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Thermal Decomposition Study of Monovarietal Extra Virgin Olive Oil by Simultaneous Thermogravimetry/Differential Scanning Calorimetry: Relation with Chemical Composition

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Thermal decomposition of 12 monovarietal extra virgin olive oils from different geographical origins (eight from Italy, two from Spain, and the others from Tunisia) was evaluated by simultaneous thermogravimetry (TG) and differential scanning calorimetry (DSC) analyses. All extra virgin olive oils showed a complex multistep decomposition pattern with the first step that exhibited a quite different profile among samples. Thermal properties of the two peaks obtained by the deconvolution of the first step of decomposition by DSC were related to the chemical composition of the samples (triacylglycerols, fatty acids, total phenols and antioxidant activity). Onset temperatures of the thermal decomposition transition and T_p values of both deconvoluted peaks as well as the sum of enthalpy were found to exhibit statistically significant correlations with chemical components of the samples, in particular palmitic and oleic acids and related triacylglycerols. Activation energy values of the second deconvoluted peak obtained by the application of kinetic procedure to the first step of decomposition were also found to be highly statistically correlated to the chemical composition, and a stability scale among samples was proposed on the basis of its values.

KEYWORDS: Extra virgin olive oil; monovarietal; triacylglycerols; fatty acids; phenols; thermal decomposition; kinetic analysis

INTRODUCTION

Extra virgin olive oil (EvoO) is a high-quality vegetable oil traditionally produced in the country of Mediterranean areas. This fat source is extremely appreciated not only for its organoleptic attributes but also for its health and nutritional properties (*1*, *2*).

The chemical composition of EvoO is well-known to exhibit a greater variability than other vegetable oils as it is largely influenced by different drupe cultivars, agronomical practices, geographical origins, harvesting periods, and processing technologies (*3*, *4*). In particular, the effect of the cultivar−environment interaction on the amounts of major [i.e., triacylglycerols (TAGs) and fatty acids (FAs)] and minor (e.g., antioxidant molecules as phenols) chemical components are considered of great importance to define the final quality of the product and to guarantee a high stability to auto- and thermal oxidation processes (*4*). In Italy, a new regulation was recently introduced that imposes virgin and extra virgin olive oil producers to obligatorily make geographical indications about olive picking and oil production on the label (*5*). More recently, the European Community (EC) Council of Regulation has established compulsory marketing standards on olive oil making regarding the labeling of the origin for extra virgin and virgin olive oils (*6*).

Chemical methods are most commonly applied for the evaluation of EvoO quality and thermal stability, but they are known to be expensive, to be time-consuming, and to have a high environmental impact. The availability of new/additional analytical techniques as supporting tools for currently used methods may be helpful to improve EvoO classification according to quality and to ensure correct information to the consumers.

Calorimetric techniques are currently applied in the field of oils and fats for several purposes. In particular, auto and thermal oxidative decomposition of vegetable oils were largely investigated by means of differential scanning calorimetry (DSC) and pressure differential scanning calorimetry (PDSC), also providing predictive models for oil stability with kinetic data (*7*−*9*).

Buzás and Kurucz evaluated the thermal decomposition of fresh and thermally treated sunflower and rapeseed oils by means of thermogravimetry (TG), derivative thermogravimetry (DTG), and differential thermal analysis (DTA) in the past, finding three steps of decomposition for fresh oils (*10*). Dweck and Sampaio evaluated the thermal decomposition of several vegetable oils by means of the same thermoanalytical techniques, finding good correlation between the onset temperature of decomposition and the heat of combustion of the oils (*11*). Santos et al. compared

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TG/DTG and DSC curves of vegetable oils attributing the three steps for thermal decomposition of the oils to the decomposition of FA classes at different saturation degrees (*12*). More recently, the thermal stability of three oils obtained by Brazilian Cerrado plants was also evaluated by means of TG/DTG curves by Garcia et al. (*13*). However, results of these studies were often contradictory, as chemical analyses on samples were only partially considered in these papers.

To the authors' best knowledge, only one study dealt with the evaluation of thermal decomposition of EvoO by thermal analysis. Vecchio et al. (*14*) examined the thermal decomposition of commercial extra virgin olive oil samples by means of TG/DTG and DSC profiles, also processing data with kinetic procedures. These authors compared the thermal profiles of the samples with those obtained on pure TAG standards (tristearin, triolein, trilinolein, and trilinolenin) for a better comprehension of the thermal degradation mechanism and a clear attribution of the different steps of mass loss observed. However, the chemical composition of EvoO samples was not considered in this work.

The aim of this work was to study the thermoxidation of EvoO from different geographical proveniences by simultaneous TG/DTG and DSC analysis and to relate thermal properties and kinetic data obtained by thermoanalytical techniques to chemical composition (TAGs, FAs, total phenols, and antioxidant activities of phenolic fractions) of the monovarietal oils obtained by three of the major-producing Mediterranean countries (Italy, Spain, and Tunisia) (*15*).

MATERIALS AND METHODS

Reagents and Standards. The standards used for high-performance liquid chromatography (HPLC) quantification (3,4-dihydroxyphenylacetic acid) and for evaluation of the antioxidant capacity of phenolic extracts (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid, Trolox) were obtained from Sigma-Aldrich (St. Louis, MO) as were ABTS [2,2′-azinobis(3-ethylbenzothiazoline)-6-sulfonic acid, diammonium salt] and potassium persulfate. All solvents used were analytical or HPLC grade (Merck & Co. Inc., Darmstadt, Germany).

Samples. Twelve monovarietal EvoO samples achieved from olives handpicked in 2007 were analyzed. Eight of them were obtained from drupes grown in three different regions of Southern Italy (Abruzzo, Puglia, and Basilicata), two from the Spanish regions of Andalusia and Castilla-La Mancha, and the others from Sfax (Tunisia). General information about the samples is reported in **Table 1**, where the abbreviations used to refer to the different samples in the remainder of the text are also shown. The samples were all produced using different continuous systems. Samples were stored in dark bottles without headspace at room temperature before analysis.

Chemical Analyses. HPLC analysis of TAG was performed according to Chiavaro et al. (*16*). Briefly, HPLC analysis of TAG was performed on a Luna C18 (Phenomenex, Torrance, CA) column (25 cm × 3.0 mm i.d.) of a 5 μm particle size equipped with a C18 precolumn filter (Phenomenex). The mobile phase flow rate was 0.7 mL/min. The gradient elution was performed by using 2-propanol and acetonitrile as reported in Chiavaro et al. (*16*). TAGs were tentatively identified based on their UV−vis and mass spectra obtained by high-performance liquid chromatography interfaced with atmospheric pressure chemical ionization mass spectrometer detection (HPLC-APCI-MSD) and literature data (*17*). The limit of quantitation (LOQ) was 0.01 g 100 g^{-1} of TAG. TAGs were grouped according to the type of FA bonded to the glycerol structure as disaturated triacylglycerol (DSTAG), monosaturated triacylglycerol (MSTAG), and triunsaturated triacylglycerol (TUTAG).

The FA composition was determined according to Bendini et al. (*18*) as methyl esters by capillary GC equipped with a flame ionization detector (FID), after alkaline treatment. Briefly, 1 μL of FA methyl ester was injected into a split/splitless 1:20 GC port set at 240 °C, and separation was performed on a fused silica capillary column (50 m length, 0.25 mm i.d.), coated with CPSil-88 (0.25 μm film thickness, Varian, Palo Alto, CA). A flow rate of 1.25 mL min^{-1} of helium as a carrier gas was used. The FID detector was set at 240 °C. The initial oven temperature was kept at 120 °C for 1 min, raised to 240 °C at a rate of 4.0 °C/min, and maintained for 4 min. The results were expressed as area normalization in percent (%). The LOQ was 0.01 g 100 g^{-1} of FAs. FAs were expressed according to their unsaturation degree as saturated fatty acids (SFAs), monounsaturated fatty acids (MUFAs), and polyunsaturated fatty acids (PUFAs).

Table 1. Description of the EvoO Samples

sample codes	area of production	olive cultivar
It1	Abruzzo (Italy)	Gentile
It2	Abruzzo (Italy)	Tortiglione
It3	Abruzzo (Italy)	Leccino
It4	Puglia (Italy)	Leccino
It5	Puglia (Italy)	Coratina
It6	Puglia (Italy)	Leccino
It7	Puglia (Italy)	Nociara
It8	Basilicata (Italy)	Coratina
Sp1	Castilla-La Mancha (Spain)	Cornicabra
Sp2	Andalusia (Spain)	Picual
Tu1	Sfax (Tunisia)	Chemlali
Tu2	Sfax (Tunisia)	Chétoui

Phenolic compounds were extracted from oil samples by liquid−liquid extraction (LLE), using a modified version of the method suggested by Pirisi et al. (*19*). HPLC analyses of phenolic extracts were performed with a HP 1100 series (Agilent Technologies, Palo Alto, CA), equipped with a binary pump delivery system, a degasser, an autosampler, diode array UV−vis (DAD) and MSD detectors, and a 5 μm Luna C18 (Phenomenex, Castel Maggiore-BO, Italy) column (25 cm × 3.0 mm i.d.), as previously reported (*17*). The phenolic compounds were quantified using a 3,4-dihydroxyphenylacetic acid calibration curve (r^2 = 0.999). Data were expressed as mg 3,4-dihydroxyphenylacetic acid kg^{-1} oil.

$ABTS^{\bullet+}$ was determined on phenolic extract according to Re et al. (*20*). Briefly, ABTS was dissolved in H_2O to a concentration of 7 mM. The radical cation of ABTS was obtained by reaction with 2.45 mM potassium persulfate (final concentration), allowing the stock solution to stand in the dark at room temperature for at least 12 h. Before use, the $ABTS^{\bullet+}$ solution was diluted with ethanol to an absorbance of 0.70 ± 0.02 at 734 nm at 30 °C. Next, 1 mL of this $ABTS^{\bullet+}$ solution was added to 0.01 mL of extract, and the decrease in absorbance was recorded for 10 min. The absorbance values were corrected for radical decay using a blank solution (0.01 mL of 50% aqueous MeOH). The antioxidant activity was calculated as the Trolox equivalent antioxidant capacity (TEAC) (r^2 = 0.981). Three replicates were prepared and analyzed per sample for all determinations.

TG/DSC Protocol and Kinetic Procedure. The TG/DSC measurements were carried out at different heating rates (2.5, 5, 7.5, and 10 K min^{-1}) using a simultaneous Stanton Redcroft STA 625 TG/DSC equipment in the temperature range between 293 and 873 K. The corresponding DTG curves were derived by operating a first-order derivative of the experimental TG data. All thermal analysis runs were performed on 9÷12 mg of sample under a 100 cm^3 min^{-1} stream of air. Three replicates were analyzed per sample.

Deconvolution of the DSC curves was performed using an Excel spreadsheet (Microsoft Office 2003) suitably designed to approximate as closely as possible the experimental values to the predicted ones. The goodness of fit among experimental and predicted values was determined by varying some peak shape parameters of the model selected, related mainly to peak temperature, height, and width of Gaussian peaks (considered as a model function in this study) through an iterative procedure, to minimize the sum of squared residuals between experimental and predicted values using a nonlinear regression method. The sum of the enthalpies associated to the first two-step decomposition process, calculated by numerical integration of the area corresponding to the first nondeconvoluted DSC peak (which can be resolved into two deconvoluted Gaussian peaks) is denoted as $\Delta h_{(p1+p2)}$ (J g^{-1}).

The proposed kinetic analysis, which is based on dynamic model-free methods that use data performed at different heating rates β, seems to be the most reliable approach. Because of the complexity of the decomposi-

Table 2. Chemical Composition of the EvoO Samples[a]

	It1	It2	It3	It4	It5	It6	It7	It8	Sp1	Sp2	Tu1	Tu2
						TAG (% of total TAG)						
LLL + LLPo	1.5 d	1.4 d	1.3 d	1.4 b	1.3 d	1.2 d	2.4 b	2.5 ab	1.1 e	1.7 cd	2.1 bc	4.7 a
OLLn	0.5 ef	0.6 de	0.9 b	0.7 bcd	0.5 ef	0.8 bc	0.5 ef	0.5 ef	0.3 f	0.4 f	1.9 a	0.6 de
OLL + OLPo	11.3 de	11.2 de	10.8 de	10.6 de	11.8 bcd	9.6 de	12.1 bc	13.9 b	9.5 e	6.7 f	11.0 de	19.9 a
LLP + OLnO	7.5 b	6.4 b	5.0 c	4.3 c	4.3 c	4.8 c	4.7 c	2.6 d	2.6 d	1.7 d	12.6 a	7.6 b
OLO	20.6 bc	18.3 cde	15.8 fg	15.8 fg	21.9 ab	14.8 g	17.1 def	24.6 a	20.5 bc	19.2 bcd	16.5 fg	17.0 def
OLP + OOPo	15.7 ab	14.2 bcd	13.8 bcd	13.7 bcd	12.9 de	12.8 de	13.2 cde	11.6 ef	10.6 f	13.8 bcd	17.6 a	15.1 bc
POPo	3.1 bc	2.7 bc	3.0 bc	3.5 bc	1.6 c	2.3 bc	2.4 bc	0.8 d	1.3 c	2.5 bc	7.7 a	3.1 bc
OOO	22.0 e	22.9 de	22.3 e	22.7 de	24.7 cd	25.6 bc	21.3 e	27.1 b	32.9 a	27.0 b	11.2 g	17.7 f
SLO + POO	12.3 cd	15.7 b	19.0 a	18.5 a	15.2 b	19.3 a	17.5 ab	10.6 de	15.0 bc	19.0 a	12.3 cd	8.3 e
POP	1.8 ghi	2.7 cde	3.8 ab	3.8 ab	2.1 efg	3.3 bc	2.8 bcd	0.8 i	1.6 hi	2.3 cdef	4.7 a	3.0 bcd
SOP	0.3 c	0.8 ab	0.9 ab	0.8 ab	1.0 ab	0.9 ab	0.8 ab	0.9 ab	0.7 ab	0.9 ab	0.6 bc	1.1 a
SOO	3.4 bc	3.2 c	3.3 bc	4.2 b	3.0 c	4.7 ab	5.1 a	4.2 b	4.0 bc	5.0 a	5.0 a	2.0 d
DSTAG	2.1 c	3.5 b	4.7 a	4.6 a	3.1 bc	4.1 ab	3.6 b	1.7 c	2.3 c	3.2 b	4.3 ab	4.1 ab
MSTAG	42.0 bc	42.1 bc	44.3 bc	44.2 bc	36.8 d	43.8 bc	43.0 bc	29.8 e	33.5 d	41.9 bc	54.0 a	36.0 d
TUTAG	55.9 c	54.4 cd	51.1 e	51.2 e	60.8 b	52.1 de	53.4 de	68.6 a	64.2 ab	54.9 cd	41.0 f	59.9 b
						FA (%)						
palmitic acid	15.1 c	15.2 c	15.6 bc	14.8 d	12.6 e	14.0 d	13.9 d	10.2 f	10.9 f	12.4 e	19.1 a	11.7 ef
stearic acid	3.0 b	2.1 cd	2.0 cd	1.7 d	2.2 c	1.8 d	1.7 d	3.9 a	2.5 bc	2.5 bc	2.9 b	2.6 bc
oleic acid	66.1 e	70.1 d	71.9 cd	72.9 bc	75.2 ab	75.3 ab	69.9 e	73.2 b	79.0 a	74.9 ab	58.1 f	67.0 e
linoleic acid	12.8 c	9.7 d	7.4 e	7.2 e	7.4 e	5.7 f	10.0 d	9.6 b	5.2 f	7.3 e	18.6 a	16.6 b
linolenic acid	0.7 a	0.8 a	0.8 a	0.7 a	0.8 a	0.7 a	0.8 a	0.9 a	0.6 a	0.6 a	0.7 a	0.6 a
SFA	19.0 b	16.8 c	18.2 b	17.1 bc	15.4 d	16.3 c	17.5 bc	15.1 d	13.9 e	15.6 d	21.9 a	14.9 de
MUFA	67.8 d	73.6 c	73.8 c	75.0 bc	76.5 b	77.3 b	71.2 cd	74.5 bc	80.4 a	76.4 b	58.9 e	67.9 d
PUFA	13.3 b	9.8 c	8.0 cd	7.9 cd	8.0 cd	6.4 d	11.3 ab	10.5 b	5.7 d	7.9 cd	19.2 a	17.2 ab
total phenols (mg kg^{-1})	181.4 d	273.0 ab	129.8 e	98.1 g	319.0 a	260.1 b	282.6 ab	60.8 h	107.8 f	141.8 de	91.6 g	220.0 c
total *o*-diphenols (mg 3,4-DHPAA kg^{-1})	24.5 ef	99.0 a	29.9 e	33.1 de	97.2 a	55.3 b	48.0 c	3.4 g	15.7 f	27.1 e	13.9 f	38.6 d
$ABTS^{\bullet+}$(mmol Trolox kg^{-1})	0.9 c	1.6 a	0.9 c	0.8 c	1.4 a	0.8 c	1.1 b	0.4 d	0.6 d	0.6 d	0.5 d	1.5 a

[a] Data are expressed as means of three determinations. The RSDs of TAG, FA, total phenols, *o*-diphenols, and $ABTS^{\bullet+}$ are ≤8.0, ≤2.5, ≤6.2, ≤9.9, and ≤5.5%, respectively. For letters a−g, the same letters in the same row do not significantly differ ($p < 0.05$).

tion patterns of the materials examined, the kinetic study was carried out using the Kissinger equation (*21*):

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{AR}{E}\right) - \left(\frac{E}{R}\right) \times \left(\frac{10^3}{T_p}\right) \quad (1)$$

where T_p is the peak temperature of each deconvoluted DSC peak, A is the pre-exponential factor, E is the activation energy, and R is the gas constant. This equation gives a single value of the kinetic parameters (A and E) for each thermal event recorded by the DSC curve as a single well-separated or deconvoluted peak.

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 (ANOVA) and Tukey's honest significant difference test at a 95% confidence level ($p < 0.05$) to identify the significance of mean differences among different samples for chemical and thermal parameters. Pearson correlation coefficients were calculated among chemical and thermal variables at a 95% confidence level ($p < 0.05$).

RESULTS AND DISCUSSION

Chemical Analysis Results. EvoO samples evaluated in this study were collected from different productions areas; in particular, eight of them came from three regions of Southern Italy, two samples from the most productive Spanish regions, and the last two from Tunisia, as summarized in **Table 1**. Among Italian VOO samples, It3, It4, and It6 were produced from the same olive cultivar (Leccino), while It5 and It8 were produced from olives of cultivar Coratina; for both cultivars, olives were grown in different areas. Coratina and Leccino are typical Italian cultivars; the first is widespread in the South of Italy, and the second is in all Italian regions. Sp1 and Sp2 were obtained from Cornicabra and Picual Spanish cvs., which can be considered the most quantitatively important olive variety in the world (*22*). Chemlali cv. (Tu1) is the most representative variety both in the Centre and in the South of Tunisia, while Chétoui, used for Tu2 production, is principally diffused in the North region (*23*).

This set of monovarietal EvoO samples was representative of a wide interval of chemical composition in both major and minor components, as shown in **Table 2**. TAG profiles changed in the set of monovarietal oils: Among the main TAGs [dioleoyl-linoleoyl-glycerol (OLO), palmitoyl-oleoyl-linoleoyl-glycerol (OLP) + dioleoyl-palmitoleoyl-glycerol (OOPo), triolein (OOO), and stearoyl-oleoyl-linoleoyl-glycerol (SLO) + dioleoyl-palmitoyl-glycerol (POO)], the level of OOO was remarkably high, ranging from 11.2 to 32.9%. In particular, both of the Tunisian samples were characterized by a significantly lower OOO percentage, while Spanish oils exhibited the highest triolein content, in accordance with the oleic acid amount. The second TAG in order of quantitative importance corresponded to OLO, which ranged from 14.8 to 24.6%, but in this case, the lowest percentages were shown by three Italian samples (It3, It4, and It6). Among the TAG group, TUTAG was the most representative class of triglycerides for all oils except for Chemlali monovarietal olive oil, where MSTAG exhibited the highest percentage. The two Italian samples from Leccino also showed the highest DSTAG amount. In any case, the TAG composition of samples was in

agreement with literature data for Italian, Spanish, and Tunisian virgin olive oils (*4*, *24*, *25*).

FAs also showed significant compositional differences among samples, in accordance with those evidenced for TAGs. In all samples, the oleic acid was always the most abundant FA, never accounting for less than 58% of the total profile. Eight samples (It2−It6, It8, Sp1, and Sp2) were characterized by a high oleic acid content that ranged from 70.1 to 79%; two Italian samples and the Tunisian sample from Chétoui cv. exhibited an oleic acid percentage between 66.1 and 69.9%, whereas the Tu1 sample showed the lowest amount (only 58.1%), according to the typical composition of Chemlali virgin olive oil (*24*). The Spanish sample from Cornicabra showed a significantly higher oleic acid percentage, in accordance with literature data (*25*). Margaric, margaroleic, behenic, gadoleic, and lignoceric were present at a percentage lower than 0.2% in all monovarietal olive oils and were not reported in **Table 2**. The content of linolenic acid was always lower than 1%, as generally shown for oils obtained by olives (*26*). Tunisian virgin olive oils were characterized by a significantly higher value of linoleic acid (18.6 and 16.6% for Tu1 and Tu2), while Chemlali monovarietal virgin olive oil exhibited the highest percentage of palmitic acid that reached 19.1%, as already observed (*24*). Palmitoleic acid ranged from 0.5 to 2.5% with the lower values obtained for It5 and Tu2 and the highest values obtained for Tu1. Thus, the three classes of FAs, SFAs, MUFAs, and PUFAs, presented wide differences among samples of Spanish and Tunisian oils, showing the highest MUFA and PUFA contents, respectively.

The phenolic composition (total phenols and *o*-diphenol) as well as ABTS test were carried out on all oils to characterize the different samples, and all of the data are summarized in **Table 2**. It2 (Tortiglione, Abruzzo), It5 (Coratina, Puglia), It6 (Leccino, Puglia), It7 (Nociara, Puglia), and Tu2 (Chétoui, Sfax) exhibited a phenol content higher than 200 mg 3,4-dihydroxyphenylacetic acid (3,4-DHPAA) kg^{-1} oil, also showing high values of *o*-diphenols and antioxidant activity (ABTS). In particular, *o*-diphenols, which were found to show a greater ability to enhance the oxidative stability of virgin olive oil (*27*), ranged from 3.4 to 99.0 mg 3,4-DHPAA for kg of oil. The Coratina sample from Basilicata (It8) was characterized by particularly low amounts of total phenols, *o*-diphenols, and antioxidant activities. This is not commonly found for this cultivar that generally exhibited both high phenolic contents and antioxidant activities (*28*). Total phenols as well as total *o*-diphenols of Sp1 samples from Cornicabra were in the range already observed for this cultivar (*29*). Picual oil exhibited a higher content of total phenols and *o*-diphenols than Cornicabra, although data were lower than those reported in literature (*30*). Data relative to phenolic compounds and antioxidant power for the two Tunisian monovarietal oils confirmed previous observations already reported in literature (*23*) that highlighted a major phenolic content for oils produced from Chétoui (Tu2) than from Chemlali (Tu1).

Thermoanalysis and Kinetic Results. The TG and DTG curves of samples It1, Sp1, and Tu1 at 10 K min^{-1} were reported in **Figure 1**, as representative of the thermal profiles shown by all of the other extra virgin olive oil samples considered in this study. TG profiles did not vary at the other three lower heating rates (2.5, 5, and 7.5 K min^{-1}) adopted for all samples except for peak temperatures that had lowered decreasing heating rates.

The absence of any step of mass loss recorded up to 473 K revealed the limited content of water in these samples, detectable only by higher sensitivity thermal analysis equipments, as expected in vegetable oil (*31*). The thermal oxidative decomposition processes occurred in all samples as several consecutive and simultaneous steps of mass loss (mainly three or four) in the temperature range between 473 and 873 K. The first decomposition step occurred in the temperature range 473−640 K for all of the tested samples (with the DTG peak temperature increasing in the following order: Sp1, It1, and Tu1) and can be considered as the sum of two overlapping processes, the former of which is characterized by a broad DTG peak between 473 and 623 K, while the latter is sharp and intense. The mass loss corresponding to this step was found to be comparable for all of the samples within percentages of mass ranging between 35 and 40%. In the previous study (*14*), where commercial EvoO samples were analyzed, the first step of the decomposition process developed over a larger temperature range from 430 to 640 K. The presence of lipid oxidation products and molecules from TAG lysis (e.g., mono- and diacylglycerols, free FAs) that were generally contained in commercial EvoO samples in higher amounts than those monovarietal may have probably shifted the onset temperature of the first step toward the lower temperature, as these molecules should probably be more easily destroyed by heat (*32*).

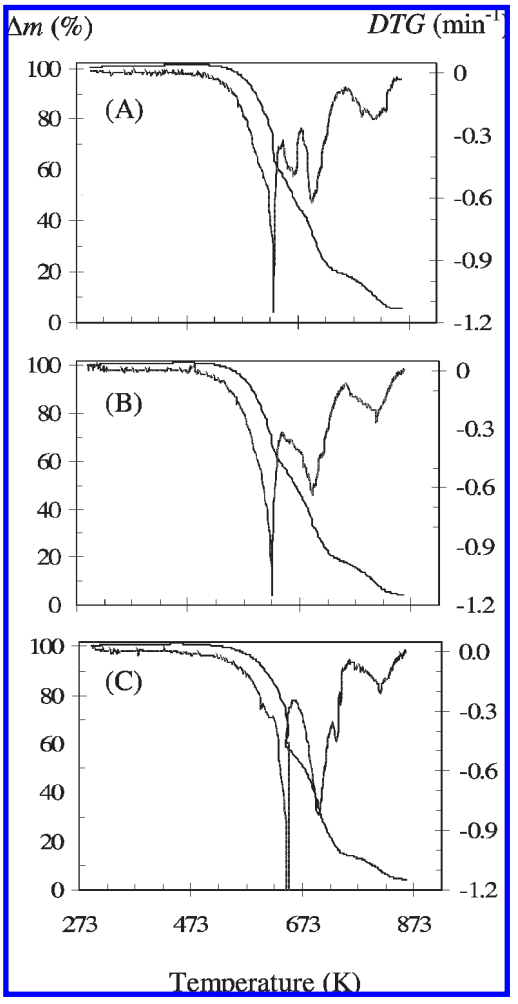

Figure 1. TG and DTG curves (solid and thin lines, respectively) at 10 K min^{-1}: (**A**) sample It1, (**B**) sample Sp1, and (**C**) sample Tu1.

The first thermal decomposition step was followed by a second event (one or two overlapping oxidation processes) in the range of 650−770 K (within percentages of mass loss ranging between 35 and 40%) in which the thermal decomposition of lipid molecules previously started was completed. The third step occurred in the range of 770−870 K (within percentages of mass loss ranging between 15 and 20%), and it is probably attributable to the oxidation of the carbonaceous residue, as previously reported (*14*).

Several contradictory hypotheses were reported in the literature about the attribution of the peaks by TG/DTG to the

thermal decomposition of vegetable oils in relation with chemical composition. Santos et al. (*12*) observed a relation between mass loss of FAs and TG/DTG data of commercial vegetable oils (olive oil among them), attributing the first step to the thermal decomposition of the most unsaturated FA moieties, whereas the second and the third were related to the monosaturated and saturated fatty acid decomposition, respectively. On the contrary, the last decomposition step was attributed by other authors (*10*, *11*) to the oxidation of the carbonaceous residue. Garcia et al. related the first and the second mass loss steps of TG/DTG curves to the oxidation of unsaturated and saturated fatty acids, respectively, whereas the third was attributed by the same authors to the decomposition of polymers formed during the oxidation process (*13*).

Vecchio et al. observed a single decomposition step between 443 and 643 K in TG/DTG profiles of pure standard of trisaturated TAG (tristearin), whereas two superimposed steps occurred for triolein in the same temperature range as well as for EvoO commercial samples (*14*).

EvoO exhibited a very complex chemical composition as several macro- (i.e., TAG and FA) and minor components (e.g., lipid oxidation products, diacylglycerols, free FAs, and phenols) are present in different percentages. A clear attribution of each decomposition event to a single chemical species appeared to be hardly achieved analyzing only DTG profiles as mass losses of several chemical components, due to decomposition of lipids, which probably occurred during each step at the same time.

DSC thermograms of all samples were also obtained and deconvoluted into constituent peaks to obtain more information about the thermal decomposition of EvoO relating thermal properties to chemical composition. All EvoO samples showed a quite complex profile with multistep overlapping exothermic transitions where the first decomposition step appeared to exhibit some differences among samples. This first thermal event, at lower temperature, may be considered as the most significant as it influenced the following exothermic processes (the second and third events at higher temperatures) that could not be clearly distinguished by it and took place consecutively. Therefore, when a stability parameter must be selected on the basis of the thermal activated reactions occurring in all EvoO samples, it seems reasonable to focus the attention on the first one. In addition, it may be hypothesized that the first step of decomposition was mainly related to the thermal oxidation process of lipids as a total decomposition of TAGs molecules and that combustion events did not occur in the range of temperature of this event (*10*).

Representative experimental DSC curves recorded at 10 K min^{-1} were reported in **Figure 2** for samples It1 (plot **A**), Sp1 (plot **B**), and Tu1 (plot **C**), which presented quite different chemical compositions (**Table 2**). DSC profiles did not vary at the other heating rates (2.5, 5, and 7.5 K min^{-1}) except for peak temperatures as reported above for TG curves.

The first DSC peak of the Tu1 sample was sharper, higher, and occurred at a higher temperature than the other two oils. On the contrary, the other DSC peaks exhibited lower heights, although temperatures were practically the same as observed in the other two samples. Comparable DSC profiles were recorded for all of the other EvoO samples (not shown) with three characteristic overlapping peaks occurring, with negligible differences, in the same temperature range observed for samples It1, Sp1, and Tu1.

All thermograms were best deconvoluted into six Gaussian peaks, as reported in **Figure 2**. Two of them were obtained by the first decomposition step and were reported as a gray area in each plot of **Figure 2**. The first exothermic step of thermal decomposition of vegetable oils by DSC was previously found to exhibit two

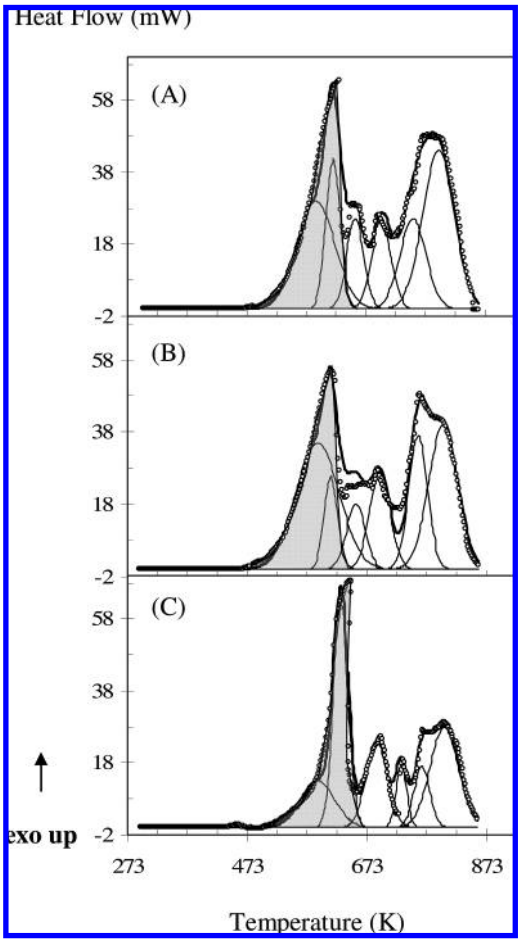

Figure 2. Experimental DSC curves (white circles) at 10 K min^{-1}: (**A**) sample It1, (**B**) sample Sp1, and (**C**) sample Tu1. Deconvoluted (solid lines) DSC peaks along with their sums (bold line) are also given for each sample considered.

not well distinct peaks (*7*, *9*). These two peaks were attributed to the oxidation of lipid molecules forming peroxides (first peak) that quickly decomposed into further products (second peak) (*8*, *9*).

Thermal properties (onset temperature of transition, peak temperature, and sum of the enthalpies) of the two deconvoluted peaks obtained by the first step of the thermal degradation of EvoO samples are summarized in **Table 3**. T_{on} and T_p of both deconvoluted peaks obtained by the first step of thermal degradation of EvoO appeared to be significantly different among Italian samples. Comparable onset temperatures of thermooxidation were exhibited by Spanish samples (T_{on} of the first peak, **Table 3**) for the first deconvoluted peak as well as T_p of the second peak. T_{on} and T_p for both peaks were markedly different for Tu1 and Tu2 samples.

Thermal properties for both deconvoluted peaks were statistically correlated with the chemical composition and the content of antioxidant molecules. Significant correlations were found for thermal properties of both deconvoluted peaks and chemical components (saturated and unsaturated lipid molecules), although correlation coefficient values ≤ 0.60 were obtained. Thus, both deconvoluted peaks appeared to be probably involved in the formation of primary and secondary lipid oxidation products from EvoO chemical components without a clear distinction of these chemical reactions on the basis of the two deconvoluted events. Correlation coefficients among TAG and FA composition and thermal parameters for both deconvoluted peaks, including activation energy values (E) discussed above, are reported in **Table 4**.

Table 3. Thermal Properties (Onset and Peak Temperatures and Sum of the Enthalpies) of the Deconvoluted Peaks Obtained by the First Step of the Thermal Degradation of EvoO Samples[a]

	I deconvoluted peak		II deconvoluted peak		
samples	T_{on} (K)	T_p (K)	T_{on} (K)	T_p (K)	$-\Delta h_{(p1+p2)}$ (J g^{-1})
It1	530.2 ± 0.7 b	594.2 ± 0.3 e	592.1 ± 0.4 c	620.5 ± 0.4 c	2006 ± 351
It2	507.2 ± 0.2 i	561.6 ± 0.2 l	557.9 ± 0.2 l	608.9 ± 0.2 h	1850 ± 372
It3	526.2 ± 0.2 c	580.8 ± 0.1 f	578.7 ± 0.2 e	617.6 ± 0.2 e	1709 ± 368
It4	516.5 ± 0.2 g	581.1 ± 0.2 f	575.6 ± 0.2 f	606.5 ± 0.2 i	1710 ± 368
It5	536.1 ± 0.2 a	609.4 ± 0.1 a	598.6 ± 0.3 b	617.5 ± 0.2 e	1839 ± 366
It6	512.2 ± 0.3 h	601.2 ± 0.2 b	603.1 ± 0.2 a	623.2 ± 0.1 b	1757 ± 366
It7	524.7 ± 0.2 d	577.1 ± 0.2 g	566.1 ± 0.2 h	617.8 ± 0.2 de	1803 ± 365
It8	520.7 ± 0.2 e	574.1 ± 0.2 h	572.6 ± 0.2 g	613.6 ± 0.2 g	1736 ± 365
Sp1	519.5 ± 0.2 f	595.6 ± 0.2 d	589.6 ± 0.2 d	615.7 ± 0.2 f	1961 ± 365
Sp2	521.3 ± 0.3 e	578.2 ± 0.2 g	565.2 ± 0.3 i	618.3 ± 0.3 d	1816 ± 365
Tu1	536.5 ± 0.2 a	597.7 ± 0.2 c	603.3 ± 0.2 a	632.8 ± 0.2 a	1288 ± 365
Tu2	508.0 ± 0.3 i	566.1 ± 0.3 i	558.5 ± 0.4 l	606.5 ± 0.3 i	1808 ± 474

[a] The associated uncertainties are standard deviations. For letters a−l, the same letters in the same column do not significantly differ ($p < 0.05$ and $n = 3$ for each heating rate).

Table 4. Pearson Correlation Coefficients (R) between Chemical Indices and Thermal Properties of the Deconvoluted Peaks

	I deconvoluted peak			II deconvoluted peak		
	T_{on} (K)	T_p (K)	E (kJ mol^{-1})	T_{on} (K)	T_p (K)	E (kJ mol^{-1})
			TAG			
LLL + LLPo	−0.31	−0.53[a]	−0.30	−0.60[b]	−0.32	−0.10
OLLn	0.40	0.24	0.26	0.44	0.30	0.39
OLL + OLPo	−0.27	−0.43[a]	−0.24	−0.50[a]	−0.40	−0.16
LLP + OLnO	0.18	0.02	0.13	0.21	0.38	0.71[b]
OLO	0.09	−0.09	0.39	−0.16	−0.21	−0.26
OLP + OOPo	0.09	−0.19	−0.06	−0.06	0.22	0.60[b]
POPo	0.26	0.05	0.11	0.21	0.60[b]	0.81[b]
OOO	−0.20	0.13	0.02	−0.01	−0.28	−0.65[b]
SLO + POO	0.50[a]	0.33	−0.16	0.24	0.22	0.10
POP	0.24	0.20	−0.18	0.29	0.50[a]	0.65[b]
SOP	0.10	0.24	−0.15	0.13	−0.04	−0.27
SOO	−0.24	−0.09	−0.21	−0.21	0.16	−0.32
DSTAG	−0.31	−0.28	−0.39	−0.28	−0.29	−0.16
MSTAG	0.20	0.13	0.02	0.20	0.56[a]	0.65[b]
TUTAG	0.13	0.16	0.37	0.10	−0.03	−0.20
			FA			
palmitic acid	0.50[a]	0.17	0.11	0.40[a]	0.58[b]	0.74[b]
stearic acid	−0.18	−0.34	0.20	−0.43	−0.22	−0.17
oleic acid	−0.18	0.21	−0.14	0.02	−0.33	−0.70[b]
linoleic acid	0.02	−0.53[a]	0.08	−0.19	0.13	0.43
linolenic acid	0.35	0.05	0.28	0.08	0.08	−0.05
SFA	0.30	−0.03	0.13	0.16	0.48[a]	0.78[b]
MUFA	−0.14	0.25	−0.11	0.08	−0.28	−0.73[b]
PUFA	0.03	−0.53[a]	0.08	−0.19	0.14	0.39

[a] Significance at the 0.05 level ($p < 0.05$). [b] Significance at the 0.01 level ($p < 0.01$).

Oil samples that exhibited the highest content of linoleic acid and PUFA as well as such TAG such as trilinolein (LLL) + dilinoleoyl-palmitoleoyl-glycerol (LLPo) and dilinoleoyl-oleoyl-glycerol (OLL) + palmitoleoyl-oleoyl-linoleoyl-glycerol (OLPo) also showed the lowest T_p values for the first deconvoluted peak. At the same time, EvoO with the highest contents of both palmitic acid and SLO + POO also exhibited the highest onset temperature of thermooxidation, as shown by the correlation coefficients reported in **Table 4**.

T_{on} and T_p values of the second deconvoluted peak were also found to be statistically correlated to the chemical composition. In particular, a positive correlation was found between the onset temperature of the second deconvoluted peak and the palmitic acid content, as well as for the first peak. In addition, oil samples with the lowest contents of LLL + LLPo and OLL + OLPo also exhibited the highest T_{on} for this peak. T_p values of this deconvoluted peak were also found to be positively correlated with MSTAG, SFA, palmitic acid, and such TAGs as dipalmitoyl-oleoyl-glycerol (POP) and palmitoyl-palmitoleoyl-oleoyl-glycerol (POPo). On the contrary, a negative correlation was found between the oleic acid content and the T_p value of the second deconvoluted peak.

No significant differences were observed for the sum of enthalpies associated with the two deconvoluted peaks of the first step of thermal degradation of EvoO samples. Anyway, among all samples, It1 showed the highest and Tu1 the lowest values. A positive correlation value was found between the enthalpy of oxidation and the thermal oxidative decomposition of EvoO and OOO and oleic acid, as a consequence ($R = 0.50$ for both chemical components; $p \leq 0.05$), whereas palmitic acid, dilinoleoyl-palmitoyl-glycerol (LLP) + dioleoyl-linolenoyl-glycerol (OLnO), OLP + OOPo, and linolenoyl-oleoyl-linoleoyl-glycerol (OLLn) were found to be negatively correlated to $\Delta h_{(p1+p2)}$ ($R = -0.45$ for all chemical components; $p \leq 0.05$). The complex chemical composition of lipids for EvoO where TAGs with FA moieties exhibiting different saturation degrees (e.g., palmitic, stearic, oleic, linoleic, and linolenic acids) were present in different percentages at the same time may explain the apparent contradiction of these results with previous findings, where the heat of combustion of vegetable oils, extrapolated by the total area of the exothermic DTA peaks, was previously reported to increase according to the degree of saturation of the FA composition (*12*). The contribution of other chemical components to enthalpy of thermoxidation cannot be excluded, as lipid oxidation products and molecules derived from TAG lysis (mono- and diacylglycerols and free FAs) are present in unheated EvoO in higher amounts than in all other vegetable oils.

Thermal properties of the two peaks obtained by deconvolution of the first thermal degradation event were not found to be statistically correlated with chemical parameters related with the antioxidant content of EvoO ($ABTS^{\bullet+}$, total phenol, and *o*-diphenol) for all samples. Thermal degradation of phenolic compounds that are partially dispersed in the water content in EvoO (*2*, *33*) probably occurred at a temperature lower than 470 K, and this could not be detected under the experimental conditions of this study (*34*).

Table 5. Kinetic Parameters of the Deconvoluted Peaks Obtained by the First Step of the Thermal Degradation of EvoO Samples[a]

	E (kJ mol^{-1})	
samples	I deconvoluted peak	II deconvoluted peak
It1	130 ± 2 c	78 ± 2 e
It2	63 ± 2 f	64 ± 2 fg
It3	56 ± 2 g	80 ± 3 de
It4	52 ± 3 g	98 ± 3 b
It5	145 ± 2 b	54 ± 2 hi
It6	52 ± 2 g	90 ± 3 c
It7	89 ± 3 e	66 ± 2 f
It8	128 ± 3 c	87 ± 3 cd
Sp1	121 ± 3 d	58 ± 2 gh
Sp2	85 ± 2 e	50 ± 2 i
Tu1	158 ± 3 a	278 ± 4 a
Tu2	27 ± 2 h	31 ± 2 l

[a] The associated uncertainties are standard deviations. For letters a−1, the same letters in the same column do not significantly differ ($p < 0.05$ and $n = 3$ for each heating rate).

In this study, kinetic procedures were applied on the first decomposition step of all samples in an attempt to establish a stability scale among samples relating parameters to the chemical composition. The activation energy (E) values were determined using eq 1 for each deconvoluted peak of the first decomposition step, and they were all summarized in **Table 5** for both deconvoluted peaks. E values significantly varied from 27 to 158 kJ mol^{-1} and from 31 to 278 kJ mol^{-1} for the first and second deconvoluted peaks, respectively. In particular, Tu1 exhibited the highest E values for both deconvoluted peaks among samples, and Tu1 showed the lowest. Higher E values for the first peak were exhibited for both Spanish oils in comparison with the second event. Among Italian samples, It1, It5, It7, and It8 showed higher E values for the first peak in comparison with the second, too. The pre-exponential factor (A) values were also calculated for each deconvoluted peak of the first thermal event of oil decomposition. Values of the ln(A/min^{-1}) varied in the range of 3−31 and 4−58 for the first and second deconvoluted peaks, respectively (data not shown).

Correlation coefficients, calculated among activation energy values and chemical compositions for all samples, were also summarized in **Table 4**. TAG and FA compositions were found to be highly statistically correlated with E values for the second deconvoluted peak, and a stability scale was proposed among samples on the basis of this kinetic parameter, considering the chemical composition of oils.

Considering the second deconvoluted peak, a high positive correlation was found between E values and MSTAG, SFA, palmitic acid contents, and such related TAGs as LLP + OLnO, OLP + OOPo, POPo, and POP. On the contrary, E values were found to be negatively correlated with OOO, MUFAs, and oleic acid contents. E values were not found to be statistically correlated with antioxidant contents as well as for DSC thermal properties. Thus, the following stability scale may be proposed, decreasing E values: Tu1 > It4 > It6 > It8 > It3 > It1 > It7 > It2 > Sp1 > It5 > Sp2 > Tu2. Italian oil samples exhibited a higher stability than both Spanish and Tunisian oils from Chetoui cultivar, with the exception of the sample from the Coratina cultivar (It5). EvoO from the Chemlali variety appeared to be the most stable oil among samples.

In conclusion, the assessment of the thermal properties obtained by the deconvolution of the first step of thermal decomposition of monovarietal EvoO seemed to be an efficient tool to evaluate differences in thermal decomposition of oils according to their composition as T_{on} and T_p of both deconvoluted peaks exhibited statistically significative correlations with chemical components (i.e., palmitic and oleic acid content and related TAGs). The enthalpy of thermal degradation also appeared to be influenced by the chemical composition of the samples, in particular by the OOO content. On the contrary, the relation between thermal degradation events and antioxidant molecules, phenols in particular, needs further investigation, applying different experimental conditions and/or other calorimetric techniques.

The application of a kinetic model using thermal analysis seemed to be an interesting approach for the construction of a stability scale of monovarietal EvoO oils on the basis of activation energy values for the most important decomposition step, taking into account differences of chemical composition due to geographical proveniences of the fruit. Anyway, these results should be confirmed by the analysis of a larger set of samples, taking into account the influence of other important factors such as agronomical practices, on−off years, and different ripening indices on the chemical composition of extra virgin olive oil.

ABBREVIATIONS USED

A, pre-exponential factor; ABTS, 2,2′-azinobis(3-ethylbenzothiazoline)-6-sulfonic acid; DAD, diode array detector; Δh, enthalpy of transition; DSC, differential scanning calorimeter; DSTAG, disaturated triacylglycerol; 3,4-DHPAA, 3,4-dihydroxyphenylacetic acid; DTG, (first-order) derivative thermogravimetry; DTA, differential thermal analysis; E, activation energy; EC, European Community; EvoO, extra virgin olive oil; FAs, fatty acids; FID, flame ionization detector; HPLC, high-performance liquid chromatography; HPLC-APCI-MSD, high-performance liquid chromatography interfaced with atmospheric pressure chemical ionization mass spectrometer detection; LLE, liquid−liquid extraction; LLL, trilinolein; LLP, dilinoleoyl-palmitoyl-glycerol; LLPo, dilinoleoyl-palmitoleoyl-glycerol; LOQ, limit of quantitation; MSTAGs, monosaturated triacylglycerols; MUFA, monounsaturated fatty acid; OLL, dilinoleoyl-oleoyl-glycerol; OLLn, linolenoyl-oleoyl-linoleoyl-glycerol; OLO, dioleoyl-linoleoyl-glycerol; OLnO, dioleoyl-linolenoyl-glycerol; OLP, palmitoyl-oleoyl-linoleoyl-glycerol; OLPo, palmitoleoyl-oleoyl-linoleoyl-glycerol; OOO, triolein; POO, dioleoyl-palmitoyl-glycerol; OOPo, dioleoyl-palmitoleoyl-glycerol; PDSC, pressure differential scanning calorimeter; POP, dipalmitoyl-oleoyl-glycerol; POPo, palmitoyl-palmitoleoyl-oleoyl-glycerol; PUFA, polyunsaturated fatty acid; SFA, saturated fatty acid; SLO, stearoyl-oleoyl-linoleoyl-glycerol; SOO, dioleoyl-stearoyl-glycerol; SOP, palmitoyl-stearoyl-oleoyl-glycerol; TAG, triacylglycerol; TG, thermogravimetry; T_{on}, onset temperature; T_p, peak temperature; TUTAG, triunsaturated triacylglycerol.

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