Kinetic Study of Olive Oil Degradation Monitored by Fourier Transform Infrared Spectrometry. Application to Oil Characterization

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Ⓢ Supporting Information

ABSTRACT: A new approach for the determination of kinetic parameters of the *cis/trans* isomerization during the oxidation process of 24 virgin olive oils belonging to 8 different varieties is presented. The accelerated process of degradation at 100 °C was monitored by recording the Fourier transform infrared spectra. The parameters obtained confirm pseudo-first-order kinetics for the degradation of *cis* and the appearance of *trans* double bonds. The kinetic approach affords the induction time and the rate coefficient; these parameters are related to the fatty acid profile of the fresh olive oils. The data obtained were used to compare the oil stability of the samples with the help of multivariate statistical techniques. Fatty acid allowed a classification of the samples in five groups, one of them constituted by the cultivars with higher stability. Meanwhile, the kinetic parameters showed greater ability for the characterization of olive oils, allowing the classification in seven groups.

KEYWORDS: *olive oil, oil degradation, Fourier transform infrared spectroscopy, kinetics, oil characterization*

■ INTRODUCTION

In the Mediterranean diet olive oil is an important source of mono- and polyunsaturated fatty acids, tocopherols, and phytosterols. These components exert health benefits in terms of lowering the risk of suffering cardiovascular diseases.[1,2] Nevertheless, the composition of olive oil can be influenced by several variables such as geographical origin, olive cultivar, extractive procedure, and degradation process suffered after its extraction. Oil degradation is a very complex process strongly depending on chemical composition (both fatty acid and antioxidant contents)[3,4] and external conditions, including temperature, light, radicals, peroxides, and metals, which catalyze the degradation reactions.[5−7] In the thermal degradation of oil a wide range of reactions occur such as hydrolysis, oxidation, isomerization, and polymerization.[6] The main phases of the oil oxidation process are essentially known, although their kinetic parameters may differ markedly from oil to oil. The well-known process follows a free radical mechanism.[5,6] In the first stage, autoxidation leads to hydroperoxides, also called primary oxidation products, and later the breakdown of these compounds leads to alcohols, aldehydes (mainly responsible for flavors and odors), ketones, lactones, hydrocarbons, fatty acids (secondary and tertiary oxidation products), and, in the last stage, polymerization products.

Lipid degradation is a process that occurs fairly slowly at room temperature, and hence accelerated methods should be employed to estimate the oxidative stability of the product or the induction time of the autoxidation reaction in a relatively short period of time. Several physical or chemical parameters can be used to increase the rate of the reaction and, consequently, the development of rancidity, such as temperature. In the literature, two approaches to predict oil oxidative stability can be found depending on the interest in storage stability or processing performance. Oils are treated at 100 °C or lower to evaluate storage stability; in contrast, higher temperatures are used to evaluate oil performance in food processing such as frying.[5−7] During lipid degradation apart from the oxidation of some compounds, other degradation processes occur simultaneously such as *cis/trans* isomerization of unsaturated fatty acids and hydrolysis of triglycerides that leads to *trans* and free fatty acids, respectively.[7] Every one of these processes contributes to oil degradation.

Traditionally, oxidative oil degradation has been studied on the basis of some indices such as peroxide, acid, and anisidine. Moreover, the purity and quality of a oils is frequently evaluated by its fatty acid profile. There are numerous studies in the literature in which the fatty acid composition is used to characterize oils and to determine their possible resistance to oxidation process. However, the determination of the fatty acid profile is time-consuming , requiring both a sample preparation process and a quantification step using gas chromatography.[8]

Alternatively, Fourier transform infrared (FTIR) spectrometry is a suitable technique to follow adulteration/authentication and oil degradation, because of the excellent sensitivity and the great amount of information collected thereby in a few minutes.[9−13] Generation of oxidation products, as well as removal of transformed components, can be followed simultaneously and easily. Therefore, FTIR spectrometry allows the evaluation of oil stability in a convenient way in a short time and without sample preparation.[9]

In particular, the oxidation study of edible oils and fats by FTIR spectrometry has been successfully used previously in the literature.[9,14] This technique has been applied following both the wavenumber and the absorbance changes of typical bands in the spectra of edible oils under oxidative conditions.[15,16] Moreover, different approaches have been carried out to

quantify and compare oxidation products of different oils, and some traditional assays such as peroxide and anisidine values were correlated with parameters obtained from FTIR spectra.[9] More specifically, FTIR spectrometry has been applied, for example, to establish the thermal degradation state of heated oils by measuring the absorption band responding to the bending vibration of *trans* double bonds, which absorbs at 966 cm^{-1} in the infrared spectra,[17] and correlating it with the total polar compounds.[18]

FTIR spectrometry can also be used to determine some kinetic parameters in the forced oxidation process of oils. Kinetic data can be used to distinguish the origin of vegetable oil or to characterize the differences or similarities among different oils. Therefore, these data are very useful for predicting the oxidative stability of vegetable oils under various heat processing, storage, and distribution conditions. Nevertheless, this subject has received little attention, and very few studies can be found in the literature in which kinetic data are used to compare oxidative behaviors of different sorts of oils. In some of these studies isothermal differential scanning calorimetry data[19] and the Rancimat test have been used to characterize different vegetable oils.[20,21]

In recent years, the number of virgin oils from different olive cultivars has grown enormously in supermarkets trying to highlight the better quality of olive oils from nutritional and culinary points of view. In the case of olive, it is known that the resistance to degradation is directly related to the ratio of oleic acid to linoleic acid and also to the proportion of antioxidant components. The willingness of the producer and/or consumer demand for geographic identification has led to a regulation of the European Commission (EC, 2006) that establishes controlled labeling of food products, virgin olive oil among others, based on geographical indications such as Protected Designation of Origin (PDO). Normally in each geographic region a olive cultivar occurs predominately, so PDOs have proven to be a successful regulatory framework to protect singular virgin olive oils from a local region that have distinctive properties. In this way, it will be of interest to find composition parameters that can help to establish a classification of olive oil cultivars to their resistance to degradation and also to prevent adulteration. In this line of work, other types of samples of high fat content such as almond cultivars were differentiated by means of chemometric tools applied to fat composition by the authors.[22−24] Principal component analysis (PCA) is a useful technique to obtain uncorrelated variables, and cluster and linear discriminant analyses (LDA) are unsupervised and supervised methods of pattern recognition to classify the samples into groups attending the values of its variables.[25,26] The capacity of these statistical techniques can be used to perform characterizations based on kinetic parameters related to the process of oxidative degradation of oils.

The aim of this paper was first to compare the storage stability of different olive oil cultivars submitted to a thermal forced degradation process at 100 °C based on kinetics parameters related to oil degradation, such as the *cis/trans* isomerization of the unsaturated fatty acids measured with infrared spectroscopy. In addition, the variations in *cis* and *trans* absorption bands are correlated with the original fatty acid content of each olive oil. Finally, we explore the possibilities of establishing a classification of olive oil cultivars using multivariate statistical techniques on the basis of fatty acid profile and the values of its kinetic parameters.

Monitoring of oil degradation is followed through the changes detected in the spectra obtained by attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectrometry. A pseudo-first-order kinetics is suggested for the decrease of the absorbance maximum for the *cis* double bond band and the simultaneous increase of the absorbance maximum for the *trans* double bond band. Kinetic parameters, such as induction times and rate coefficients, were calculated for both bands. These parameters were correlated between them, and also the correlation with the fatty acid profile was studied. Finally, multivariate statistical techniques were applied to the data for the evaluation as potential variables for the characterization of monocultivar olive oils.

MATERIALS AND METHODS

Samples. A set of 24 monovarietal extra virgin olive oils from cultivars Arbequina (A1−A7), Blanqueta (B1, B2), Cornicabra (C1, C2), Empeltre (E), Hojiblanca (H1−H4), Lechin (L), Manzanilla (M1, M2), and Picual (P1−P5) available in the market (Spain) was studied. Different oil brands for the same cultivar were purchased.

Fatty Acid Determination. The determination of the fatty acid composition was carried out according to International Standard UNE-EN ISO:5508:1996.[8] A Carlo Erba series 8000 gas chromatograph with a split/splitless injector and a flame ionization detector (FID) was used to analyze the fatty acid methyl esters. The equipment was controlled by the software for data acquisition and processing Chrom-card (Fisons Instruments, Poole, UK). The chromatographic column was a cyanopropyl methyl siloxane (Quadrex Corp., New Haven, CT, USA), 30 m × 0.25 mm i.d. Samples of 1 μL were injected into the split injector at a 1:30 ratio and 230 °C. The carrier gas was helium at a flow rate of 2 mL/min. The FID was set at 300 °C. Oven temperature was maintained at 110 °C for 2 min, ramped from 110 to 170 °C at 4 °C/min, then held at 170 °C for 4 min, ramped again from 170 to 190 °C at 20 °C/min, and finally held at 220 °C for 5 min. A FAME standard mix (FAMQ005) purchased from Accustandard (New Haven, CT, USA) was used for the identification and determination of fatty acid methyl esters.

Sample Oxidation Treatment. Eighty grams of oil were weighed for each sample and one and a half grams was taken every treatment day. The samples were introduced into glass vessels of 95 mm diameter and 3 cm height without the stopper. The glass vessels with the samples were placed in a convection oven with adjustable temperature (Selecta 2000209) set to 100 ± 0.5 °C. The sample contained in each glass vessel was used to realize the everyday analyses by ATR-FTIR, until the day when sample polymerization started.

Spectra Acquisition. A FTIR spectrometer, Vector 22 (Bruker, Ettlingen, Germany) interfaced with a computer operating under OPUS NT software (version 3.1), and an attenuated total reflection device (Gateway ATR kit is a six reflection horizontal ATR sampling system with a Through Top Plate from Specac) was used with a ZnSe crystal (angle of incidence is 45°). Triplicate spectra from three aliquots of each sample were recorded daily from 4000 to 650 cm^{-1} by co-adding 128 scans at a 4 cm^{-1} resolution and a gain of 2.0, until the sample became so viscous that taking the oil with a Pasteur pipet from the vial was difficult due to the polymerization. The ATR sampling system was cleaned using a soft paper tissue moist with acetone after every measurement. A background was recorded after every sample to check the performance of the cleaning procedure.

FTIR Data Acquisition and Processing. Rutherford baseline correction was carried out from 64 baseline points excluding the carbon dioxide region. The wavenumber of the band maxima and absorbance values from the *cis* CH stretching vibration and *trans* bending vibrations around 3006 and 970 cm^{-1}, respectively, were obtained by a command of OPUS software. The absorbance data refer to peak height, measured by tracing a local baseline between two adjacent minima to reduce errors due to overlapping bands for the *cis* stretching band. On the other hand, the difference spectrum was used to measure the absorbance of the *trans* bending vibration band. The

Table 1. Fatty Acid (FA) Mean Values Obtained for Monocultivar Extra Virgin Olive Oils and Total Saturated Fatty Acids (SFA), Total Monounsaturated Fatty Acids (MUFA), and Total Polyunsaturated Fatty Acids (PUFA) and Ratio C18:1/C18:2 (O/L)

cultivar	g FA/100 g total FA[a]					SFA	MUFA	PUFA	O/L
	C16:0	C16:1	C18:0	C18:1	C18:2				
A1	14.2 (5.3%)	1.420 (4.2%)	2.27 (2.1%)	69.5 (1.0%)	10.8 (0.3%)	16.9	71.3	11.7	6.4
A2	14.2 (0.3%)	1.402 (0.9%)	2.45 (0.7%)	70.6 (<0.1%)	9.2 (0.4%)	17.3	72.5	10.2	7.7
A3	13.4 (0.3%)	1.219 (0.5%)	2.47 (1.9%)	71.3 (0.2%)	9.4 (0.5%)	16.5	73.0	10.5	7.6
A4	14.6 (1.4%)	1.478 (2.4%)	2.25 (1.3%)	69.4 (0.3%)	10.3 (0.5%)	17.5	71.3	11.2	6.7
A5	13.6 (5.5%)	1.222 (5.2%)	2.19 (5.1%)	71.8 (1.1%)	9.4 (1.6%)	16.3	73.4	10.2	7.6
A6	14.6 (0.1%)	1.449 (2.4%)	2.31 (0.8%)	69.2 (0.1%)	10.4 (0.3%)	17.5	71.2	11.3	6.7
A7	14.2 (0.3%)	1.210 (0.8%)	2.24 (0.2%)	70.0 (0.1%)	10.4 (0.5%)	17.0	71.7	11.2	6.7
B1	15.8 (0.4%)	1.329 (1.6%)	2.05 (0.9%)	62.8 (0.1%)	15.6 (0.2%)	18.5	64.8	16.7	4.0
B2	15.6 (0.4%)	1.66 (1.3%)	2.03 (1.0%)	62.5 (0.1%)	15.5 (0.2%)	18.5	64.9	16.6	4.0
C1	11.0 (1.1%)	0.771 (2.1%)	3.35 (0.9%)	78.3 (0.1%)	4.6 (0.5%)	15.0	79.5	5.5	17.1
C2	9.7 (0.3%)	0.688 (2.0%)	3.62 (0.3%)	79.1 (0.1%)	5.1 (0.9%)	14.0	80.1	5.9	15.6
E	10.8 (1.3%)	0.588 (1.1%)	2.02 (0.5%)	71.5 (0.5%)	12.8 (0.8%)	13.7	72.7	13.6	5.6
H1	11.4 (0.8%)	0.968 (0.7%)	2.88 (0.5%)	75.4 (0.1%)	7.5 (0.8%)	14.9	76.8	8.3	10.0
H2	11.3 (0.6%)	0.827 (1.2%)	2.92 (0.7%)	76.8 (0.1%)	6.4 (0.2%)	14.8	78.0	7.2	11.9
H3	11.1 (0.2%)	0.760 (1.4%)	3.04 (0.2%)	77.2 (0.1%)	6.2 (0.3%)	14.7	78.3	6.9	12.4
H4	11.1 (2.2%)	0.792 (5.9%)	3.02 (1.4%)	76.9 (0.3%)	6.8 (1.2%)	14.7	78.0	7.3	11.4
L	11.1 (0.5%)	0.752 (1.8%)	3.27 (0.3%)	79.3 (0.2%)	3.9 (1.4%)	14.9	80.4	4.7	20.3
M1	14.5 (0.8%)	1.093 (3.4%)	2.18 (0.8%)	65.0 (0.5%)	15.6 (0.6%)	17.2	66.5	16.3	4.2
M2	14.2 (0.8%)	0.943 (4.2%)	2.24 (0.8%)	66.3 (0.5%)	14.6 (0.7%)	17.0	67.7	15.3	4.5
P1	11.6 (1.9%)	0.804 (2.6%)	3.24 (1.2%)	78.0 (0.2%)	4.5 (0.4%)	15.4	79.1	5.4	17.2
P2	11.1 (0.9%)	0.736 (1.5%)	3.02 (0.2%)	78.4 (0.1%)	5.1 (0.6%)	14.7	79.5	5.9	15.4
P3	11.1 (0.7%)	0.750 (0.9%)	3.17 (0.6%)	78.8 (<0.1%)	4.3 (0.6%)	14.9	79.9	5.2	18.1
P4	11.5 (0.1%)	0.826 (0.8%)	3.19 (0.4%)	78.4 (0.5%)	4.2 (0.2%)	15.3	79.6	5.1	18.9
P5	11.5 (0.6%)	0.807 (2.7%)	2.80 (0.2%)	77.9 (10.1%)	5.2 (0.4%)	14.9	79.1	6.0	15.0

[a]In parentheses are the relative standard deviations for $n = 3$.

difference spectrum is obtained by subtracting the fresh oil spectrum from the spectrum corresponding to the day of treatment. The data reported triplicate spectra averages.

Kinetic Parameter Calculation. At moderate temperatures, due to the high oxygen concentration dissolved in the oil, the lipid autoxidation is probed to be independent of the oxygen pressure and the oxidation rate follows pseudo-first-order kinetics.[6,7] Hence, the kinetics of the *cis/trans* isomerization will probably follow the same kinetic order. If this hypothesis is true, the isomerization rate should be expressed by

$$v = \frac{d[ROOH]}{dt} = -\frac{d[RH]}{dt} = k[cis\text{-}RH]$$

Hence, the dependence of the amount with time is given by

$$[cis\text{-}RH] = [cis\text{-}RH]_0\, e^{-k(t-t_{ind})}$$

where k is the pseudo-first-order coefficient, t_{ind} is the induction time, and $[cis\text{-}RH]$ and $[cis\text{-}RH]_0$ are the concentrations of the reactant at time t and time 0. This expression is related to the FTIR signal (absorbance around 3006 cm^{-1}) by means of the Beer–Bouguer–Lambert law, and by applying logarithms the next expression is obtained:

$$\ln(S^{cis\text{-}RH}) = \ln(S_0^{cis\text{-}RH}) - k(t - t_{ind})$$

$S^{cis\text{-}RH}$ and $S_0^{cis\text{-}RH}$ are the reactant signal at time t and the apparent initial signal obtained from the straight line. Hence, when $\ln(S^{cis\text{-}RH})$ is plotted versus time (for $t > t_{ind}$), a straight line is obtained. From the slope of the adjusted line the pseudo-first-order coefficient is obtained, and from its intercept and the signal of the *cis* double bond band, the induction time is calculated:

$$t_{ind} = \frac{\ln(S_i^{cis\text{-}RH}) - \ln(S_0^{cis\text{-}RH})}{-k}$$

$S_i^{cis\text{-}RH}$ is the signal of reactant of the fresh oil.

On the other hand, the concentration of the *trans* products is related with time by

$$[trans\text{-}RH] = [trans\text{-}RH]_\infty\bigl(1 - e^{-k(t-t_{ind})}\bigr)$$

where $[trans\text{-}RH]$ and $[trans\text{-}RH]_\infty$ are the concentrations of *trans* products at time t and infinite time. By replacing the concentrations by the FTIR signal (absorbance around 970 cm^{-1}) using the Beer–Bouguer–Lambert law and applying logarithms, the next expression is obtained:

$$\ln\left(\frac{S_\infty^{trans\text{-}RH} - S^{trans\text{-}RH}}{S_\infty^{trans\text{-}RH}}\right) = -k(t - t_{ind})$$

$S^{trans\text{-}RH}$ and $S_\infty^{trans\text{-}RH}$ are the product signals at time t and infinite time, respectively. Therefore, by plotting $\ln((S_\infty^{trans\text{-}RH} - S^{trans\text{-}RH})/S_\infty^{trans\text{-}RH})$ versus time, a straight line is obtained (for $t > t_{ind}$). The slope of the straight line is the pseudo-first-order coefficient, and from the intercept and kinetic coefficient, the induction time is obtained.

Statistical Analysis. The statistical analysis was performed with the help of software package IBM SPSS statistics (version 19, SPSS Inc., Chicago, IL, USA).

■ RESULTS AND DISCUSSION

The composition of major fatty acids was determined as their fatty acid methyl esters by gas chromatography. Table 1 shows the composition of major fatty acids and content of saturated (SFA), monounsaturated (MFA), and polyunsaturated (PUFA) fatty acids and the ratio C18:1/C18:2 (O/L). Arbequina, Manzanilla. and Blanqueta cultivars contain a higher proportion of palmitic and palmitoleic acids (C16:0 and C16:1) than the rest of the cultivars;[27,28] meanwhile, the cultivars Cornicabra, Hojiblanca, Lechin, and Picual show a higher proportion of

Table 2. Correlation Matrix for Major Fatty Acids, Total Saturated Fatty Acids (SFA), Total Monounsaturated Fatty Acids (MUFA), and Total Polyunsaturated Fatty Acids (PUFA)

	C16	C16.1	C18	C18.1	C18.2	SFA	MUFA	PUFA
				correlation *significance (one-tailed)*				
C16	1.000	0.910	−0.838	−0.921	0.813	0.983	−0.910	0.822
	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
C16:1	0.910	1.000	−0.705	−0.778	0.629	0.917	−0.753	0.643
	0.000		0.000	0.000	0.000	0.000	0.000	0.000
C18	−0.838	−0.705	1.000	0.906	−0.904	−0.729	0.905	−0.906
	0.000	0.000		0.000	0.000	0.000	0.000	0.000
C18:1	−0.921	−0.778	0.906	1.000	−0.973	−0.871	0.999	−0.977
	0.000	0.000	0.000		0.000	0.000	0.000	0.000
C18:2	0.813	0.629	−0.904	−0.973	1.000	0.737	−0.980	0.999
	0.000	0.000	0.000	0.000		0.000	0.000	0.000
SFA	0.983	0.917	−0.729	−0.871	0.737	1,000	−0.857	0.748
	0.000	0.000	0.000	0.000	0.000		0.000	0.000
MUFA	−0.910	−0.753	0.905	0.999	−0.980	−0.857	1.000	−0.983
	0.000	0.000	0.000	0.000	0.000	0.000		0.000
PUFA	0.822	0.643	−0.906	−0.977	0.999	0.748	−0.983	1.000
	0.000	0.000	0.000	0.000	0.000	0.000	0.000	

stearic acid (C18:0) than the others.[27,28] This was also observed in a previous study in which Cornicabra virgin olive oil was compared on the basis of fatty acid profile to other Spanish cultivars.[27]

The samples from the Blanqueta and Empeltre cultivars showed the lowest amount of C18:0.[29] Additionally, the samples from the cultivar Blanqueta showed the highest amount of C16:0; meanwhile, the C16:0 content is very low in the Empeltre sample.[29,30] The amount of C16:0 in Cornicabra samples is the lowest.[27]

With regard to oleic and linoleic acids, which are the main fatty acids, two sets of samples are clearly differentiated, one set made up of the cultivars with a high oleic/linoleic acid ratio (O/L > 10.0) and the other with cultivars having low oleic/linoleic acid ratio (O/L < 10.0). The oleic/linoleic acid ratios for the cultivars in growing order are Blanqueta (4.0), Manzanilla (4.2−4.5), Empeltre (5.6), Arbequina (6.4−7.7), Hojiblanca (10−12.4), Picual (15.4−18.9), Cornicabra (15.6−17.1), and Lechin (20.3). Similar results were found in the literature.[27,28,30,31]

The lowest content of MUFA was observed in samples of the Blanqueta cultivar, mainly due to the low content in C18:1 fatty acid. Meanwhile, the highest contents of C18:1 were obtained for Lechin, Cornicabra, and Picual cultivars.[27,31]

The Manzanilla and Blanqueta cultivars showed the highest amount in PUFA; the lowest PUFA content was for the Lechin cultivar.

As shown in Table 2, the composition of fatty acids is highly correlated with significance $p < 0.05$. Hence, PCA was applied to obtain uncorrelated data.

PCA is a useful technique to reduce the number of original variables, keeping the maximum explained accumulated variance. The two first principal components are retained and explain 96.65% of the total variance. The communality values

obtained by applying the proposed model to the data are >0.9. The calculated scores of the different olive oils in the reduced space determined by the first two principal components were used as variables for further statistical analysis.

An unsupervised classification technique such as cluster analysis was applied to visualize the sample classification, using the average linkage method for agglomeration and the square Euclidean distance as a criterion of proximity. The resulting dendrogram classifies the olive oil samples in five groups at a rescaled distance of 6 (Figure S-1 in the Supporting Information). Four groups correspond to a single cultivar: Empeltre, Manzanilla, Blanqueta, and Arbequina. Meanwhile, the fifth group consists of Lechin, Cornicabra, Hojiblanca, and Picual cultivars.

A dendrogram similar to the former was obtained by applying cluster analysis to the calculated scores from the SFA, MUFA, and PUFA contents.

A LDA was applied to the data setting five groups as observed in the cluster analysis above. LDA establishes mathematical functions for the classification allowing differentiating groups of olive oil cultivars. The LDA was conducted stepwise by employing Wilks's statistics for variable selection. The predicted model was applied to each sample of the test set, obtaining a correct classification of the samples in the groups in 100% of the cases. The scores plot for the LDA for the samples in the space formed by the two calculated discriminant functions (DFs) can be observed in Figure 1.

The samples from the Manzanilla, Blanqueta, Arbequina, and Empeltre cultivars show positive values on DF1; meanwhile, the corresponding values for samples from the Cornicabra, Lechin, Picual, and Hojiblanca cultivars are negative. The Empeltre cultivar is differentiated from the rest because of its positive value on DF1 and the lowest value and differentiation in DF2.
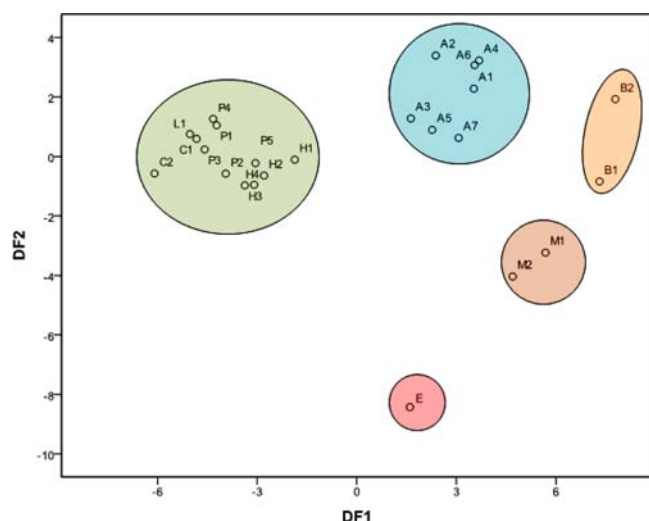
Figure 1. Scores plot of oil samples related to fatty acid composition on the two calculated discriminant functions.

Samples of the cultivar Blanqueta differ from the rest because they show higher scores on DF1. Samples of the Arbequina cultivar are differentiated from the rest by presenting the highest values on DF2 and positive values on DF1. Samples of the Manzanilla cultivar differ from the rest by presenting positive values on DF1 and negative values on DF2.

The data obtained from the FTIR spectra are shown below for monitoring the oxidative degradation of the oil samples by a thermal treatment at 100 °C. For the sake of clarity, the main infrared band assignments and the functional group and relative mode of vibration for the virgin olive oils are shown in Table 3 (the changes can be observed in the difference spectra in Figure S-2 in the Supporting Information).

With regard to the FTIR spectra of fresh oils, the higher is the content in PUFA, the higher is the absorbance and the wavenumber of the maximum corresponding to the band associated with the stretching vibration of the *cis* double bond. Therefore, the cultivars having higher percentages of linoleic acid (Blanqueta, Manzanilla, and Empeltre) show a more intense band, and the wavenumbers of the maxima are observed at higher wavenumber values, whereas cultivars having lower contents in linoleic acid show lower intensity bands and maxima of absorbance at lower wavenumbers. The changes

observed under accelerated thermal degradation conditions show similar trends; the main differences are referred to the time when the changes start and the rate of transformation. The appearance of primary (hydroperoxides) and secondary (carbonyl compounds) oxidation products is observed by spectral changes in the regions from 3700 to 3150 cm^{-1} and from 1800 to 1700 cm^{-1}, respectively. Moreover, these changes take place almost simultaneously with the disappearance of the *cis* double bond and the appearance of *trans* products, so that the oxidation process occurs concomitantly with the *cis/trans* isomerization.

The absorbance decrease in the *cis* double bond and the absorbance increase in the *trans* double bond in the FTIR spectra under oxidative conditions are shown in Figure 2.

Degradation of *cis* Unsaturated Fatty Acids. During the oxidation process, the wavenumber of the maximum absorbance associated with the stretching vibration of *cis* double bonds is shifted to lower values and the band intensity diminishes. The absorbance plot versus time shows a reactant trend, which can be fitted to a pseudo-first-order kinetics, as has been pointed out previously by other authors for the oxidation process.[6]

The kinetic parameter values, such as pseudo-first-order rate coefficient and ln S_0^{cis} from which induction time is calculated, were obtained by linear regression from the FTIR spectral data with the linear range specified in days of treatment (Table 4).

The plot of logarithms of absorbance values versus time can be fitted to a straight line with a high correlation coefficient ($r < -0.993$) during a wide range of time, varying from 14 days for the Lechin sample to 23 days for sample Arbequina 5, confirming that the degradation of the *cis* double bond follows pseudo-first-order kinetics during most of the degradation process.

The calculated rate coefficients (k) were similar for all samples, varying in the range of 0.060−0.074 day^{-1}. As a general trend, the samples that contain more PUFA show higher rate coefficients; for instance, the highest coefficients are attained for Blanqueta, Empeltre, and Manzanilla samples, whereas the lowest are obtained for the cultivars Picual, Lechin, Cornicabra, and Hojiblanca. Another parameter obtained from the straight line is induction time, determined as specified above with its error estimated by error propagation. The longest induction times are obtained for the Lechin cultivar,

Table 3. Most Important Bands for Olive Oil Degradation Study

| wavenumber region (cm^{-1})	funcional group	vibration	wavenumber variation	bandwidth variation	peak absorbance variation
3650−3100	−OH	O—H	variable	increase	increase
~3006	*cis* double bond of FA	C—H stretching	decrease	decrease	decrease
2922	aliphatic (CH$_3$)	C—H stretching	increase	increase	decrease
2853	aliphatic (CH$_2$)	C—H stretching	increase	increase	decrease
1800−1700	carbonyl compounds	C=O stretching	decrease	increase	non significant
1655	double bond	C=C stretching	increase	decrease	decrease
1635	α,β-unsaturated compounds	C=C	decrease	non significant	increase
1418	*cis* disubstituted olefins	C=C—H rocking	decrease	increase	increase
1401	olefinic group	C—H bending in plane	increase	decrease	decrease
1119	tentatively assigned to double bonds	not available	decrease	after a slight increase, decrease	decrease
965−970	*trans* isolated olefins	C—H bending	increase	after a slight decrease, increase	increase
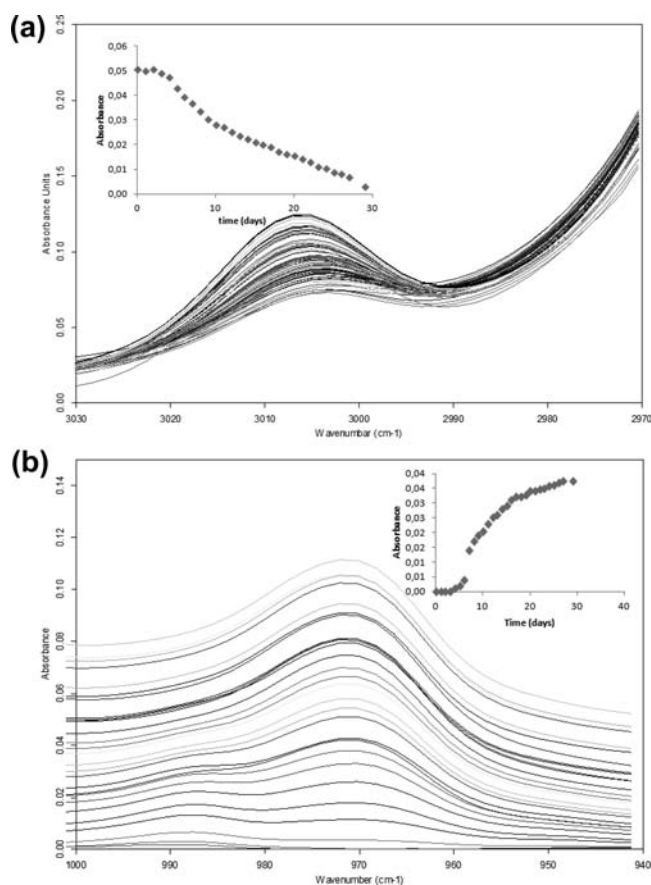
Figure 2. Changes observed for a sample of Arbequina cultivar 30 days under oxidative conditions: (a) decrease of the absorbance of stretching vibration of *cis* double bond around 3006 cm^{-1}; (b) increase of the absorbance of bending vibration of *trans* double bond around 970 cm^{-1}.

whereas the shortest ones correspond to cultivars Arbequina and Manzanilla.

Formation of *trans* Unsaturated Fatty Acids. During the oxidation process, the absorbance increase and the shift toward higher wavenumber of the bending vibration associated with the *trans* double bound are observed. The absorbance plot versus time shows the trend of a product that can be fitted to pseudo-first-order kinetics, as has been pointed out above. Then the signal of the product is fitted to a linear line plotting $\ln((S_\infty^{trans\text{-}RH} - S^{trans\text{-}RH})/S_\infty^{trans\text{-}RH})$ versus time as described above, obtaining the induction time and rate coefficient. The main trouble found is the estimation of $S_\infty^{trans\text{-}RH}$, which is assumed to be the last point measured. The usage of the difference spectra avoids the interference owing to the band that appears at 988 cm^{-1} associated with *trans–trans* and *cis–trans* conjugated double bonds during the first days under oxidative conditions and other surrounding bands. Hence, the absorbance value of difference spectra before the induction time is zero. The linearity is fulfilled during a wide range of time, with relatively high correlation coefficients between −0.995 and −0.999 (as shown in Table 5). The range varies from 14 days for the Lechin sample to 22 days some samples of Arbequina, Blanqueta, Cornicabra, Hojiblanca, and Manzanilla cultivar.

The rate coefficients vary in the range from 0.057 to 0.074 days^{-1} (Table 5). As a general trend, the highest coefficients of reaction rate are obtained by the samples with a higher linoleic acid content (i.e., Blanqueta, Manzanilla, and Empeltre),

whereas the lowest coefficients correspond with the cultivars Cornicabra, Hojiblanca, Picual, and Arbequina. This behavior was pointed out before for *cis* degradation. The induction times are determined as mentioned above from the straight line, with the associated error estimated by error propagation. The longest induction time is obtained by the sample Lechin, whereas the shortest induction times correspond with the cultivars Arbequina and Manzanilla.

Relation between Degradation of *cis* Unsaturated Fatty Acids and Formation of *trans* Unsaturated Fatty Acids. Table 6 shows the correlations between the kinetic parameters calculated for the bands of *cis* and *trans* double bond and their significance levels. Noteworthy is the high correlation between the rate coefficients of *cis* and *trans* and between the t_{ind}^{cis} and t_{ind}^{trans}, in all cases with a level of significance $p < 0.05$. Also, there is a high correlation between $\ln S_0^{cis}$ and $\ln S_0^{trans}$ with t_{ind}^{cis} and t_{ind}^{trans}, which is expected because the induction time is a point of the linearization.

From the results it can be concluded that the induction time for the bands of *cis* double bonds and *trans* double bonds are closely associated with each other, as well as the subsequent decrease in absorbance of the *cis* double bond band, which is significantly associated with the increase in the *trans* double bond band.

The correlation between the induction times and the rate coefficients is low, which indicates that the stability of oils during the first days (induction period) is not clearly associated with the subsequent degradation of the oils.

A regression study was performed to compare the kinetic parameters, induction times, and rate coefficients obtained from the *cis* and *trans* double bond bands. The values of slope and intercept with their confidence intervals, at a significance level $p = 0.05$, were 1.0 ± 0.4 and -0.00 ± 0.03 for the study of the rate coefficients. Meanwhile, the values of slope and intercept with their confidence intervals, at a significance level $p = 0.05$, were 0.9 ± 0.2 and -0.3 ± 0.7 for the regression study of the induction times. In both cases the confidence intervals estimated for the slope and the intercept include the value 1 for the slope and the value 0 for the intercept. The induction times of *cis* and *trans* double bond bands are highly correlated with each other and do not differ statistically significant at $p < 0.05$. During the oxidative degradation of the oils, the rate coefficients of the *cis* and *trans* double bonds are highly and significantly correlated ($p < 0.05$). Hence, no significant differences are observed at a confidence level of 95% between the reaction rate coefficients or between the induction times obtained from absorbance values of *cis–trans* double bond bands.

Relationship between Kinetic Parameters and Fatty Acid Composition. First, a correlation study was performed to establish any possible association between the kinetic parameters calculated and the fatty acid composition. Table 7 shows the correlation values obtained between these parameters and their significance levels. The highest correlation values correspond to the association between the rate constants of *cis* and *trans* fatty acids with MUFA and PUFA, with a value of positive association for PUFA and negative for MUFA, whereas SFA shows correlation values and positive somewhat lower, in each case with a significance level $p = 0.05$. The induction times show lower values of correlation with the fatty acids than the rate coefficients with a lower significance, but $p < 0.05$ in all cases.

Table 4. Summary of the Kinetic Parameters Obtained from the Absorbance of the Stretching Vibration Band of the *cis* Double Bond

cultivar	linear range (days)	$k \pm t_{(n-2)}s_k$ (day^{-1})	$\ln S_0^{cis} \pm t_{(n-2)}s$ ($\ln S_0^{cis}$)	r	n	t_{ind} (day) $\pm s_{t\ ind}$
A1	[3–21]	0.068 ± 0.002	−2.89 ± 0.03	−0.998	19	2.3 ± 0.4
A2	[3–22]	0.066 ± 0.003	−2.91 ± 0.03	−0.997	20	2.2 ± 0.4
A3	[3–22]	0.067 ± 0.003	−2.90 ± 0.05	−0.997	20	2.4 ± 0.5
A4	[3–24]	0.068 ± 0.001	−2.93 ± 0.02	−0.999	22	2.3 ± 0.4
A5	[3–25]	0.069 ± 0.002	−2.83 ± 0.04	−0.997	23	2.3 ± 0.5
A6	[3–19]	0.070 ± 0.003	−2.82 ± 0.04	−0.998	17	2.1 ± 0.4
A7	[3–20]	0.070 ± 0.003	−2.87 ± 0.03	−0.997	18	2.1 ± 0.4
B1	[4–22]	0.072 ± 0.003	−2.71 ± 0.04	−0.997	19	3.3 ± 0.4
B2	[4–21]	0.074 ± 0.003	−2.62 ± 0.04	−0.998	18	3.4 ± 0.4
C1	[5–23]	0.062 ± 0.004	−2.80 ± 0.06	−0.993	19	4.5 ± 0.6
C2	[5–21]	0.063 ± 0.002	−2.80 ± 0.03	−0.997	17	4.0 ± 0.4
E	[6–24]	0.070 ± 0.002	−2.56 ± 0.04	−0.998	19	5.1 ± 0.4
H1	[5–22]	0.065 ± 0.002	−2.77 ± 0.03	−0.998	18	3.9 ± 0.4
H2	[5–22]	0.064 ± 0.004	−2.78 ± 0.06	−0.996	18	3.7 ± 0.4
H3	[5–22]	0.063 ± 0.003	−2.80 ± 0.04	−0.997	18	3.9 ± 0.4
H4	[5–21]	0.066 ± 0.003	−2.59 ± 0.05	−0.997	17	4.1 ± 0.4
L	[8–21]	0.064 ± 0.004	−2.62 ± 0.06	−0.995	14	7.0 ± 0.6
M1	[3–23]	0.070 ± 0.003	−2.82 ± 0.04	−0.997	21	2.4 ± 0.4
M2	[3–21]	0.073 ± 0.002	−2.81 ± 0.02	−0.998	19	2.5 ± 0.4
P1	[5–21]	0.060 ± 0.005	−2.85 ± 0.07	−0.993	17	3.3 ± 0.6
P2	[5–22]	0.061 ± 0.002	−2.78 ± 0.03	−0.998	18	4.2 ± 0.4
P3	[5–21]	0.064 ± 0.006	−2.78 ± 0.09	0.993	17	3.6 ± 0.7
P4	[5–19]	0.062 ± 0.002	−2.87 ± 0.03	−0.998	15	3.9 ± 0.5
P5	[5–22]	0.061 ± 0.002	−2.78 ± 0.04	−0.998	18	4.2 ± 0.4

Table 5. Summary of the Kinetic Parameters Obtained from the Absorbance of the Bending Vibration Band of *trans* Double Bond

cultivar	linear range (days)	$k \pm t_{(n-2)}s_k$ (day^{-1})	$\ln S_0^{trans} \pm t_{(n-2)}s_{\ln S0}^{trans}$	r	n	t_{ind} (day) $\pm s_{t\ ind}$
A1	[3–24]	0.061 ± 0.002	0.15 ± 0.03	−0.997	22	2.5 ± 0.2
A2	[3–24]	0.066 ± 0.001	0.14 ± 0.02	−0.999	22	2.2 ± 0.2
A3	[3–20]	0.059 ± 0.002	0.14 ± 0.03	−0.998	18	2.4 ± 0.2
A4	[3–23]	0.070 ± 0.001	0.14 ± 0.01	−0.9997	21	2.0 ± 0.1
A5	[3–24]	0.065 ± 0.001	0.13 ± 0.02	−0.999	22	2.0 ± 0.2
A6	[4–21]	0.065 ± 0.002	0.13 ± 0.02	−0.999	18	3.5 ± 0.1
A7	[3–24]	0.068 ± 0.002	0.14 ± 0.03	−0.998	22	2.1 ± 0.2
B1	[3–22]	0.074 ± 0.003	0.31 ± 0.04	−0.997	20	2.9 ± 0.3
B2	[4–23]	0.072 ± 0.004	0.34 ± 0.06	−0.996	20	3.4 ± 0.4
C1	[4–25]	0.057 ± 0.002	0.20 ± 0.04	−0.996	22	3.5 ± 0.3
C2	[4–23]	0.068 ± 0.003	0.12 ± 0.03	−0.997	20	3.8 ± 0.2
E	[5–23]	0.070 ± 0.002	0.50 ± 0.03	−0.999	19	4.0 ± 0.2
H1	[4–24]	0.065 ± 0.001	0.21 ± 0.02	−0.999	21	3.3 ± 0.2
H2	[4–23]	0.069 ± 0.004	0.22 ± 0.05	−0.995	20	3.5 ± 0.4
H3	[4–21]	0.066 ± 0.004	0.23 ± 0.05	−0.995	18	3.4 ± 0.3
H4	[4–23]	0.068 ± 0.003	0.23 ± 0.05	−0.996	20	3.5 ± 0.3
L	[8–24]	0.059 ± 0.003	0.44 ± 0.06	−0.997	14	7.4 ± 0.5
M1	[3–21]	0.072 ± 0.002	0.17 ± 0.03	−0.999	19	2.3 ± 0.2
M2	[3–24]	0.073 ± 0.002	0.16 ± 0.02	−0.999	22	2.4 ± 0.2
P1	[4–22]	0.070 ± 0.004	0.17 ± 0.04	−0.997	19	2.7 ± 0.3
P2	[4–21]	0.062 ± 0.002	0.20 ± 0.03	−0.998	18	3.3 ± 0.2
P3	[4–23]	0.060 ± 0.003	0.19 ± 0.05	−0.997	20	3.2 ± 0.4
P4	[4–24]	0.061 ± 0.001	0.22 ± 0.02	−0.999	21	3.1 ± 0.2
P5	[4–22]	0.060 ± 0.002	0.20 ± 0.03	−0.998	19	3.3 ± 0.2

Therefore, it follows that the kinetic parameters of the oil samples, mainly the rate constants, are highly associated with the initial fat composition of the oil samples. In particular, once the induction time passed, the greater the concentration of PUFA, the lower the oxidative stability of oils, whereas the higher the content of MUFA, the higher the oxidative stability.

The induction times are correlated with the initial fat composition, but their values are lower, so this may indicate that there are other substances in the oil composition which clearly affect the initial oxidative stability, such as the presence of antioxidants.

Table 6. Correlation Matrix between the Kinetic Parameters of *cis* and *trans* Double Bond Bands

	correlation significance (one-tailed)					
	K_{cis}	k_{trans}	t_{ind}^{cis}	t_{ind}^{trans}	$\ln S_0^{cis}$	$\ln S_0^{trans}$
K_{cis}	1.000	0.749	−0.454	−0.272	0.194	0.135
		0.000	0.013	0.099	0.182	0.265
k_{trans}	0.749	1.000	−0.340	−0.322	0.188	0.204
	0.000		0.052	0.062	0.189	0.170
t_{ind}^{cis}	−0.454	−0.340	1.000	0.890	0.702	0.742
	0.013	0.052		0.000	0.000	0.000
t_{ind}^{trans}	−0.272	−0.322	0.890	1.000	0.677	0.682
	0.099	0.062	0.000		0.000	0.000
$\ln S_0^{cis}$	0.194	0.188	0.702	0.677	1.000	0.897
	0.182	0.189	0.000	0.000		0.000
$\ln S_0^{trans}$	0.135	0.204	0.742	0.682	0.897	1.000
	0.265	0.170	0.000	0.000	0.000	

The high correlation between the kinetic parameters, mainly rate coefficients, and the initial fatty acid composition of oils highlights the dependence of the oxidative stability of oils on the fatty acid composition. The induction times of oils exhibit a certain dependence, not very marked, on the fatty acid composition; thus, to explain the stability of the oils during this initial period should be considered other compositional substances such as antioxidants present in the olive oil from each cultivar. Once after the induction time of oxidative degradation, high values of rate coefficients, for both reduction of the maximum absorbance of the *cis* double bond band and the maximum absorbance increase of the *trans* double bond band, are associated with low values of MUFA and at the same time high PUFA values.

Classification of Oil Samples Based on the Kinetic Parameters. Subsequently, the possibility of establishing a mathematical model based on the kinetic parameters for classifying the oils in the corresponding cultivar membership is studied.

As previously mentioned, the correlations between the kinetic parameters are high; the Bartlett test of sphericity to the data is applied, obtaining a significance level of $p < 0.001$, indicating the adequacy of the data for PCA application. PCA provides the scores of samples on new uncorrelated variables with each other. The communality values of the original variables in all cases exceed the value of 0.8. In the proposed model, the first two principal components are retained, applying Kaiser's criterion, which accumulate 90% of the total explained variance.

The scores of the principal components are used to display a classification of samples using a method of unsupervised

Table 7. Correlation Matrix between Kinetic Parameters and Fatty Acid Composition

	correlation significance (one-tailed)								
	SFA	MUFA	PUFA	k_{cis}	k_{trans}	t_{ind}^{cis}	t_{ind}^{trans}	$\ln S_0^{cis}$	$\ln S_0^{trans}$
SFA	1.000	−0.857	0.748	0.721	0.530	−0.681	−0.468	−0.255	−0.242
		0.000	0.000	0.000	0.004	0.000	0.011	0.114	0.127
MUFA	−0.857	1.000	−0.983	−0.922	−0.756	0.576	0.434	−0.045	−0.022
	0.000		0.000	0.000	0.000	0.002	0.017	0.417	0.459
PUFA	0.748	−0.983	1.000	0.931	0.785	−0.500	−0.393	0.149	0.115
	0.000	0.000		0.000	0.000	0.006	0.029	0.244	0.297
O/L	−0.701	0.919	−0.934	−0.886	−0.745	0.641	0.529	0.035	0.061
	0.000	0.000	0.000	0.000	0.000	0.000	0.004	0.436	0.388
k_{cis}	0.721	−0.922	0.931	1.000	0.749	−0.454	−0.272	0.194	0.135
	0.000	0.000	0.000		0.000	0.013	0.099	0.182	0.265
k_{trans}	0.530	−0.756	0.785	0.749	1.000	−0.340	−0.322	0.188	0.204
	0.004	0.000	0.000	0.000		0.052	0.062	0.189	0.170
t_{ind}^{cis}	−0.681	0.576	−0.500	−0.454	−0.340	1.000	0.890	0.702	0.742
	0.000	0.002	0.006	0.013	0.052		0.000	0.000	0.000
t_{ind}^{trans}	−0.468	0.434	−0.393	−0.272	−0.322	0.890	1.000	0.677	0.682
	0.011	0.017	0.029	0.099	0.062	0.000		0.000	0.000
$\ln S_0^{cis}$	−0.255	−0.045	0.149	0.194	0.188	0.702	0.677	1.000	0.897
	0.114	0.417	0.244	0.182	0.189	0.000	0.000		0.000
$\ln S_0^{trans}$	−0.242	−0.022	0.115	0.135	0.204	0.742	0.682	0.897	1.000
	0.127	0.459	0.297	0.265	0.170	0.000	0.000	0.000	

pattern recognition such as cluster analysis. A dendrogram was obtained using the squared Euclidean distance as a criterion of distance, and as an agglomeration method, the average linkage between groups (Figure S-3 in the Supporting Information). The dendrogram displays a classification of samples into seven differentiated groups for a rescaled distance of 3. Six of the groups consist of samples belonging to a single variety of oil, particularly the Lechin, Empeltre, Blanqueta, Arbequina, Manzanilla, and Hojiblanca cultivars. The seventh group consists of samples from the Picual and Cornicabra cultivars.

This classification is to be considered to apply LDA to the data to establish discriminant functions and therefore classify oil samples depending on the cultivar. The LDA was conducted stepwise by employing the Wilks' lambda statistic. DF1 is the one with the highest absolute correlation with the first principal component (0.966), whereas DF2 presents the highest absolute correlation with the second principal component (0.994). The classification functions assign each sample to its membership group in a completely correct way, showing 100% of cases correctly classified.

Figure 3 shows the values of the scores of the discriminant functions obtained for each oil sample on the calculated discriminant functions.
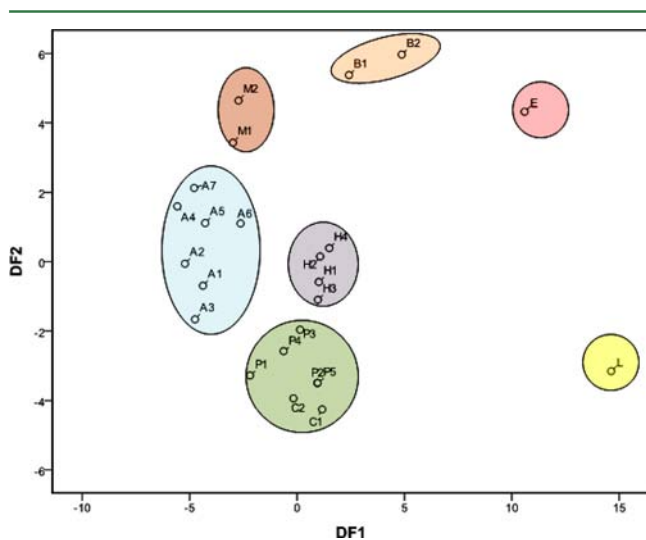

Figure 3. Scores plot of oil samples related to the values of the kinetic parameters on the two calculated discriminant functions.

Samples from the Lechin and Empeltre cultivars differ from the rest by presenting the highest score values on DF1. The difference between them is established because the variety Lechin presents a negative score on DF2, whereas Empeltre presents a positive value.

Samples from the Blanqueta cultivar differ from the rest because they show the highest score values and positive values on DF2.

The samples of the Arbequina and Hojiblanca cultivars show score values close to zero on DF2; they differentiate between them because the score values on DF1 for Hojiblanca samples are positive (close to zero), but they are negative for Arbequina samples.

Samples from the Manzanilla cultivar differ from the rest by presenting negative score values on DF1 and positive and higher values than those of Arbequina on DF2. Samples from the Picual and Cornicabra cultivars are classified jointly, being

characterized by score values close to zero on DF1 and the lower average score values on DF2, but more negative for Cornicabra cultivar.

Comparison between the Classifications of the Olive Oil Samples in the Cultivars Produced by the Initial Composition of Fatty Acids and Kinetic Parameters. The classification of olive oils obtained on the basis of data from the initial composition of fatty acids allows establishing five differentiated groups. A group of oils from the Lechin, Hojiblanca, Cornicabra, and Picual cultivars are those with higher content of MUFA and at the same time lower PUFA. Another consists of the Empeltre cultivar, which stands out for showing a lower content of SFA. Samples from the Blanqueta cultivar differ from the rest because they have the highest content of SFA and PUFA and at the same time lower values of MUFA. Finally, the Arbequina and Manzanilla cultivars show similar SFA contents, but the MUFA content is higher for the Arbequina cultivar and the PUFA content is higher in Manzanilla.

The classification of olive oils obtained on the basis of the kinetic parameters allows us to establish seven differentiated groups. Each of the six differentiated groups consists of samples of a single cultivar, namely, Lechin, Empeltre, Blanqueta, Arbequina, Manzanilla, and Hojiblanca cultivars.

The first two cultivars (Lechin and Empeltre) stand out from the rest for presenting the greatest induction times, that is, the longest period of initial resistance among the samples studied, which means a higher initial resistance to the oxidative degradation. The samples from Blanqueta and Manzanilla cultivars stand out for showing the highest values of rate coefficients for both *cis* and *trans*, which is indicative of a more rapid degradation of the oil after the induction period. The samples from Arbequina cultivar are distinguished by presenting lower induction times, which is indicative of lower resistance to oxidative degradation during the first days of treatment. The samples from Hojiblanca cultivar show both rate coefficients and induction times intermediate. The samples from Cornicabra and Picual cultivars that are classified together highlight for presenting lower values of rate coefficients, so that once the induction time is exceeded, these samples show greater resistance to oxidative degradation.

Pseudo-first-order kinetics for both the decrease in absorbance band related to the *cis* double bond and for the increase in absorbance of the band of *trans* double bond are shown. The high oxidative stability of oils during the initial period is not necessarily linked to a high stability during the second part of the oxidative degradation prior to polymerization of the oil.

Fat composition data of the oils allow a classification of them into five differentiated groups according to their variety of origin, whereas the classification based on kinetic parameters allows a classification into seven differentiated groups. Therefore, the classification established on the basis of the kinetic parameters allows more cultivars to be distinguished. The data of the kinetic parameters differentiate between oils of cultivars Arbequina, Blanqueta, Manzanilla, Empeltre, Lechin, and Hojiblanca; oils from Picual and Cornicabra cultivars are the only ones that cannot be distinguished between them. In contrast to the classification obtained using the data of fatty acids, when using kinetic data, oil from the Lechin cultivar differs very clearly from the rest. This oil presents the greatest oxidative resistance associated with the longest induction time

and with the highest MUFA content and at the same time the lowest PUFA content.

The kinetic parameters obtained from the data of absorbance bands at 3006 cm^{-1} for the disappearance of the *cis* double bond and at 966 cm^{-1} for the appearance of *trans* double bond constitute a valuable tool for cultivar classification of olive oil, offering advantages over the characterization based on fatty acid profile.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

ABBREVIATIONS USED

FTIR spectrometry, Fourier transform infrared spectrometry; PDO, Protected Designation of Origin; PCA, principal component analysis; LDA, linear discriminant analysis; ATR-FTIR spectrometry, attenuated total reflectance-Fourier transform infrared spectrometry; FAME, fatty acid methyl esters; DF, discriminant function; FA, fatty acid; SFA, saturated fatty acids; MUFA, monounsaturated fatty acids; PUFA, polyunsaturated fatty acids; O/L, ratio C18:1/C18:2.

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