), could have influenced the melting point of the deconvoluted peaks characteristics of the higher melting molecules (peaks 5 and 6). It has been reported that 1,2 DAG affected the melting temperature of palm oil and its products (*26*). However, no literature data were found about DAG influence on the melting of olive oil to support the proposed hypothesis.

The same oil samples were previously studied by DSC upon cooling in an attempt to characterize the crystallization process (*16*). The cooling thermograms were found to be less complex than the heating profiles, that were, on the contrary, more distinctive for each cultivar, providing important qualitative information to investigate monovarietal EVOOs. In particular, the line shape of the small peak (B) seems to be a very promising parameter to discriminate among EVOOs from different olive cultivars, as its profile is affected by MSTAG and/or cooperation among less saturated TAG fractions (MSTAG and DSTAG).

Deconvolution of the thermograms into their constituent peaks was found to be more effective in the discrimination of the crystallization process, whereas the complexity of the melting process made it difficult to attribute each deconvoluted peak to the different TAG polymorphic forms of EVOO. Additional

Table 2. Deconvolution Parameters of Heating Thermograms of the Monovarietal Extra Virgin Olive Oils at Three Harvesting Periods[a]

peak[b]	cultivar	T_{on} (°C)	T_p (°C)	T_{off} (°C)	range[c] (°C)
		Harvesting Period A			
1	Biancolilla	−28.5 ± 0.2 b	−19.7 ± 0.1 b	−13.5 ± 0.2 b	15.1 ± 0.5 ab
	Cerasuola	−26.9 ± 0.5 a	−18.6 ± 0.3 a	−12.9 ± 0.7 b	13.9 ± 0.4 b
	Nocellara del Belice	−27.7 ± 0.6 ab	−19.4 ± 0.2 a	−8.5 ± 1.9 a	19.2 ± 2.5 a
2	Biancolilla	−18.4 ± 0.5 a	−10.8 ± 0.4 ab	0.2 ± 1.1 a	18.7 ± 0.8 a
	Cerasuola	−21.2 ± 1.5 b	−11.3 ± 0.2 b	−4.4 ± 1.2 a	17.2 ± 0.4 a
	Nocellara del Belice	−17.5 ± 0.4 a	−10.0 ± 0.2 a	−2.5 ± 1.6 a	18.8 ± 0.9 a
3	Biancolilla	−14.0 ± 0.5 ab	−4.9 ± 0.2 a	4.7 ± 0.9 b	18.6 ± 0.8 b
	Cerasuola	−16.2 ± 1.1 b	−4.8 ± 0.6 a	6.2 ± 0.8 ab	22.3 ± 1.2 a
	Nocellara del Belice	−12.1 ± 1.1 a	−3.8 ± 0.2 a	9.2 ± 0.1 a	21.3 ± 1.0 ab
4	Biancolilla	−11.8 ± 0.9 b	−1.2 ± 0.2 a	2.8 ± 0.4 a	13.1 ± 1.5 a
	Cerasuola	−10.1 ± 1.2 ab	−0.7 ± 0.3 ab	2.1 ± 0.3 a	12.0 ± 1.8 a
	Nocellara del Belice	−8.5 ± 0.9 a	−0.4 ± 0.2 a	2.9 ± 0.7 a	12.6 ± 1.9 a
5	Biancolilla	1.5 ± 0.9 ab	7.0 ± 0.3 a	14.2 ± 1.2 b	12.7 ± 0.5 a
	Cerasuola	1.3 ± 0.7 b	5.8 ± 0.6 a	10.1 ± 0.6 b	8.8 ± 0.2 b
	Nocellara del Belice	3.0 ± 0.1 a	7.0 ± 0.8 a	12.6 ± 1.1 ab	9.6 ± 1.1 b
6	Biancolilla	0.1 ± 1.8 a	10.4 ± 0.2 a	14.2 ± 0.4 a	14.2 ± 2.1 a
	Cerasuola	2.9 ± 1.1 a	8.0 ± 0.6 b	12.6 ± 0.2 b	9.7 ± 1.1 b
	Nocellara del Belice	1.8 ± 2.1 a	9.5 ± 0.5 a	13.5 ± 1.1 ab	11.6 ± 3.2 ab
		Harvesting Period B			
1	Biancolilla	−28.5 ± 0.2 xy	−20.3 ± 0.2 y	−11.5 ± 0.7 x	16.9 ± 0.9 x
	Cerasuola	−26.8 ± 0.6 x	−19.2 ± 0.4 x	−14.1 ± 0.6 y	12.6 ± 0.1 y
	Nocellara del Belice	−29.1 ± 1.1 y	−20.4 ± 0.4 y	−13.8 ± 1.3 y	15.2 ± 0.6 x
2	Biancolilla	−19.8 ± 0.8 x	−11.1 ± 0.4 x	−0.7 ± 2.3 xy	19.0 ± 1.6 x
	Cerasuola	−20.6 ± 0.3 y	−12.1 ± 0.3 x	−1.6 ± 1.5 y	19.1 ± 1.5 x
	Nocellara del Belice	−19.3 ± 0.3 xy	−11.7 ± 0.4 x	−0.2 ± 2.4 x	19.1 ± 2.1 x
3	Biancolilla	−13.6 ± 0.5 x	−5.2 ± 0.2 x	4.6 ± 1.1 y	18.2 ± 0.5 y
	Cerasuola	−15.1 ± 0.8 y	−5.5 ± 0.4 x	6.7 ± 0.9 x	21.7 ± 1.0 x
	Nocellara del Belice	−14.2 ± 0.5 x	−4.6 ± 0.6 x	6.0 ± 0.7 x	21.4 ± 0.7 x
4	Biancolilla	−11.8 ± 1.2 x	−1.4 ± 0.1 x	1.6 ± 0.4 x	13.4 ± 0.6 x
	Cerasuola	−11.1 ± 1.1 x	−0.8 ± 0.6 x	1.8 ± 0.3 x	12.9 ± 0.9 x
	Nocellara del Belice	−9.6 ± 0.6 x	−0.8 ± 0.5 x	2.1 ± 0.5 x	11.6 ± 1.1 x
5	Biancolilla	0.3 ± 0.2 x	7.0 ± 0.3 x	13.1 ± 0.5 y	12.8 ± 0.4 x
	Cerasuola	1.1 ± 0.7 x	5.7 ± 0.5 y	10.5 ± 1.4 y	9.5 ± 1.6 y
	Nocellara del Belice	1.0 ± 1.2 x	7.2 ± 0.1 x	14.1 ± 1.1 x	13.1 ± 2.1 x
6	Biancolilla	−1.2 ± 1.3 y	10.4 ± 0.2 x	14.5 ± 0.3 x	15.7 ± 2.1 x
	Cerasuola	3.3 ± 0.9 x	7.8 ± 0.6 y	11.9 ± 0.5 y	8.6 ± 1.4 y
	Nocellara del Belice	−1.1 ± 1.7 y	10.0 ± 0.1 x	14.3 ± 0.9 x	15.6 ± 0.8 x
		Harvesting Period C			
1	Biancolilla	−31.0 ± 1.5 B	−20.7 ± 0.2 B	−14.4 ± 0.2 A	16.6 ± 1.7 A
	Cerasuola	−27.9 ± 0.6 A	−20.3 ± 0.9 B	−13.7 ± 2.8 A	14.2 ± 2.2 A
	Nocellara del Belice	−31.0 ± 1.7 B	−19.1 ± 0.3 A	−12.8 ± 1.3 A	15.2 ± 0.6 A
2	Biancolilla	−17.4 ± 0.4 A	−12.0 ± 0.9 A	6.9 ± 0.1 A	24.3 ± 0.4 A
	Cerasuola	−17.4 ± 0.5 A	−12.6 ± 0.3 A	4.6 ± 2.2 AB	21.9 ± 1.6 B
	Nocellara del Belice	−17.7 ± 0.2 A	−11.1 ± 0.2 A	3.9 ± 1.2 B	21.5 ± 1.1 B
3	Biancolilla	−19.0 ± 0.5 A	−5.1 ± 0.1 A	4.0 ± 1.2 A	23.0 ± 1.6 A
	Cerasuola	−17.7 ± 0.4 A	−5.7 ± 0.2 B	4.9 ± 0.3 A	22.6 ± 0.3 A
	Nocellara del Belice	−18.8 ± 1.3 A	−5.0 ± 0.2 A	5.8 ± 0.8 A	19.5 ± 1.5 A
4	Biancolilla	−10.2 ± 1.9 A	−1.0 ± 0.2 A	2.8 ± 0.6 A	13.3 ± 1.8 A
	Cerasuola	−9.9 ± 1.5 A	−0.6 ± 0.2 A	2.5 ± 0.4 A	12.5 ± 1.3 A
	Nocellara del Belice	−9.5 ± 1.5 A	−0.5 ± 0.2 A	2.7 ± 0.9 A	12.4 ± 1.2 A
5	Biancolilla	0.8 ± 0.5 AB	6.4 ± 0.2 A	11.2 ± 1.4 A	10.4 ± 1.1 A
	Cerasuola	1.7 ± 0.5 A	2.4 ± 0.3 B	4.6 ± 1.1 B	2.8 ± 0.8 B
	Nocellara del Belice	−0.2 ± 0.1 B	5.5 ± 0.4 A	9.2 ± 0.9 A	9.5 ± 0.9 A
6	Biancolilla	−1.7 ± 0.9 B	8.6 ± 0.1 A	12.4 ± 0.4 A	14.1 ± 1.2 A
	Cerasuola	1.4 ± 1.1 A	6.0 ± 0.6 B	9.6 ± 0.6 B	8.3 ± 0.7 B
	Nocellara del Belice	−1.1 ± 0.5 B	7.7 ± 0.3 A	11.1 ± 0.7 AB	8.4 ± 1.0 A

[a] Data are expressed as mean ± standard deviations of three determinations. The same letters within each column for a single peak at each harvesting period do not significantly differ ($p < 0.05$). [b] See **Figure 1** for peak number assignation. [c] Temperature difference between T_{on} and T_{off}.

investigations are needed to establish this link and could be carried out, for example, coupling DSC with other analytical techniques (e.g., DSC−X-ray diffraction). In addition, DSC analysis of custom-made lipid mixtures, with chemical composition similar to that of olive oil, may be useful in elucidating the influence of minor chemical components on thermal properties of heating thermograms.

This preliminary work indicated that thermal properties during heating are largely influenced by the chemical composition of EVOO. Discrimination of oil samples from different olive varieties could be performed by DSC when major components (i.e., TAG and fatty acids) of samples exhibited different unsaturation degree. Thermal properties of EVOO can also be influenced by changes in chemical composition due to different harvesting period of olives that can affect the attribution of sensorial and oxidative quality to the final product. To validate the results reported in this work, a larger number of EVOOs should be analyzed accounting for the variability of chemical composition originated by olive cultivar, geographical origin, seasonality, and agronomical and technological oil production conditions.

ABBREVIATIONS USED

DAG, diacylglycerols; ΔH, enthalpy of transition; DSC, differential scanning calorimeter; DSTAG, disaturated triacylglycerols; EVOO, extra virgin olive oil; FA, fatty acids; FFA, free fatty acids; HPLC, high-performance liquid chromatography; MSTAG, monosaturated triacylglycerols; MUFA, monounsaturated fatty acids; OLL, dilinoleoyl-oleoyl-glycerol; OOL, dioleoyl-linoleoyl-glycerol; OOO, triolein; OOP, dioleoyl-palmitoyl-glycerol; PLL, dilinoleoyl-palmitoyl-glycerol; POL, palmitoyl-oleoyl-linoleoyl-glycerol; POLn, palmitoyl-oleoyl-linolenoyl-glycerol; PPO, dipalmitoyl-oleoyl-glycerol; PUFA, polyunsaturated fatty acids; SFA, saturated fatty acids; SOO, dioleoyl-stearoyl-glycerol; TAG, triacylglycerols; T_{on}, onset temperature; T_{off}, offset temperature; T_p, peak temperature; TUTAG, triunsaturated triacylglycerols.

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