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Kinetic-thermodynamic study of the oxidative stability of Arbequina olive oils flavored with lemon verbena essential oil

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ABSTRACT

Arbequina extra-virgin olive oils were flavored with lemon verbena (*Aloysia citrodora*) essential oil (0.1–0.4%, w/w), being evaluated quality parameters (free acidity, peroxide value, UV-extinction coefficients), oxidative stability, antioxidant and total reducing capacity. The kinetic-thermodynamic nature of the lipid oxidation was evaluated by Rancimat (110–150 °C). The essential oil addition promoted the antioxidant and total reducing capacities but, unfortunately, increased primary and secondary related quality parameters. Moreover, flavoring decreased the oils' oxidative stability. The kinetic-thermodynamic data showed that unflavored oils had significantly lower oxidation reaction rates (0.055–0.06492 h^{-1}), more negative temperature coefficient ($-0.0268°C^{-1}$), higher temperature acceleration factor (1.852), greater activation energy (82.7 kJ mol^{-1}) and frequency factor (10.9×10^9 h^{-1}), higher positive enthalpy of activation (79.4 $kJmol^{-1}$), lower negative entropy of activation (-131.8 J $mol^{-1}K^{-1}$) and greater positive Gibbs free energy of activation (129.95–135.23 kJ mol^{-1}), showing that oils' oxidation was negatively influenced by the essential oil incorporation. Overall, oxidation had a non-spontaneous, endothermic and endergonic nature. Finally, olive oils could be satisfactorily classified (principal component and linear discriminant analysis) according to the flavoring level, using quality-antioxidant-stability or kinetic-thermodynamic datasets. The latter showed a less predictive performance, although ensuring the full discrimination of unflavored from flavored oils.

1. Introduction

Olive oil (*Olea europea* L.) is of utmost economic relevance in Mediterranean region, being widely used in the food, health and cosmetics fields (Rossi et al., 2017). Several positive nutritional and health effects related to the olive oil consumption have been reported in the literature, which are mainly linked to the richness in oleic acid and to the oil's phenolic fraction (Granados-Principal, Quiles, Ramirez-Tortosa, Sanchez-Rovira, & Ramirez-Tortosa, 2010). Olive oils' phenolic compounds are responsible for antioxidant, anti-inflammatory and antimicrobial activities as well as for the oxidative stability of the oils (Piqué, 2014). Extra-virgin olive oils (EVOO) are prone to oxidation regardless its high unsaturation level and rich content in antioxidant compounds. The level of oxidation is significantly influenced by the chemical composition, as well as on several endogenous and exogenous factors like the maturation index of the olive at harvest, cultivar, agronomic practices, climatic conditions, extraction process, storage and packaging conditions (Giuffrè, Capocasale, & Zappia, 2017; Pristouri, Badeka, & Kontominas, 2010).

Among the large variety of olive oils commercially available, Arbequina olive oils (a worldwide widespread olive cultivar) are known to possess low phenolic contents and so, a more limited shelf-life with less intense sensory attributes. A possible strategy to improve the overall quality and to ensure an optimal intake of polyphenols through the usual Mediterranean diet would be to consume Arbequina oils fortified with well-known bioactive polyphenolics. Olive oils have been fortified/flavored with their own phenolics or with phenolic compounds from other vegetable sources (Piqué, 2014). Thus, different matrices have been used, namely spices and aromatic herbs (basil, pepper, garlic, and laurel), fruits (apple, banana, lemon, and orange), mushrooms, and nuts

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(almonds, and hazelnuts), being evaluated the impact at chemical and sensory levels (Ayadi, Grati-Kamun, & Attia, 2009; Sousa et al., 2015). Essential oils (EOs; e.g., mint and thyme) and purified extracts have been also used as flavorings agents (Baiano, Terracone, Gambacorta, & La Notte, 2009; Caponio et al., 2016; Khemakhem, Yaiche, Ayadi, & Bouaziz, 2015). In fortification/flavoring process it should be kept in mind the need to set the precise amount of the flavoring agent, in order to ensure its beneficial effect (e.g., phenolics may have antioxidant or pro-oxidant activities) and to minimize the risk of over-fortification, which result into an extreme enhancement of the bitter and pungent sensations, not always appreciated by consumers, particularly those from non-Mediterranean areas (Reboredo-Rodríguez et al., 2017). Nevertheless, according to the European Union regulations, a flavored olive oil cannot be commercialized as extra virgin olive oil (EVOO) (European Union Commission, Regulation CE 1989/2003, 2003; Baiano, Gambacorta, & Notte, 2010; Issaoui et al., 2016). The flavored oil could only be commercialized as a processed olive oil with vegetables, fruits, herbs or spices, with specific nutritional-sensory properties (Issaoui et al., 2016).

In this framework, Arbequina EVOO were flavored with pre-established amounts of lemon verbena EO (*Aloysia citrodora*). This EO was selected as the flavoring agent, since the plant (from the Verbenaceae family) is one of the most valuable aromatic and medicinal plants (Combrinck et al., 2019). Several studies reported its beneficial effects, including antimicrobial, neuroprotective, cardioprotective, anticonvulsant, anti-inflammatory, and antigenotoxic (Bahramsoltani et al., 2018). The flavoring was studied taking into account the effect on the usual olive oil quality parameters, antioxidant activity, total reducing capacity (TRC) as well as the oxidative stability (OS). The lipid oxidation was further evaluated based on the activated complex theory, aiming to establish, for the first time, a kinetic-thermodynamic insight regarding the impact of the flavoring on the oils' oxidation process. This kinetic-thermodynamic approach has been previously used, for example, to assess different olive oils' stabilities and to compare them with those of other vegetable oils evaluating, in some cases, the effect of indigenous antioxidant compounds or fatty acid composition, to evaluate the oxidation kinetics of purified compounds, to establish an olive oil adulteration index for recognizing adulterations with palm olein and sunflower oil or to develop unsupervised/supervised classification models for monovarietal and blend olive oils discrimination according to the cultivar/total phenols content (Ciemniewska-Żytkiewicz, Ratusz, Bryś, Reder, & Koczoń, 2014; Farhoosh & Hoseini-Yazdi, 2014; Farhoosh, Niazmand, Rezaei, & Sarabi, 2008; Gharby et al., 2016; Heidarpour & Farhoosh, 2018; Mahdavianmehr, Farhoosh, & Sharif, 2016; Ostrowska-Ligeza et al., 2010; Veloso et al., 2020). In this context, the main aim of this study was the kinetic-thermodynamic evaluation of the lipid oxidation of *cv.* Arbequina olive oils flavored with lemon verbena essential oil.

2. Materials and methods

2.1. Olive oil samples and essential oil

The *cv.* Arbequina EVOOs were produced from olives grown in an olive grove with high density production mode located in Trás-os-Montes region. The olives were collected in 2019, and the oil extracted in an olive mill (Olimontes) located in Macedo de Cavaleiros (Portugal), using a two-phase centrifugation system. The olive oils were kept in their original amber glass bottles (approximately 500 mL), during 4 months, in a dark environment, at room temperature (18–25 °C), being filtrated before analysis. Then lemon verbena EO was added in different amounts allowing to obtain flavored oils with 0.1, 0.2, 0.3 and 0.4% (w/w) of essential oil). In total, 5 independent closed amber glass bottles (with approximately 100 mL of oil) were also stored in dark at 18-25 °C during two weeks before being analyzed, for each flavoring concentration, plus other 5 bottles without no essential oil addition (0.0%, w/w), used as the control samples. The oil from each independent bottle was analyzed in duplicate (5 concentrations × 5 independent bottles × 2 replicates = 50 assays), two weeks after being flavored, regarding the quality parameters, the antioxidant activity and the oxidative stability at different temperatures. The essential oil was purchased in a local specialty store devoted to the commercialization of essential oils for the food industry. According to the label information, the essential oil had a lemony profile and sweet fresh aroma. Although no sensory analysis was performed, all flavored oils could be easily recognized by non-trained consumers due to the perception of a lemony profile and sweet fresh taste/aroma, which sensory attributes are in accordance with the labelled information. Lemon verbena EO was chosen due to its well-documented richness in polyphenols (Ishkeh, Asghari, Shirzad, Alirezalu, & Ghasemi et al., 2019; Rocha et al., 2019).

2.2. Chemical composition of lemon verbena essential oil

The composition of the lemon verbena EO was determined by gas chromatography with mass spectrometry detection (GC/MS) according to the method previously described by Teles et al. (2014), with some modifications. Before injection, 15 μL of essential oil were diluted in 2 mL of methanol, and then 1.5 μL was injected. The gas chromatograph (Shimadzu GC-2010 model) was coupled to a GC/MS-QP 2010 Shimadzu mass detector. For the separation, a nonpolar low bleed column was used (Agilent J&W DB-5: 30 m × 0.25 mm i.d., with a film thickness of 0.25 μm). The injector port temperature was set equal to 220 °C and injections were carried out in split mode (ratio of 1:20). The temperature of the oven was programmed at 60 °C and then increased to 240 °C at a temperature rate of 3 °C/min, and kept at that temperature for 20 min. The carrier gas was helium, at a constant flow of 1 mL/min. The ion source was maintained at 240 °C, the ionization energy at 70 eV, and the ionization current at 0.7 kV. Retention indices (RI) were calculated based on the chromatographic profiles of n-alkenes (C_6–C_{20}), injected at the same experimental conditions. The components were identified by comparison of their mass spectra with the spectrometer database of the NIST 11 Library (National Institute of Standards and Technology, Gaithersburg, MD, USA). For each identified compound, the relative abundance was calculated by the area normalization method, without considering the response factors (percentage of the compound peak area relative to the total peak areas from all compounds).

2.3. Physicochemical analysis of unflavored and flavored olive oils

The physicochemical quality parameters, namely, free acidity (FA), peroxide value (PV) and specific coefficients of extinction at 232 nm and 268 nm (K_{232} and K_{268}) were determined according to the standard methodologies described in the EC regulation (Commission Delegated Regulation [EU] 2015/1830, 2015). These parameters allow assessing the oil's acidity (% of oleic acid) as well as the primary and the secondary oxidation products.

2.4. Antioxidant stability of unflavored and flavored olive oils

The antioxidant capacity of olive oil samples was investigated using two tests, namely the total reducing capacity (TRC) and the radical scavenging activity (2,2- diphenyl-1-picrylhydrazyl) (DPPH). The TRC was expressed as mg of caffeic acid equivalents per kg of olive oil (mg CAE/kg) and it was assessed following the methodology described by Capannesi, Palchetti, Mascini, and Parenti (2000) with some modifications. For quantification purposes a calibration curve of caffeic acid in methanol was used. In which concern the DPPH, 1 g of olive oil was dissolved in 10 mL of ethyl acetate and shacked. Then, 1 mL was taken from the mother solution and 4 mL of the DPPH solution (0.039 g of DPPH/100 mL of ethyl acetate) was added. The mixture was then shacked and let it stand for 30 min in the dark. Afterwards, the samples were spectrophotometrically analyzed at 515 nm, using 10 mL of ethyl

acetate plus 4 mL of the DPPH solution as the blank solution. For auto-zero purposes the ethyl acetate solution was used.

2.5. Oxidative stability of unflavored and flavored olive oils

The oxidative stability (OS) of the oils at different temperatures (110, 120, 130, 140 and 150 °C) were assessed using the Rancimat method (Rancimat 743 apparatus from Metrohm CH, Switzerland) following the methodology previous described by Veloso et al. (2020). This experimental data allows to calculate the kinetic-thermodynamic parameters.

2.6. Kinetic-thermodynamic parameters of unflavored and flavored olive oils

A kinetic-thermodynamic approach was applied, based on the OS experimental data recorded at different temperatures (110, 120, 130, 140, 150 °C), under Rancimat test conditions (Ciemniewska-Żytkiewicz et al., 2014; Farhoosh et al., 2008; Farhoosh & Hoseini-Yazdi, 2014; Heidarpour & Farhoosh, 2018; Mahdavianmehr et al., 2016; Trapani et al., 2017; Malvis et al., 2019; Veloso et al., 2020). This methodology allowed to calculate (Veloso et al., 2020):

i. The temperature coefficient T_C ($°C^{-1}$), equal to the slope of the linear regression line established between the decimal logarithmic of the OS (in h) and the temperature T (in °C);
ii. The temperature acceleration factor, the Q_{10} number, calculated as $10^{-10\times T_C}$;
iii. The activation energy E_a (J/mol) and the frequency factor A (h^{-1}) calculated from the Arrhenius equation after linearization (i.e., natural logarithm of the reaction rate constant k, in h^{-1}, versus the inverse of the absolute temperature, in K^{-1}), being equal to the product of the slope value by the universal gas constant ($R = 8.314$ J mol^{-1} K^{-1}) and the natural exponential (Euler number basis) of the intercept value, respectively;
iv. The enthalpies (ΔH^{++}) and entropies (ΔS^{++}) of activation, calculated from the slope and intercept values of the linear regression line established between $log_{10}\left(\frac{k}{T}\right)$ versus the inverse of the absolute temperature ($1/T$, in K^{-1}), respectively as '$\Delta H^{++} = -slope \times ln(10) \times R$' and '$\Delta S^{++} = ln(10) \times R \times \left[intercept - log_{10}\left(\frac{k_B}{h}\right)\right]$', were k_B and h are the Boltzman and the Planck's constants, respectively;
v. The Gibbs free energy (ΔG^{++}, in J mol^{-1}) of activation at a given temperature T (in K) as '$\Delta G^{++} = \Delta H^{++} - T \times \Delta S^{++}$'.

2.7. Statistical analysis

The parameters experimentally assessed (FA, PV, K_{232}, K_{268}, DPPH, TRC and OS) as well as the kinetic-thermodynamic data calculated from the OS, were expressed as the mean value ± standard deviation (SD). The significance level was set equal to 5%. One-way ANOVA was applied to determine the statistical significant effect of the olive oils' flavoring, with known amounts of essential oil. When a significant effect was found (P-value < 0.05), the post-hoc multiple comparison Tukey's test was used to establish which flavoring levels were significantly different from each other. The possibility of using the physicochemical quality parameters or the kinetic-thermodynamic data as olive oil classifiers was evaluated using the principal component analysis (PCA, an unsupervised pattern recognition multivariate technique). The physicochemical or kinetic-thermodynamic parameters that possessed the most discriminant potential were identified using a linear discriminant analysis (LDA) coupled with the simulated annealing (SA) meta-heuristic variable selection algorithm, which was applied as a supervised pattern recognition multivariate technique. The quality performance of the LDA-SA models established based on the best sub-sets of independent parameters (selected by the SA algorithm) was checked using the leave-one-out cross-validation (LOO-CV) procedure, by calculating the correct classification rate (i.e., the model's sensitivity) and by visual inspection of the 2D plots of the main discriminant functions and of the class membership ellipses established using the posterior probabilities, computed using the Bayes' theorem (Bishop, 2006). The statistical analysis was performed using the Subselect and MASS packages of the open source statistical program R (version 3.6.2) (Cadima, Cerdeira, & Minhoto, 2004; Venables & Ripley, 2002).

3. Results and discussion

3.1. Chemical analysis of lemon verbena essential oil

Gas chromatography revealed that it was possible to detect more than 50 peaks on the analysis of the commercial lemon verbena EO used. Among the detected peaks, only those that returned a similarity equal or greater than 95% and had a relative abundance greater than 0.4% were considered. Thus, 14 compounds were identified (Table 1), which areas corresponded to 96% of the total area of the detected chromatographic peaks. Table 1 shows that the most abundant chemotypes are α- and β-citral (51.35 ± 0.08% and 23.86 ± 0.04%, respectively), followed by geraniol (6.16 ± 0.01%) and geranyl acetate (5.95 ± 0.02%). It should be remarked that the number of identified compounds and their relative abundance greatly depend on the EO extraction conditions, storage conditions, harvest periods and geographical origin, being limonene, citral, caryophyllene, neral and/or geranial the most commonly found (Elechosa et al., 2017; Farahmandfar, Asnaashari, Pourshayegan, Maghsoudi, & Moniri, 2018; Ishkeh, Asghari, Shirzad, Alirezalu, & Ghasemi, 2019; Kizil et al., 2018; Ebadollahi and Razmjou, 2019; Krzyśko-Łupicka, Sokół, & Piekarska-Stachowiak, 2020).

3.2. Physicochemical analysis of unflavored and flavored olive oils

The physicochemical evaluation of the *cv*. Arbequina olive oils without EO addition (0.0%, control) and flavored with known amounts of lemon verbena EO (0.1, 0.2, 0.3 and 0.4% w/w) was performed being

Table 1
Chemical composition of the commercial lemon verbena essential oil (relative abundance mean value ± standard deviation calculated based on the GC/MS spectra profile of three injections).

Identified compound[a]	Empririal formula	Retention Index[b]	Relative abundance (%)[c]
Camphene	$C_{10}H_{16}$	830	0.88 ± 0.01
Methyl heptenone	$C_8H_{14}O$	855	1.19 ± 0.01
β-Myrcene	$C_{10}H_{16}$	859	0.45 ± 0.01
Limonene	$C_{10}H_{16}$	887	0.76 ± 0.01
Propyl amyl ketone	$C_9H_{18}O$	931	0.66 ± 0.01
Linalool	$C_{10}H_{18}O$	942	1.08 ± 0.02
α-Terpineol	$C_{10}H_{18}O$	995	0.74 ± 0.01
cis-Geraniol	$C_{10}H_{18}O$	1023	0.63 ± 0.02
β-Citral	$C_{10}H_{16}O$	1034	23.86 ± 0.04
Geraniol	$C_{10}H_{18}O$	1042	6.16 ± 0.01
α-Citral	$C_{10}H_{16}O$	1055	51.45 ± 0.08
Geranyl acetate	$C_{12}H_{20}O_2$	1119	5.95 ± 0.02
Caryophyllene	$C_{15}H_{24}$	1146	1.52 ± 0.01
γ-Muurolene	$C_{15}H_{24}$	1197	0.64 ± 0.01

[a] Peaks identification based on mass spectra comparison with the spectrometer database of the NIST 11 Library (National Institute of Standards and Technology, Gaithersburg, MD, USA) and by comparison of their retention index calculated against n-alkanes (C_6–C_{20}), being set a minimum similarity of 95% and a relative abundance greater than 0.4%.
[b] Retention index calculated based on n-alkenes (C_6–C_{20}) injected at the same experimental conditions.
[c] Relative abundance of each compound, in percentage, calculated by the area normalization method, without considering the response factors.

the results shown in Table 2. Based on the results it was found that the oils' flavored with the EO had a statistical significant effect on the FA, PV, K_{232} and K_{268} (P-value < 0.05, for the one-way ANOVA). No appreciable changes were observed on the FA due to the oils' flavoring process. Regarding the other three quality parameters (PV, K_{232} and K_{268}) an increase trend was observed with EO flavoring level (PV: from 7.80 (0.0% EO) to 9.05 mEq O_2 kg^{-1} (0.4%f EO); K_{232}; from 0.99 (0.0% EO) to 4.65 (0.4% EO); and, K_{268}: from 0.084 (0.0% EO) to 0.221 (0.4% EO)). This latter finding showed that the addition of the lemon verbena EO to the studied oils promoted undesirable primary and secondary oxidation reactions, contributing to decrease the oils' quality. Similar findings were reported in the literature, for oils flavored with fruits, spices or aromatic herbs, which flavoring processes in general increased the PV, K_{232} and/or K_{268} (Baiano et al., 2009; Caponio et al., 2016; Sacchi, Medaglia, Paduano, Caporaso, & Genovese, 2017). Opposite trends, *i.e.*, a significant decrease of the PV, K_{232} and/or K_{268} or no significant change of the parameters' values, were reported after olive oils flavoring with different aromatic herbs, EO, rosemary leaves or olive leaves (Bobiano et al., 2019; Sousa et al., 2015; Tarchoune et al., 2019). However, as pointed out by Taoudiat, Djenane, Ferhat, and Spigno (2018), the above-mentioned changes (decrease or increase) may only be observed after a minimum storage period (after a 60-days period). Even so, it is interesting to observe that the *cv*. Arbequina olive oil fulfilled the legal thresholds established by the European Commission (EC) regulations for EVOO quality grade classification (Commission Delegated Regulation [EU] 2015/1830, 2015; Sacchi et al., 2017). For the flavored oils, although according to the EC Regulation they cannot be labelled as EVOO, only the oils flavored with 0.1% of EO would meet the above-mentioned thresholds (European Union Commission, Regulation CE 1989/2003, 2003; Issaoui et al., 2016). Finally, it would be important to remark that, according to the results of this study and based on the different findings reported in the literature, a detailed evaluation must be performed when olive oil producers intend to implement a flavoring process.

Table 2
Physicochemical (free acidity, extinction coefficients and peroxide values), total reducing capacity and oxidative stability data of the *cv*. Arbequina olive oils studied without (0.0% essential oil) and with the addition (0.1, 0.2, 0.3 and 0.4%) of pre-established amounts of essential oil (mean value ± standard deviation calculated based on the data determined for five independent samples of each olive oil type).

Parameters	*cv*. Arbequina olive oil class[a]					*P*-value[b] (one-way ANOVA)
	Not flavored (control)	Flavored olive oils with Lemon Verbena essential oil				
	0.0% essential oil	0.1% (w/w)	0.2% (w/w)	0.3% (w/w)	0.4% (w/w)	
FA (%)	0.32 ± 0.04a	0.29 ± 0.02 ab	0.30 ± 0.03 ab	0.28 ± 0.02b	0.29 ± 0.03 ab	***0.0259***
PV (mEq O_2 kg^{-1})	7.80 ± 0.58b	8.87 ± 0.40a	8.31 ± 0.57 ab	8.31 ± 0.02 ab	9.05 ± 1.38a	***0.0037***
K_{232}	0.99 ± 0.14d	2.34 ± 0.18c	2.50 ± 0.08c	3.78 ± 0.16b	4.65 ± 0.36a	< ***0.0001***
K_{268}	0.084 ± 0.010d	0.142 ± 0.012c	0.135 ± 0.023c	0.196 ± 0.026b	0.221 ± 0.016a	< ***0.0001***
TRC (mg CAE/kg)	148 ± 11d	159 ± 4c	164 ± 5bc	169 ± 4 ab	173 ± 4a	< ***0.0001***
DPPH (%)	40 ± 2c	44 ± 1b	45 ± 3b	48 ± 1a	49 ± 2a	< ***0.0001***
$OS_{110\,°C}$ (h)	18.3 ± 0.8 aA	17.1 ± 0.9bA	16.2 ± 0.7bcA	16.0 ± 0.6Ca	14.9 ± 0.4 dA	< ***0.0001***
$OS_{120\,°C}$ (h)	9.5 ± 0.2 aB	8.7 ± 0.3bB	8.1 ± 0.4 cB	7.6 ± 0.2 dB	7.2 ± 0.4 dB	< ***0.0001***
$OS_{130\,°C}$ (h)	4.9 ± 0.1 aC	4.8 ± 0.1abC	4.6 ± 0.1bcC	4.5 ± 0.1 cC	4.2 ± 0.3 dC	< ***0.0001***
$OS_{140\,°C}$ (h)	2.8 ± 0.1aD	2.6 ± 0.1bD	2.6 ± 0.1bcD	2.4 ± 0.1cdD	2.4 ± 0.2dD	< ***0.0001***
$OS_{150\,°C}$ (h)	1.5 ± 0.1E	1.5 ± 0.1E	1.5 ± 0.1E	1.4 ± 0.1E	1.5 ± 0.1E	0.0643
P-value[c] (one-way ANOVA)	< ***0.0001***	< ***0.0001***	< ***0.0001***	< ***0.0001***	< ***0.0001***	

[a] Monovarietal *cv*. Arbequina olive oil flavored with Lemon Verbena *(Aloysia citrodora)* essential oil (0.1, 0.2, 0.3 and 0.4% w/w) or not (0.0%, control).

[b] For each line, a P-value < 0.05 (bold and italic) means that the mean value of the evaluated parameter of at least one olive oil type significantly differ from the others, according to the one-way ANOVA. In each line, different lowercase letters mean significant statistical differences of the parameter under evaluation, at a 5% significance level, according to multiple comparison Tukey's HSD test.

[c] For each column, a P-value < 0.05 (bold and italic) means that the mean value of the oxidative stability (OS) determined at least one oxidation temperature significantly differ from the others, according to the one-way ANOVA. In each column, different uppercase letters mean significant statistical differences of the parameter under evaluation, at a 5% significance level, according to multiple comparison Tukey's HSD test.

3.3. Antioxidant activity of unflavored and flavored olive oils

The results showed that the flavoring Arbequina olive oil with lemon verbena EO enhanced the antioxidant stability, with a significant increase (P-value < 0.05) of TRC levels (varying from 148 (0.0% EO) to 173 mg CAE/kg (0.4% EO)) as well as of the DPPH values (with an increase of the inhibition rate from 40 (0.0% EO) to 49% (0.4% EO). These results are in-line with the literature regarding the flavoring of olive oils with laurel EO or rosemary EO, basil and oregano, sweet orange and sweet lemon peels) or olive leaves (Ayadi, Grati-Kamoun, & Attia, 2009; Dambolena et al., 2010; Khemakhem et al., 2015; Rached, Abdallah, & Guerfel, 2014; Taoudiat et al., 2018; Tarchoune et al., 2019). An opposite finding was reported for olive oils flavored with spices or aromatic herbs (e.g., hot chili peppers, pepper, garlic, laurel or oregano), which led to a significant decrease of the TRC but to an increase or decrease of the DPPH, depending on the type of flavoring agent used (Baiano et al., 2009; Sousa et al., 2015). In brief, the data of this study demonstrated that lemon verbena EO promoted the antioxidant nature of the flavored *cv*. Arbequina olive oils studied.

3.4. Oxidative stability of unflavored and flavored olive oils

The effect of the temperature and of the oils' flavoring on the oils stability was evaluated using the Rancimat test. Table 2 clearly shows that the OS is significantly influenced by both factors, with significant decrease (P-value < 0.05) when the temperature rise (from 110 to 150 °C, for all EO flavoring levels) as well as with the increase of the EO flavoring level (from 0.0 to 0.4% EO, except for 150 °C), pointing out that the oil lipid oxidation is faster at higher temperatures and when higher amounts of EO were added (in-line with the results found for the PV, K_{232} and K_{268} but in disagreement with the TRC). The observed temperature decreasing effect is in accordance with the literature data for olive oils (Farhoosh & Hoseini-Yazdi, 2014; Heidarpour & Farhoosh, 2018; Veloso et al., 2020). Similar decreasing trends were also reported found for olive oils flavored with lemon, dried chili pepper, hot pepper, rosemary, sweet lime/orange, oregano or basil (Baiano et al., 2009; Bobiano et al., 2019; Caporaso, Paduano, Nicoletti, & Sacchi, 2013; Khemakhem et al., 2015). Opposite findings (i.e., higher OS values for higher content of the flavoring agent) were also reported in the literature, which are in general linked to higher TRC values (Ayadi et al., 2009; Farhoosh & Hoseini-Yazdi, 2014; Sousa et al., 2015; Veloso et al., 2020). Thus, once again, based on the contradictory literature data, no clear trend can be theorized regarding the positive/negative effect of oils' flavoring process on their OS. In summary, for the oils studied, it was verified that the addition of lemon verbena EO had a negative effect on the oils stability, hypothetically due to a possible pro-oxidant behavior of some phenolic compounds of the lemon verbena EO. The mentioned negative impact of the EO addition could also be tentatively

attributed to some oxidation level of the EO, although no visual or olfactory evidence could corroborate this possibility.

3.5. Kinetic-thermodynamic parameters of unflavored and flavored olive oils

The k values of the lipid oxidation at temperatures ranging from 110 to 150 °C were determined based on the OS values, being listed in Table 3. The results showed that the k values significantly increased with the temperature (P-value < 0.05), in-line with the literature data (Aktar & Adal, 2019; Gharby et al., 2016; Gülmez & Şahin, 2019; Veloso et al., 2020). Also, flavoring *cv*. Arbequina oil with lemon verbena EO significantly increased the k values (P-value < 0.05), for each studied temperature. This trend is opposite to the literature data reported that described a decrease of the k values for soybean oil or hazelnut oil flavored with different additive, namely, catmint (Nepeta) extracts (Gülmez & Şahin, 2019; Mahalleh, Sharayei, Azarpazhooh, & Ramaswamy, 2019).

Table 3 also shows the T_C and Q_{10} values calculated after linearization (determination coefficients, R^2, varying between 0.9884 and 0.9982), being not observed a significant effect of EO flavoring level (P-value > 0.05), pointing out that no significant increase in the reaction rates could be attributed to a 10 °C rise. However, the literature reported a decreasing trend of the T_C and Q_{10} values of soybean or hazelnut oils flavored with catmint extract or with pomegranate peels and seeds (Golmakani, Keramat, & Leila, 2020; Mahalleh et al., 2019).

The E_a and A values, calculated after the linearization of the Arrhenius equation ($0.9948 \leq R^2 \leq 0.9993$), are also shown in Table 3. As can be seen from the results, the A and the E_a values significantly decreased (P-value < 0.05), as the EO level increased, pointing out that the lipid oxidation of olive oils with higher EO amounts would require a lower minimum energy turning promoting the onset of the initial oxidation process (Farhoosh et al., 2008). Once again, these findings are opposite to those reported in the literature for flavored soybean or hazelnut oils (Mahalleh et al., 2019; Gülmez & Şahin, 2019). Table 3 also presents the values of ΔH^{++} and ΔS^{++} calculated based on the activated complex theory, by logarithmic linearization of k/T dependency with the temperature ($0.9968 \leq R^2 \leq 0.9996$). For all studied oils, ΔH^{++} were positive, confirming the endothermic nature of the lipid oxidation reaction previously reported for not flavored olive oils (Farhoosh et al., 2008; Farhoosh & Hoseini-Yazdi, 2014, Gharby et al., 2016; Heidarpour & Farhoosh, 2018, Veloso et al., 2020). Besides, the ΔH^{++} decreased significantly (P-value < 0.05), from 79.4 to 74.1 kJ mol^{-1}, with the increase of EO level (from 0.0 to 0.4% EO, w/w), which is in agreement with the results of Mahalleh et al. (2019) for flavored soybean oil and of Golmakani, Keramat, Darniyani, and Leila (2020) for flavored linseed oil, but contrary to the findings of Gülmez and Şahin (2019) for flavored hazelnut oils. The higher ΔH^{++} values for the *cv*. Arbequina unflavored oils pointed out that the flavoring process promotes the decrease of the energy needed to remake the bonds during the formation of the activated complexes (Mahalleh et al., 2019). On the other hand, the negative sign of ΔS^{++} (varying from −131.1 to −144.0 J mol^{-1} K^{-1} for 0.0 and 0.4% EO; Table 3) indicates that, as previously reported for not flavored olive oils, the lipid oxidation is an endergonic process leading to more ordered transition state structures in comparison with the reactants in the ground state, suggesting an association mechanism among the reactant species to form the transition states (Farhoosh & Hoseini-Yazdi, 2014; Veloso et al., 2020). Also, the flavoring process led to oils with significantly (P-value < 0.05) more negative ΔS^{++} values, implying that fewer reactants participate in the activated complex state of the oils flavored with lemon verbena EO and thus the activated complex state was more prone to oxidation. Globally, these observations are in agreement with those reported in the literature for flavored soybean and linseed oils, but contrary to those found for flavored hazelnut

Table 3
Reaction rate constants, temperature coefficients, temperature acceleration factors, frequency factors, activation energies, enthalpies and entropies of activation, and free Gibbs energies (mean value ± standard deviation) of *cv*. Arbequina olive oils flavored or not with essential oil.

Kinetic and Thermodynamic parameters	*cv*. Arbequina olive oil class[a]					*P*-value[b] (one-way ANOVA)
	Not flavored (control)	Flavored olive oils with Lemon Verbena essential oil				
	0.0% essential oil	0.1% (w/w)	0.2% (w/w)	0.3% (w/w)	0.4% (w/w)	
$k_{110\ °C}$ (h^{-1})	0.055 ± 0.002 dE	0.059 ± 0.003 cE	0.0617 ± 0.002bcE	0.063 ± 0.002bE	0.067 ± 0.002 aE	***< 0.0001***
$k_{120\ °C}$ (h^{-1})	0.106 ± 0.002eD	0.115 ± 0.004dD	0.124 ± 0.006cD	0.132 ± 0.004bD	0.139 ± 0.007aD	***< 0.0001***
$k_{130\ °C}$ (h^{-1})	0.205 ± 0.005 cC	0.210 ± 0.005bcC	0.216 ± 0.007bcC	0.221 ± 0.007bC	0.238 ± 0.016 aC	***< 0.0001***
$k_{140\ °C}$ (h^{-1})	0.355 ± 0.008 dB	0.387 ± 0.008 cB	0.389 ± 0.018bcB	0.411 ± 0.016abB	0.416 ± 0.03 aB	***< 0.0001***
$k_{150\ °C}$ (h^{-1})	0.649 ± 0.020A	0.657 ± 0.030A	0.683 ± 0.048A	0.687 ± 0.033A	0.682 ± 0.031A	***0.0482***
P-value[c] (one-way ANOVA)	***< 0.0001***	***< 0.0001***	***< 0.0001***	***< 0.0001***	***< 0.0001***	
T_C (°C^{-1})	−0.0268 ± 0.0002	−0.02635 ± 0.0002	−0.2582 ± 0.0005	−0.02584 ± 0.0004	−0.02556 ± 0.0016	0.1480
Q_{10}	1.852 ± 0.008	1.834 ± 0.007	1.812 ± 0.022	1.813 ± 0.019	1.802 ± 0.067	0.1610
$A \times 10^9$ (h^{-1})	10.9 ± 3.2a	7.9 ± 0.9 ab	5.9 ± 2.7bc	5.1 ± 1.1bc	2.6 ± 0.8c	***< 0.0001***
E_a (kJ mol^{-1})	82.7 ± 1.1a	81.6 ± 0.4 ab	80.2 ± 1.6b	79.8 ± 0.8b	77.4 ± 0.9c	***< 0.0001***
ΔH^{++} (kJ mol^{-1})	79.4 ± 1.1a	78.3 ± 0.4 ab	76.8 ± 1.6b	76.5 ± 0.8b	74.1 ± 0.9c	***< 0.0001***
ΔS^{++} (J mol^{-1} K^{-1})	−131.8 ± 2.6a	−134.4 ± 0.9 ab	−137.4 ± 4.1b	−138.2 ± 1.8b	−144.0 ± 2.4c	***< 0.0001***
$\Delta G^{++}_{110\ °C}$ (kJ mol^{-1})	129.95 ± 0.08 aE	129.73 ± 0.04bE	129.53 ± 0.11 cE	129.41 ± 0.09 cE	129.17 ± 0.08 dE	***< 0.0001***
$\Delta G^{++}_{120\ °C}$ (kJ mol^{-1})	131.27 ± 0.05aD	131.07 ± 0.04bD	130.09 ± 0.09cD	130.79 ± 0.08cD	130.61 ± 0.09dD	***< 0.0001***
$\Delta G^{++}_{130\ °C}$ (kJ mol^{-1})	132.59 ± 0.03 aC	132.41 ± 0.04bC	132.28 ± 0.07 cC	132.17 ± 0.07cdC	132.05 ± 0.10 dC	***< 0.0001***
$\Delta G^{++}_{140\ °C}$ (kJ mol^{-1})	133.91 ± 0.02 aB	133.76 ± 0.04bB	133.66 ± 0.08bcB	133.55 ± 0.07cdB	133.49 ± 0.11 dB	***< 0.0001***
$\Delta G^{++}_{150\ °C}$ (kJ mol^{-1})	135.23 ± 0.04 aA	135.10 ± 0.04abA	135.03 ± 0.10bcA	134.93 ± 0.07 cA	134.92 ± 0.13 cA	***< 0.0001***
P-value[c] (one-way ANOVA)	***< 0.0001***	***< 0.0001***	***< 0.0001***	***< 0.0001***	***< 0.0001***	

[a] Monovarietal *cv*. Arbequina olive oil flavored with Lemon Verbena (*Aloysia citrodora*) essential oil (0.1, 0.2, 0.3 and 0.4% w/w) or not (0.0%, control).

[b] For each line, a P-value < 0.05 (bold and italic) means that the mean value of the evaluated parameter of at least one olive oil type significantly differ from the others, according to the one-way ANOVA. In each line, different lowercase letters mean significant statistical differences of the parameter under evaluation, at a 5% significance level, according to multiple comparison Tukey's HSD test.

[c] For each column, a P-value < 0.05 (bold and italic) means that the of reaction rate constant (k) or the mean value of the free Gibbs energy (ΔG^{++}) calculated at least one oxidation temperature significantly differ from the others, according to the one-way ANOVA. In each column, different uppercase letters mean significant statistical differences of the parameter under evaluation, at a 5% significance level, according to multiple comparison Tukey's HSD test.

oils (Golmakani et al., 2020; Gülmez & Şahin, 2019; Mahalleh et al., 2019). It should also be noticed that $A/\Delta S^{++}$ ratio linearly increase (in absolute value, due to its negative nature, $R^2 = 0.9656$) with the EO addition, strengthen the higher tendency of the more flavored oils (greater percentage of EO) to undergo oxidation reactions. Contrary, $E_a/\Delta H^{++}$ ratio was almost constant for all the studied olive oils. Moreover, linear and polynomial correlations could be established for E_a versus ΔH^{++} and A versus ΔS^{++} ($R^2 = 1.000$ and 0.9998, respectively), which is in agreement with the reaction rate transition-state theory (Farhoosh & Hoseini-Yazdi, 2014; Heidarpour & Farhoosh, 2018). In the present study, a linear behavior ($0.8298 \leq R^2 \leq 0.9816$) was observed between those two parameters, similarly to that previously reported by Veloso et al. (2020) for not flavored olive oils. Other researchers did not find any marked relationship between E_a and OS values (Farhoosh &

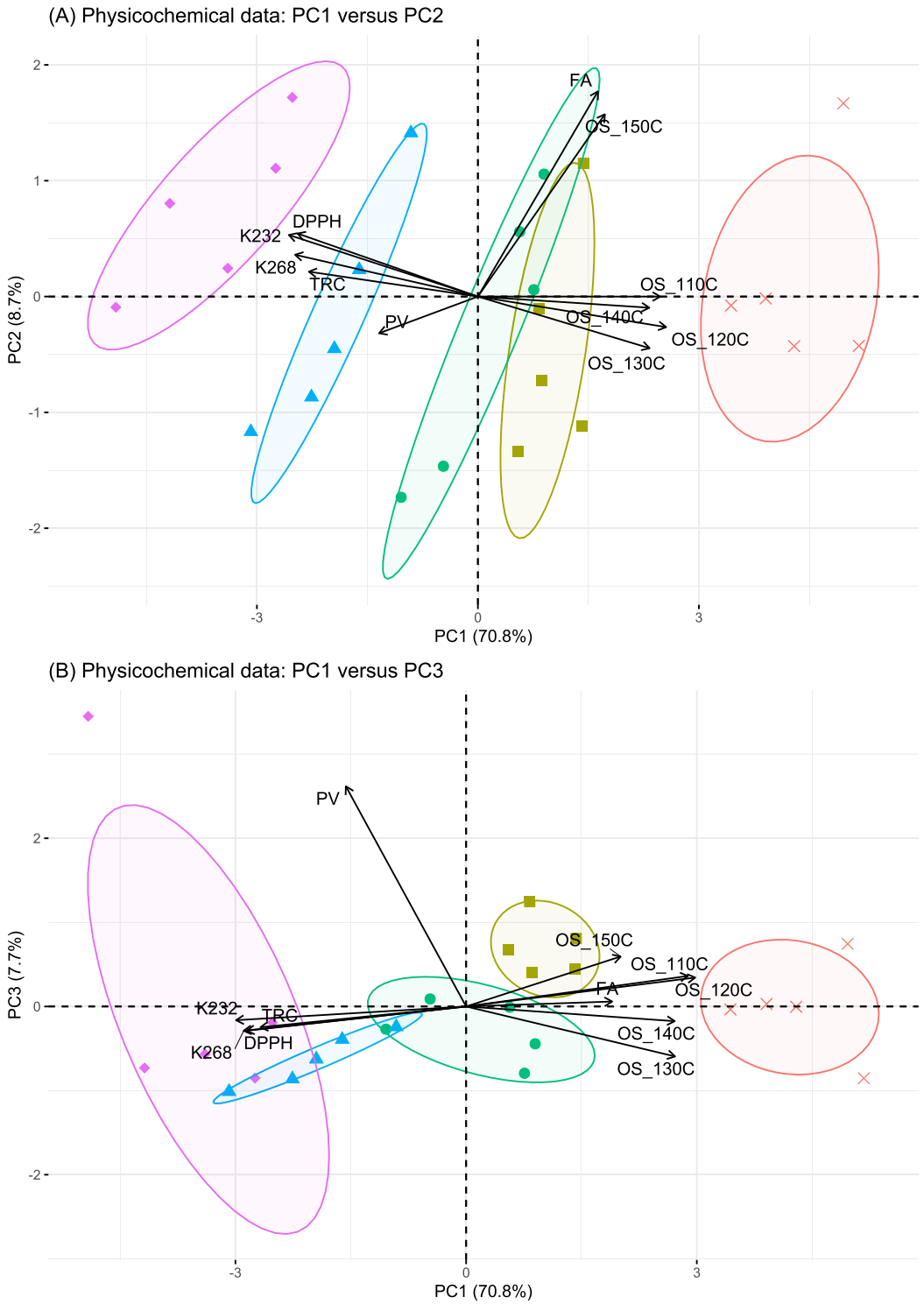

Fig. 1. Principal component analysis (PCA) for *cv*. Arbequina olive oils (×: 0% EO, w/w) or flavored (■: 0.1% EO; ●: 0.2% EO; ▲: 0.3% EO; ♦ 0.4% EO, w/w) with lemon verbena essential oil (EO), based on physicochemical quality parameters (FA, PV, K_{232}, and K_{268}), antioxidant stability data (TRC and DPPH) and oxidative stability at different temperatures (OS at 110, 120, 130, 140 and 150 °C).

Hoseini-Yazdi, 2014; Gharby et al., 2016).

Finally, the ΔG^{++} (Table 3) were also calculated for each of the five temperatures studied (110–150 °C), allowing the simultaneous assessment of the effect of ΔH^{++} and ΔS^{++} on the oxidation rate and oxidative stability of the oils (Mahalleh et al., 2019). The ΔG^{++} values were positive for both unflavored and flavored *cv*. Arbequina oils, and for all the temperatures studied, indicating the non-spontaneous nature of the lipid oxidation reaction, which is in agreement with the literature data for not flavored olive oils (Ong et al., 2013; Veloso et al., 2020). This behavior was expected considering the negative entropy along with positive enthalpy (Gülmez & Şahin, 2019). For all studied oils, a significant increase (P-value < 0.05) of the ΔG^{++} occurred with the temperature rise, pointing out the lowered levels of disorder among the reactants that comprise the activated complexes during the oxidation

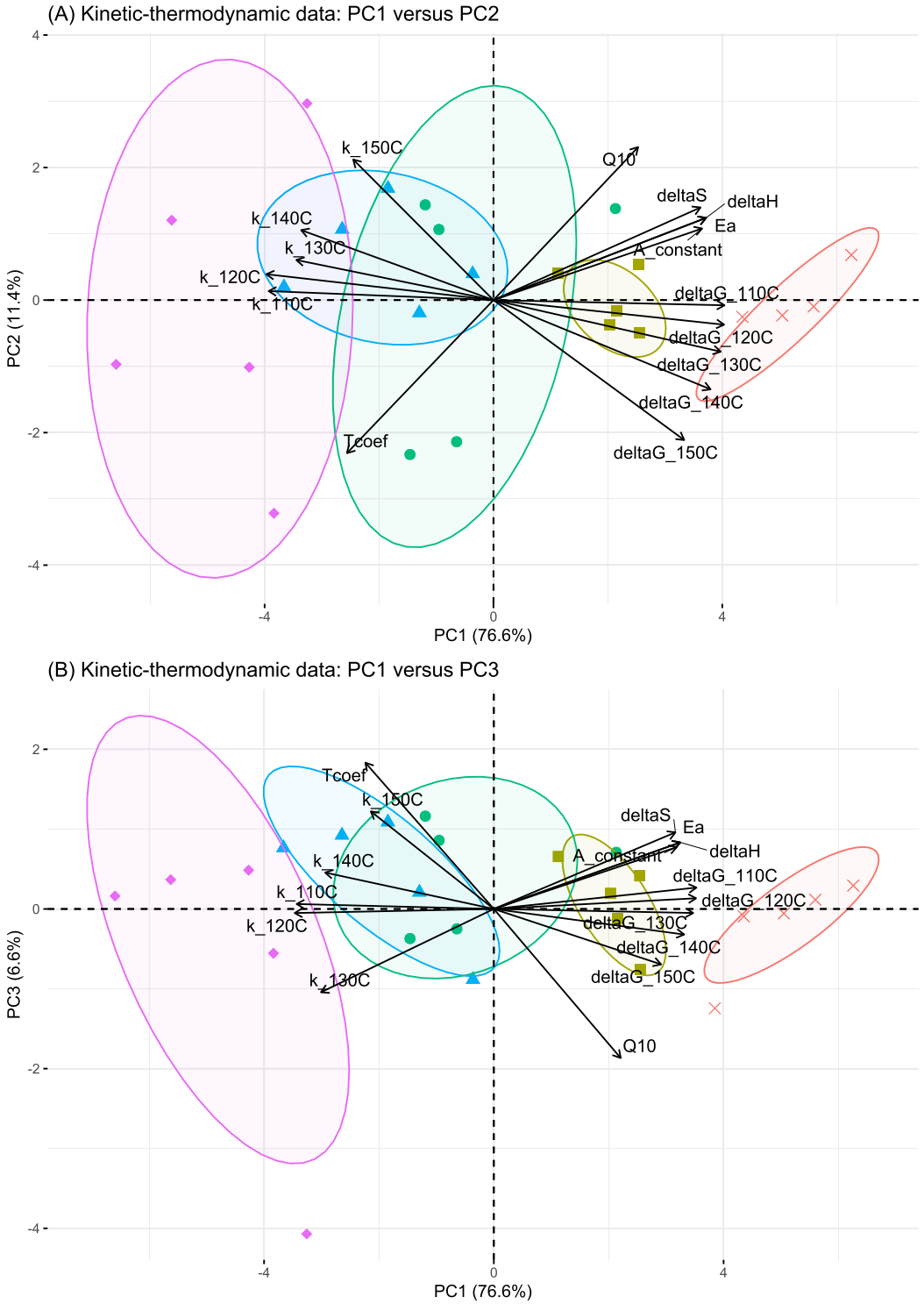

Fig. 2. Principal component analysis (PCA) for *cv*. Arbequina olive oils unflavored (×: 0% EO, w/w) or flavored (■: 0.1% EO; ●: 0.2% EO; ▲: 0.3% EO; ♦: 0.4% EO, w/w) with lemon verbena essential oil (EO), based on kinetic-thermodynamic data (T_C, Q_{10}, E_a, A coefficient, ΔH^{++}, ΔS^{++}, k and ΔG^{++} at 110, 120, 130, 140 and 150 °C).

reaction (Farhoosh & Hoseini-Yazdi, 2014; Mahdavianmehr et al., 2016). On the other hand, a significant but slight decrease of the ΔG^{++} was observed with the EO flavoring level, which is in disagreement with the literature data (Golmakani et al., 2020; Mahalleh et al., 2019).

Briefly, the kinetic-thermodynamic results confirmed that the lipid oxidation was a non-spontaneous, endergonic, and endothermic process, showing that the addition of EO (and so, the increase of the TRC) delayed the formation of the activated complexes and thus, the energy needed to the formation of the activated complexes was lower. On the other hand, the oxidation reaction rate was faster which is in accordance with the OS values observed, and that could be tentatively attributed to the possible pro-oxidant nature of the EO phenolic compounds or to some possible slight oxidation of the EO added. Finally, to the Authors' best knowledge, the literature evidenced a lack of data regarding kinetic-thermodynamic parameters of flavored olive oils, strengthening the relevance of the present study.

3.6. Unsupervised and supervised olive oil classification according to the flavored level using physicochemical or kinetic-thermodynamic data

As previously discussed, flavoring *cv*. Arbequina oils with lemon verbena EO greatly influenced the physicochemical, antioxidant and oxidative characteristics as well as the kinetic-thermodynamic parameters. Thus, the feasibility of distinguish the studied oils according to the flavoring level using the referred data was further evaluated. The unsupervised pattern analysis performed highlighted the potential use of both sets of data for distinguishing the oils according to the flavoring level. The PCA results clearly showed that the set of FA, PV, K_{232}, K_{268}, TRC, DPPH and OS (Fig. 1) or that comprising k, T_C, Q_{10}, E_a, A, ΔH^{++}, ΔS^{++} and ΔG^{++} (Fig. 2) would allow the recognition and differentiation of the olive oils in relation to the lemon verbena flavoring level. In both cases, the first principal component (PC1) allowed explaining the majority of the data variability (70.8 and 76.6%, respectively), being the oils assembled along the PC1 into unsupervised groups according to the decrease level of EO, showing that both datasets enabled a clear differentiation of unflavored and flavored oils. In more detail, the use of the physicochemical-stability dataset resulted into a slight overlapping of the flavored levels being possible to withdraw two main groups, one corresponding to the oils flavored with 0.1–0.2% of EO and the other for 0.3–0.4% of EO. On the other hand, the kinetic-thermodynamic dataset also led to an overlapping of the flavored groups, although this was more evident for oils flavored with 0.2–0.3% of EO. Overall, PCA allowed inferring that both type of data could be used as a preliminary recognition tool for distinguish unflavored *cv*. Arbequina oils from those flavored with lemon verbena EO, although the former dataset seemed to have a higher *a priori* classification potential. Nevertheless, it should be remarked, that the kinetic-thermodynamic data were calculated from the reaction rates and so, indirectly from the OS data, only requiring a single analysis, turning the procedure less time-consuming and practical if a routine recognition protocol is envisaged.

To deeper evaluate the classification potential of the physicochemical or the kinetic-thermodynamic data, a LDA-SA approach was further implemented. In each case, the supervised LDA coupled with the SA algorithm, allowed to identify the most powerful non-redundant discriminant parameters. For the physicochemical data, the best LDA-SA model was established based on four parameters (PV, K_{232}, TRC and OS at 140 °C). The first two linear discriminant functions explained 99.6 and 0.2% of the original data variance, with sensitivities (i.e., correct classification rates) of 100 and 96% for the original data group (Fig. 3) and for the LOO-CV, respectively. The predictive performance was satisfactory, being only one olive oil flavored with 0.2% of EO misclassified, as belonging to the 0.1% of EO group. In which concerns the kinetic-thermodynamic data the best LDA-SA model included seven non-redundant variables (k at 130, 140 and 150 °C, E_a, ΔH^{++}, ΔG^{++} at 110 and 140 °C), explaining the first two discriminant functions 94.1 and 4.6% of the original data variance. The supervised linear

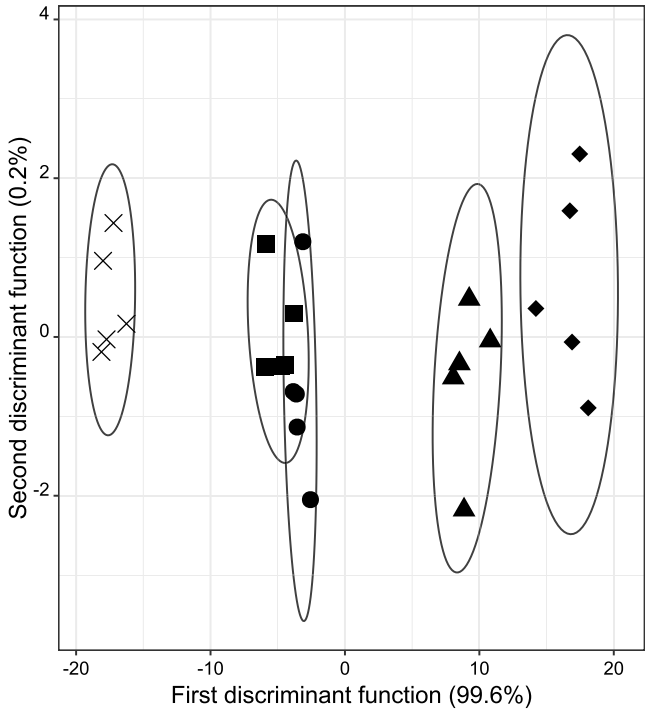

Fig. 3. Linear discriminant analysis-simulated annealing (LDA-SA) model for *cv*. Arbequina olive oil discrimination according to the lemon Verbena essential oil level (×: unflavored oil, 0.0% EO; ■: 0.1% EO; ●: 0.2% EO; ▲: 0.3% EO; ◆: 0.4% EO, w/w): first and second discriminant function based on four non-redundant physicochemical parameters (PV, K_{232}, TRC and OS at 140 °C) and respective class membership regions limited by the confidence ellipses calculated from the posterior probabilities, computed by the Bayes' theorem.

classification model had sensitivities of 100 and 80% for the original data group (Fig. 4) and for the LOO-CV. As can be inferred, the predictive performance of the kinetic-thermodynamic data was less satisfactory, although all unflavored olive oil samples were correctly classified being the misclassifications observed among the flavored olive oil samples with 0.2–0.4% of EO. Thus, the selected kinetic-thermodynamic data could be used as preliminary putative discriminant biomarkers, although with a low discrimination power than the physicochemical-stability parameters.

4. Conclusions

Flavoring *cv*. Arbequina olive oils with lemon verbena essential oil enhanced the antioxidant capacity and the total reducing capacity of the unflavored oil. However, the flavoring agent had a negative effect on the oils' oxidative stability promoting the primary and secondary lipid oxidation (greater peroxide values and extinction coefficients), which may reflect a hypothetical pro-oxidant effect or a possible slight oxidation of the essential oil. The kinetic-thermodynamic study confirmed the negative impact of the oils' flavoring process, leading to higher reaction rates, lower activation energies and frequency factors (i.e., lower resistance to lipid oxidation accelerating the onset of the initial oxidation process, responsible for the bond scission that results on the formation of primary oxidation products), lower positive enthalpy of activation, more negative entropies of activation and lower positive Gibbs free energies of activation. In conclusion, the lipid oxidation of both flavored and unflavored oils had a non-spontaneous, endergonic, and endothermic nature. Regarding the flavored oils, the study contributed to minimize the lack of kinetic-thermodynamic data, allowing a deeper insight regarding the oils' lipid oxidation. On the other hand, the study also pointed out the feasibility of using the collected data (physicochemical-

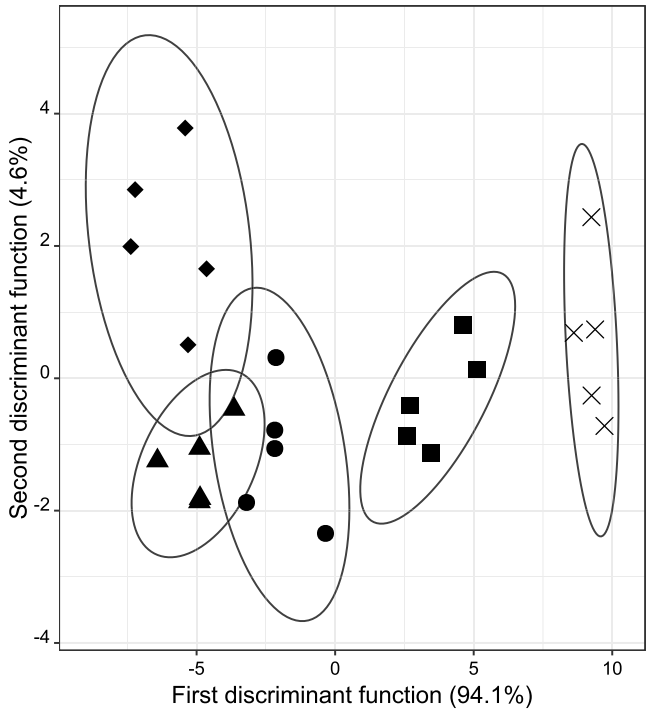

Fig. 4. Linear discriminant analysis-simulated annealing (LDA-SA) model for *cv*. Arbequina olive discrimination according to the lemon Verbena essential oil level (×: unflavored oil, 0.0% EO; ■: 0.1% EO; ●: 0.2% EO; ▲: 0.3% EO; ◆: 0.4% EO, w/w): first and second discriminant function based on eight non-redundant kinetic-thermodynamic data (*k* at 140 and 150 °C, E_a, ΔH^{++}, ΔG^{++} at 110 and 140 °C) and respective class membership regions limited by the confidence ellipses calculated from the posterior probabilities, computed by the Bayes' theorem.

stability or kinetic-thermodynamic datasets) to differentiate (principal component analysis) as well as to discriminate (linear discriminant analysis) the *cv*. Arbequina oils according to the level of essential oil addition. Indeed, the unsupervised and supervised statistical analysis showed that both datasets could be satisfactorily used to identify unflavored oils and discriminating them from the flavored ones, allowing foreseeing their possible use (namely of the kinetic-thermodynamic approach, which only requires the oxidative stability evaluation) as a preliminary but practical tool for routine analysis of olive oils.

CRediT authorship contribution statement

Marwa Cherif: Investigation, Writing - original draft, Writing - review & editing. **Nuno Rodrigues:** Conceptualization, Funding acquisition, Writing - original draft, Writing - review & editing. **Ana C.A. Veloso:** Software, Writing - review & editing. **Khalil Zaghdoudi:** Conceptualization, Writing - review & editing. **José A. Pereira:** Funding acquisition, Resources, Conceptualization, Writing - review & editing. **António M. Peres:** Funding acquisition, Conceptualization, Software, Writing - review & editing.

Declaration of competing interest

The authors declare no conflict of interest.

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