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ORIGINAL PAPER

# Classification of Four Almond Cultivars Using Oil Degradation Parameters Based on FTIR and GC Data

**A. Beltrán Sanahuja · M. S. Prats Moya · S. E. Maestre Pérez · N. Grané Teruel · M. L. Martín Carratalá**

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**Abstract** Four almond cultivars (Marcona, Guara, Garrigues and Butte) have been classified using attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) and gas chromatography (GC) data. The data were obtained by completing the first stages of a thermal oxidative degradation process. The degradation process was monitored by using the variations in the main fatty acid methyl esters (FAME) content determined by GC and to changes in the infrared spectra recorded using the ATR-FTIR technique. In order to classify the almond cultivars, a stepwise linear discriminant analysis was applied to the data. The results indicated that, although the four almond oils evaluated here have a similar fatty acid composition, differences in linoleic acid content may be linked to oxidative stability. Butte cultivar samples had higher linoleic acid content and were more prone to oxidative deterioration.

**Keywords** *Prunus dulcis* · Almond oil · Oxidative stability · GC · FAME · ATR-FTIR · Multivariate data analysis

## Introduction

Almond nuts (*Prunus dulcis*) are grown to be eaten on their own as a snack or incorporated into a variety of manufactured food products such as nougat, chocolate and ice cream. In 2006, over 1.1 million tons of almonds were produced throughout the world. California currently dominates the world almond market, producing more than 63.5% of all almonds grown, followed by Spain (18.6%), Italy (10.5%), Greece (4.2%) and Turkey (4.0%) [1].

Despite their high fat content (ranging from 53 to 63% dry weight basis) [2, 3], almonds contain many valuable nutritional components [4]. The health benefits they offer are attributed to their influence on the serum lipid profile and reduced cardiovascular risk in humans [5]. These effects have been linked to their fatty acid composition (i.e. mainly mono and polyunsaturated fatty acids) and to the presence of other minor compounds which have been linked to antioxidant activity (i.e. polyphenols [6] and tocopherols [7]) and to the cholesterol lowering effects of phytosterols [8].

The high unsaturated fatty acid content of these nuts makes almond oil quite susceptible to oxidative degradation resulting in a reduction in almond shelf life. The oxidation processes in several fats have been monitored using different instrumental techniques and several chemical parameters such as iodine, peroxide [9] and anisidine [10] values or changes in the conductivity value of the fat [11]. While monitoring of chemical parameters is often included in standard methods, instrumental techniques can help to carry out a thorough analysis of the changes in fatty acid components throughout the oxidation process.

FTIR spectroscopy has been increasingly used for studying the oxidative stability of oils and fats. [12, 13]. This technique has proved to have several advantages because of its low cost, simple sample preparation and reduced analysis time in comparison with other instrumental techniques such as GC or HPLC.

A number of studies have been published which compare the oxidative stability of different nut oils using FTIR [14]. However, to the best of our knowledge, a comparison

A. Beltrán Sanahuja (✉) · M. S. Prats Moya · S. E. Maestre Pérez · N. Grané Teruel · M. L. Martín Carratalá
Departamento de Química Analítica, Nutrición y Bromatología, Universidad de Alicante, 03080 Alicante, Spain
e-mail: abs12@alu.ua.es

between different almond cultivars has not yet been described in the literature. Since almonds are used as ingredients in food products which are processed at rather high temperature, a study of the thermal stability of almond oil can be useful for identifying the almond cultivars that are most resistant to oxidative degradation.

The aim of the present work was to classify the four almond cultivars studied according to their resistance to a forced oxidative treatment. To this end, the major fatty acid concentration and the FTIR spectrum of almond oil were monitored during the oxidation treatment. In order to classify the almond cultivars a stepwise linear discriminant analysis was applied to the data.

## Experimental Procedures

### Samples

The set of samples characterized in this work consisted of 31 samples from 4 different almond cultivars: 12 Marcona, 9 Guara, 4 Garrigues and 6 Butte samples. The Marcona, Guara and Garrigues cultivars were selected as they are representative of the cultivars grown in Spain and Butte was chosen because it is one of the most widely grown cultivars in the world [15].

All of the samples were from cultivars grown in the same crop year and different samples for the same cultivar were collected from different geographical areas. The first three cultivars were obtained from different Spanish localities i.e. Reus (Tarragona), Santomera (Murcia), Córdoba, Alicante, Agost (Alicante), Xixona (Alicante), Pinoso (Alicante), Zaragoza, Alcañiz (Teruel) and Velez Rubio (Almeria). The Butte samples were grown in California and they were obtained from a Spanish importer (Colefruse, San Juan, Alicante).

### Preparation of the Samples

The samples were acquired with shells and the shells were removed immediately. The kernels were then stored at 7 °C to retain freshness until the oil was extracted.

Just before the oil was extracted, the seeds were ground in a domestic electric grinder (Moulinex, Barcelona, Spain). The seed fragments which passed through a 1.5 mm sieve were stored in a desiccator. Afterwards, 5 g of the ground almond seeds were extracted using a commercial fat extractor (Selecta, Barcelona, Spain) for a period of 90 min with 40 mL of analytical grade petroleum ether (Panreac, Barcelona, Spain). According to the instrument's manufacturer, the temperature of the heating module was set at 135 °C, i.e. roughly two times the boiling point of the extraction solvent. However, the actual temperature of the extraction process was fixed at 60 °C because of the boiling point of the petroleum ether.

The oil obtained was dried under a nitrogen current and kept sealed in an amber vial at −21 °C in the freezer until the treatment or the analysis was carried out. The oil obtained from each sample was a mixture of twelve independent fat extractions.

### Oxidative Treatment

Two grams of almond oil were put into a 3 cm high glass vial (25 mm o.d.) without a lid. The vial was then placed in a Selecta oven at 75 °C in order to accelerate the lipid oxidation process. The temperature was monitored using an external thermometer. A quantity of few drops of oil was sampled at the beginning of the oxidative treatment and every 5 days until the secondary oxidation products appeared (i.e. around the 20th day of the treatment).

As oxidative processes depend on the amount of sample and the surface area in contact with the air, different vials were used for each sample treatment day. Oil for a particular day of treatment was therefore sampled from a new vial which always contained the same amount of oil (i.e. approximately 2 g). This fraction of oil was used for the analysis of fatty acids using GC and for collecting the FTIR spectrum.

### Derivatization of the Fatty Acids

The methylation of the fatty acids was carried out according to the American Oil Chemists' Society method CE-2-66 [16]. The fatty acids contained in 0.3 g of almond oil were transformed into their respective fatty acid methyl esters (FAME) by adding 6 mL of sodium methylate solution and heating the mixture under reflux until one phase was obtained. The sodium methylate solution was prepared by dissolving 3.4 g of sodium (Panreac, Barcelona, Spain) in 1 L of HPLC grade methanol (Scharlau, Barcelona, Spain). A 5% solution of analytical grade sulphuric acid (Panreac) in methanol (Scharlau) was then added to the mixture. After completion of the methylation reaction, the FAME were extracted using 6 mL of hexane (96% GC grade, Scharlau, Barcelona, Spain). A saturated sodium chloride solution (25 mL) was added to the mixture to facilitate the separation of the two layers. A 1-mL sample of the organic layer was mixed with 1 mL of the internal standard solution and the volume made up to 10 mL with hexane in a volumetric flask. A 730 mg/L solution of methyl tridecanoate (98% GC, Sigma, Steingeim, Germany) was used as internal standard as this fatty acid was not present in almonds [17].

### Gas Chromatography

The FAME were analyzed using a Carlo Erba Series 8000 gas chromatograph equipped with a split/splitless injector and a flame-ionization detector (FID). This was connected to a computer equipped with a program for data acquisition and processing (Chrom-card; Fisons Instruments, Poole, UK). The FAME standards were purchased from Sigma. Calibration solution standards were prepared by mixing different amounts of these standards to cover the different concentration range of the almonds' FAME. An internal standard was added to all samples and standard solutions.

The chromatographic column selected was a BPX70 (70% cyanopropyl polysilphenylene-siloxane SGE, 30 m × 0.25 i.d). Experimental conditions were optimized to obtain a good separation of all fatty acid methyl esters. Samples (1 μL) were injected into the split injector at a ratio of 1:30 and a temperature of 230 °C. Helium was used as the carrier gas at a flow rate of 2 mL/min.

The FID temperature was set at 250 °C. The oven temperature was set at 110 °C for 2 min, increased from 110 to 170 °C at 3.0 °C/min and then kept at 170 °C for 4 min. It was then increased to 190 °C at 2.0 °C/min and to 220 °C at 20.0 °C/min, where it was kept for 4 min. At the end of the analysis, the temperature oven returned to the initial temperature (110 °C).

### FTIR Spectroscopy

The IR spectra were collected using a Vector 22 FTIR spectrometer (Bruker Optic Gmbh, Ettlingen, Germany) with OPUS software (version 3.1). A film of a small amount of the oil (five drops) was placed on the ATR device, which was equipped with a ZnSe crystal [18]. The spectra were obtained using 128 scans and ratioed against the spectrum of the clean crystal. The range from 4,000 to 400 $cm^{-1}$, with a resolution of 4 $cm^{-1}$, was used to obtain spectral information. After each measurement, the ATR plate was carefully cleaned by wiping it with analytical grade acetone (Panreac) and dried with a soft tissue before it was filled with the next sample. Three spectra replicates were obtained for each sample.

### Statistical Analysis

Experimental data were processed with the aid of the SPSS statistical package Version 15.0 [19]. The presence of different categories within the almond samples was investigated using linear discriminant analysis (LDA). This is a supervised pattern recognition technique used not only to recognize different classes in a set of data but to obtain classification functions (i.e. vectors) that make it possible to predict to which group a sample belongs using the appropriate latent variables [20]. These latent variables are linear combinations of the initial selected variables that maximize the resolution among the groups. One basic problem encountered when using LDA is deciding which variables should be included in the analysis. This problem can be solved with a stepwise LDA. This criterion is usually applied by minimizing the Wilks' lambda statistics ($\lambda_w$). This parameter is calculated as the sum of the squares of the distances between points belonging to the same category divided by the total sum of the squares. Values of $\lambda_w$ approaching zero are obtained with well-resolved categories, whereas overlapped categories make $\lambda_w$ approach a value of one.

In order to construct the LDA vectors, only the means of the replicates of the samples were included. In this way, the internal dispersion of the categories was reduced. This was important in order to reduce the number of variables selected by the SPSS stepwise algorithm during the construction of the model. According to this algorithm, a predictor variable is selected when the reduction of the $\lambda_w$ produced after its inclusion in the model exceeds an $F$ to enter value, the entrance threshold of a variance comparison test or $F$ test. However, the inclusion of a new predictor modifies the significance of the predictor variables which are already present in the model. For this reason, after the inclusion of a new variable, a rejection threshold, $F$ is used to decide if one of the other predictors should be removed from the model. The process comes to an end when no further predictors are being introduced to or eliminated from the model. A tolerance level of 0.001 was selected in order to set the $F$ to enter (i.e. 1.000) and to remove (i.e. 0.999) thresholds [20].

## Results and Discussion

### Major Fatty Acid Composition Data

The composition of different almond oils was determined by measuring their major fatty acid content i.e. the content of oleic (C 18:1), linoleic (C 18:2), palmitic (C 16:0), stearic (C18:0), and palmitoleic (C16:1) acids. It is widely known that the oil oxidative rate is related to the proportion of poly- and mono-unsaturated fatty acids [21] that are present in the oil sample. Samples that were collected on 0, 11 and 20 days of the oxidative treatment were used for the analyses as notable changes in the FTIR spectra were observed over these periods of the treatment.

The results for the FAME that make up more than 90% of the total fatty acid content of the four almond cultivars are shown in Table 1. The most abundant fatty acid in almond oil was oleic acid (57–74%) followed by linoleic acid (16–28%). There were also smaller amounts of palmitic (6–7%), stearic (1.7–2.7%) and palmitoleic (0.37–0.54%) acids. The

**Table 1** Major fatty acid content (g/100 g of oil) of the four almond cultivars at different days of the oxidative treatment

| Cultivar | Fatty acid methyl esters | Days | | |
|---|---|---|---|---|
| | | 0 | 11 | 20 |
| Marcona | Palmitic (C 16.0) | 6.046 ± 0.368b | 5.580 ± 0.300c | 5.451 ± 0.315c |
| Garrigues | Palmitic (C 16.0) | 6.935 ± 0.256b | 6.380 ± 0.088c | 6.110 ± 0.201c |
| Guara | Palmitic (C 16.0) | 6.055 ± 0.439b | 5.719 ± 0.303bc | 5.469 ± 0.369c |
| Butte | Palmitic (C 16.0) | 6.368 ± 0.590b | 5.916 ± 0.438bc | 5.272 ± 0.536c |
| Marcona | Palmitoleic (C 16.1) | 0.541 ± 0.058b | 0.498 ± 0.051bc | 0.457 ± 0.032c |
| Garrigues | Palmitoleic (C 16.1) | 0.494 ± 0.018b | 0.450 ± 0.015c | 0.369 ± 0.015d |
| Guara | Palmitoleic (C 16.1) | 0.371 ± 0.023b | 0.348 ± 0.025b | 0.313 ± 0.026c |
| Butte | Palmitoleic (C 16.1) | 0.447 ± 0.029b | 0.402 ± 0.032c | 0.332 ± 0.030d |
| Marcona | Stearic (C18.0) | 2.029 ± 0.224b | 1.861 ± 0.235bc | 1.724 ± 0.220c |
| Garrigues | Stearic (C18.0) | 1.948 ± 0.103b | 1.759 ± 0.275b | 1.669 ± 0.208b |
| Guara | Stearic (C18.0) | 2.690 ± 0.162b | 2.449 ± 0.143c | 2.335 ± 0.092c |
| Butte | Stearic (C18.0) | 1.711 ± 0.144b | 1.554 ± 0.104bc | 1.454 ± 0.046c |
| Marcona | Oleic (C 18.1) | 65.876 ± 3.569b | 59.987 ± 4.399c | 54.698 ± 4.083d |
| Garrigues | Oleic (C 18.1) | 74.090 ± 1.045b | 69.387 ± 2.276c | 56.933 ± 1.107d |
| Guara | Oleic (C 18.1) | 67.427 ± 2.124b | 59.811 ± 2.479c | 53.590 ± 4.252d |
| Butte | Oleic (C 18.1) | 57.258 ± 1.111b | 50.610 ± 2.631c | 43.360 ± 1.689d |
| Marcona | Linoleic (C18.2) | 16.728 ± 1.581b | 13.082 ± 1.826c | 3.685 ± 0.937d |
| Garrigues | Linoleic (C18.2) | 20.626 ± 1.933b | 18.105 ± 1.461b | 4.716 ± 0.249c |
| Guara | Linoleic (C18.2) | 16.090 ± 1.026b | 13.634 ± 1.196c | 4.102 ± 1.657d |
| Butte | Linoleic (C18.2) | 28.317 ± 2.066b | 14.953 ± 3.277c | 2.914 ± 1.077d |

Mean ± $SD_m$, $n = 12$ (Marcona), $n = 4$ (Garrigues), $n = 9$ (Guara) and $n = 6$ (Butte). Values followed by different letters in the same row are significantly different at the 5% level

relative standard deviation (RSD) of the determinations was always lower than 10% for each cultivar at different stages of the oxidation process. These results fall in line with data obtained previously [2]. With regard to the comparison between the different cultivars at day 0 of the oxidative treatment, the Butte cultivar had the lowest concentrations of oleic and stearic acids and the highest linoleic acid content. The Guara cultivar had the highest stearic acid content and the lowest palmitoleic acid content.

The concentration of all of the major fatty acids monitored over the course of oxidation decreased from those obtained on day 0. In relative terms, the reduction of the content followed the order linoleic > oleic ~palmitoleic acids. This order falls in line with the data published in the literature which states that linoleic acid reacts with oxygen 10 times faster than oleic acid does [22]. Finally, a small reduction in the amount of saturated fatty acids was observed in all cultivars.

When comparing the fatty acid profile for the four almond cultivars, the different behavior of Butte samples is worth highlighting as there is a greater drop from the initial concentration of linoleic acid when compared to the other three cultivars. On day 20 of the process, 90% of the linoleic acid in the Butte cultivar had degraded. This percentage was lower in samples of the Marcona (78%), Garrigues (77%) and Guara (74%) cultivars. This feature could be used to help differentiate this cultivar from the other three evaluated. However, due to the fact that all major fatty acids may help to differentiate and/or associate cultivars, multivariate techniques are likely to be the most appropriate method for this purpose.

In order to obtain a separate classification for each of the four almond cultivars, a discriminant analysis was applied to the data collected on days 0, 11 and 20 of the treatment. This analysis was conducted stepwise using the Wilk's lambda statistic for variable selection.

The discriminant analysis led to three discriminant functions for all the treatment days selected. In all cases with the first two discriminant functions, 85% of the total variance was retained. Figure 1 shows the mean scores for the almond cultivars. They are projected on the reduced space of the first two discriminant functions at different stages of the oxidation process. By using the calculated discriminant functions, samples were correctly classified in 100% of the cases using the data from days 0 or 20. Samples from day 11 were classified correctly 97% of the time. In this case, one sample was misclassified, this causing the lower correct classification value.

The sample scores in Fig. 1 show that the Garrigues and Marcona samples were very similar at the beginning of the

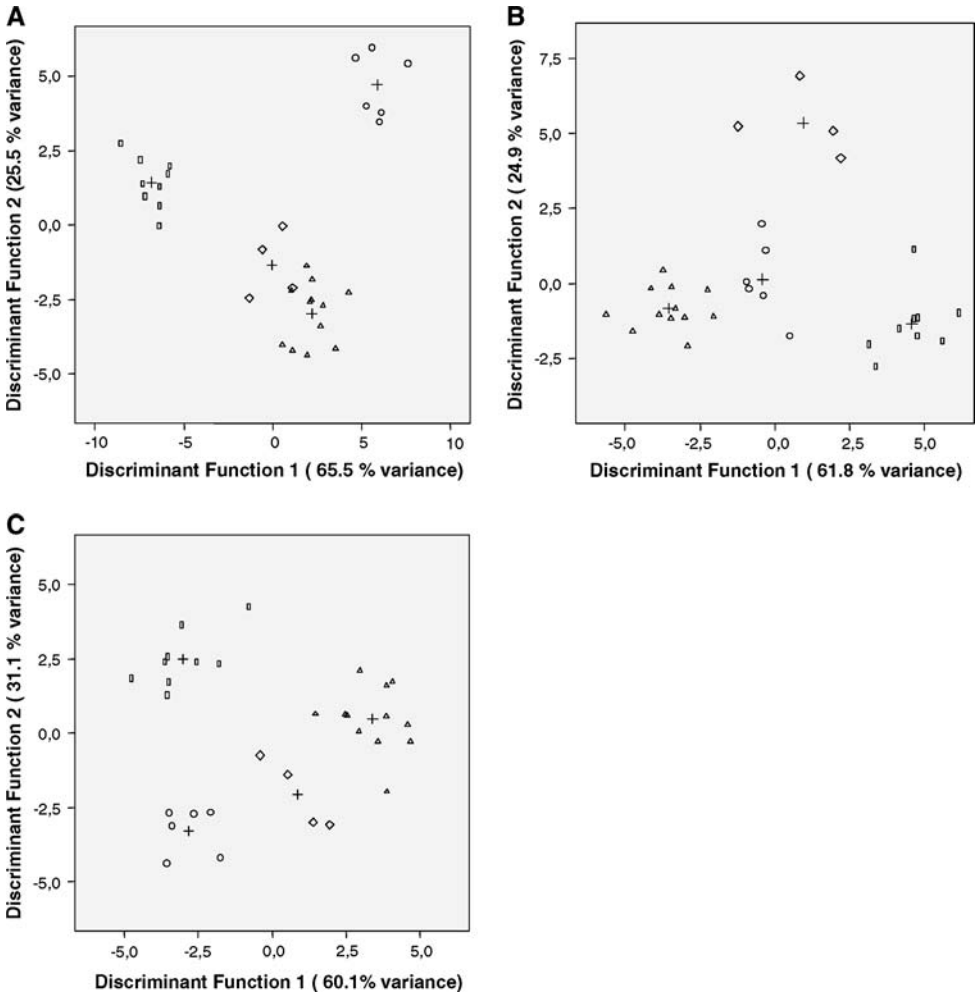


**Fig. 1** Mean scores of almond cultivars for the two discriminant functions at different stages of the oxidative process. *Plus signs* Centroid, *open triangles* Marcona, *open squares* Guara, *open diamonds* Garrigues, *open circles* Butte. **a** 0 days of treatment, **b** 11 days of treatment and **c** 20 days of treatment

process while the other two cultivars were clearly differentiated. As the oxidation progressed, the differences between the four almond cultivars became more obvious. As a result, at the end of the oxidative treatment, the four almond cultivars appeared totally separated in the reduced space formed by the first two discriminant functions.

The scores for the canonical discriminant functions, obtained from the data for day 20 samples, are shown in Table 2. The first discriminant function was influenced predominantly by the palmitoleic, oleic and linoleic acids, and the second discriminant function was determined, predominantly, by the stearic acid. The third discriminant function was influenced mainly by the oleic and palmitic acids.

The Butte cultivar could be differentiated using the initial linoleic acid content and the drop in the concentration of this fatty acid as the oxidative process progresses. However, the other three cultivars could not be differentiated based on this parameter alone. By using the discriminant analysis, based on the major fatty acid content, all four cultivars could be differentiated.

**Table 2** Standardized scores for the canonical discriminant functions obtained 20 days after the beginning of the oxidative treatment

| | Function 1 | Function 2 | Function 3 |
|---|---|---|---|
| Palmitic | 0.264 | −0.460 | 0.725 |
| Palmitoleic | 0.968 | 0.369 | −0.416 |
| Stearic | −0.254 | 1.129 | −0.309 |
| Oleic | 0.888 | 0.257 | 0.788 |
| Linoleic | −0.822 | −0.435 | 0.031 |

## FTIR Data

The FTIR spectra of almond oil showed the typical characteristic absorption bands for common vegetable oils. Figure 2 shows the FTIR spectrum for Butte almond oil at the beginning of the oxidative treatment (day 0). As the almond oils had similar compositions, the FTIR spectra for the other cultivars were very similar and they are not shown in Fig. 2. As the oxidation process progresses, several changes take place in the FTIR spectrum of almond

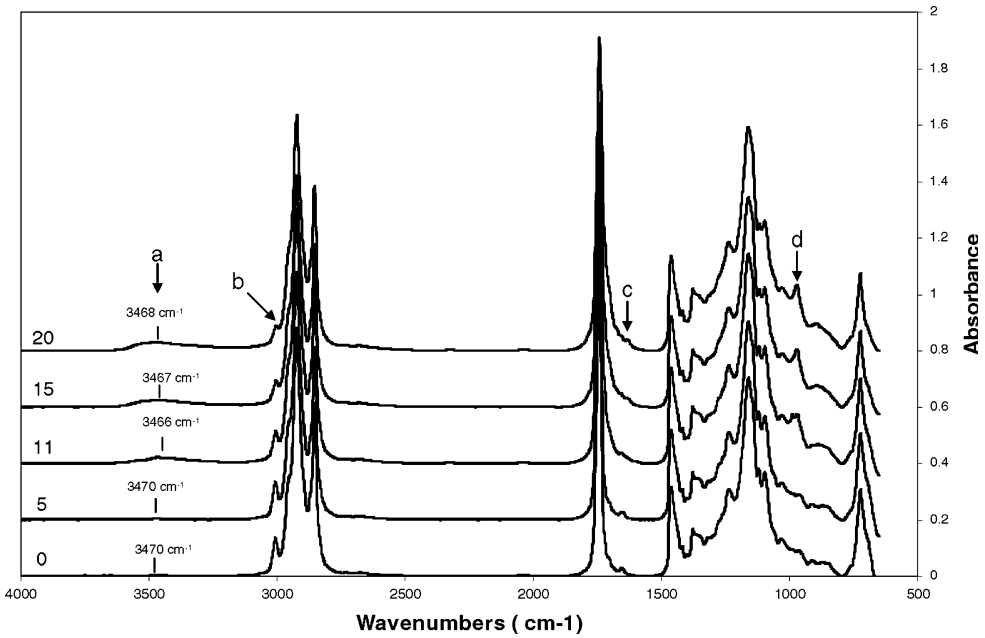


**Fig. 2** Fourier transform infrared spectra of Butte almond oil after 0, 5, 11, 15 and 20 days under oxidative conditions

oil. Figure 2 also shows the Butte oil spectra recorded on days 5, 11, 15 and 20. The spectra for these days have been manually shifted by adding a constant value to the actual absorbance value (i.e. by adding 0.2, 0.4, 0.6 and 0.8) of the spectra on days 5, 11, 15 and 20. The main changes to the spectra appeared at the following regions:

(a) 3,700–3,150 $cm^{-1}$: This region remained unaltered for the first 5 days that the sample was under the degradation conditions. After this period, the profile of this region began to change. Oxidation of the almond oil led to a wider and more intense absorption band in this region in comparison with the raw almond oil spectra. In addition, the frequency of this absorption band decreased slowly as the process progressed (from 3,470 to 3,466 $cm^{-1}$). This decrease in frequency value was due to the overlap with the original band (3,470 $cm^{-1}$) due to the overtone of the glyceride ester carbonyl absorption and new absorptions caused by hydroperoxides or primary oxidation products generated in the oxidation process. In advanced stages of oxidation, the frequency of this band increased towards values similar to those of the original band in raw samples (3,467–3,468 $cm^{-1}$). This can be attributed to the decrease in hydroperoxide concentration and the appearance of new bands due to secondary oxidation products such as alcohols or acids which overlap with those of the hydroperoxide groups. Secondary oxidation products also contributed to the morphology of this band. As such, changes in this band throughout the oxidative treatment were only able to provide us with qualitative information.

(b) 3,010–2,999 $cm^{-1}$: The absorbance of the band at approximately 3,006 $cm^{-1}$ (due to the stretching vibration of CH *cis*-olefinic groups) remained unaltered for approximately 5 days while the sample was under oxidative conditions. Oils with absorbance values lower than the original ones for this band were in advanced stages of oxidation. While the oxidative treatment was taking place, double bonds of unsaturated fatty acids underwent isomerization from *cis* to *trans*. This explained the gradual disappearance of this band as shown in Fig. 2.

(c) 1,800–1,700 $cm^{-1}$: The band which appeared at approximately 1,743 $cm^{-1}$ was due to the ester carbonyl functional group of the triacylglycerides. This band underwent an asymmetric modification throughout the oxidative treatment. Having remained practically unchanged for the first 5 days of the oxidative treatment, its frequency value began to decrease (from 1,743 to 1,741 $cm^{-1}$ approximately) at different rates depending on the oil. This change could be associated with the appearance of saturated aldehyde functional groups or of secondary oxidation products causing an absorption band at 1,728 $cm^{-1}$ which overlaps the band for the ester functional group. As a result of this overlap, the width of this band increased as the oxidative treatment progressed.

(d) 1,000–900 $cm^{-1}$: The absorbance of the band originally at 967 $cm^{-1}$, associated with bending vibrations of CH functional groups of isolated *trans*-olefins, increased at different rates depending on the oil. This band provided us with information about the gradual

*cis* to *trans* isomerization throughout the oxidative treatment.

These results are in line with those obtained for other vegetable oils [23, 24]. The extent of the changes in these regions was related to the differences in almond oil composition. As such, some specific features could be selected to compare the behavior of the cultivars throughout the oxidation process. The features selected were: the absorbance values of the bands appearing at 3,468, 3,006 and 967 $cm^{-1}$ and the width and wavenumber shift for the 1,743 $cm^{-1}$ band.

In Fig. 3 the shift in 1,743 $cm^{-1}$ band and changes in the absorbance at 3,006 $cm^{-1}$ during the oxidative treatment are presented. At the beginning of the oxidative treatment (data for days 0 and 5), no significant differences were found between the almond cultivars in the position of the 1,743 $cm^{-1}$ band (Fig. 3a). However, when the oxidative treatment progressed (data for days 11, 15 and 20) differences between the Butte cultivar and the other cultivars began to appear. The shift in this band is related to the production of some oxidation products [24] (i.e. the more the oxidation process is advanced, the lower wavenumber value of this band will be). This different behavior in the Butte oil is an indication of its lower resistance to oxidative deterioration.

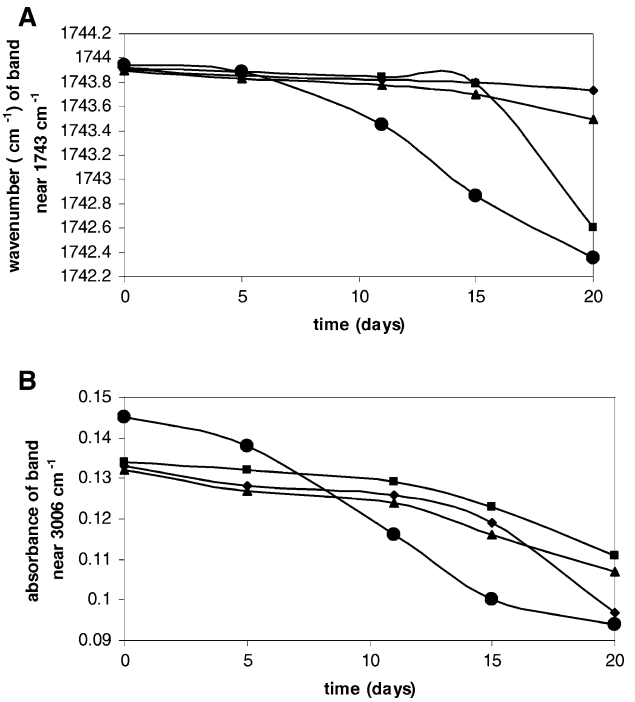


**Fig. 3** Changes in the selected features of the FTIR spectra of the four almond cultivars at different days of the oxidation process. *Filled triangles* Marcona, *filled squares* Guara, *filled diamonds* Garrigues, *filled circles* Butte. **a** Wavenumber of 1,743 $cm^{-1}$ band. **b** Absorbance of 3,006 $cm^{-1}$ band

Previous studies [12–14] had showed that the initial absorbance value of 3006 $cm^{-1}$ band is related to the composition of the oil. Almonds with a large proportion of polyunsaturated acyl groups have higher absorbance values than those with a lower amount. Since the Butte almond oil had the highest linoleic acid content at the beginning of the oxidative treatment, a higher initial absorbance value of this band was expected [24]. This fact was experimentally confirmed by data shown in Fig. 3b. As the oxidation progressed, a decrease in the absorbance value was registered for all cultivars, although the Butte cultivar showed the greatest variation of this parameter, this trend can be attributed to the higher oxidation rate of the Butte oil. It is interesting to note that there were also some differences in the absorbance at 3,006 $cm^{-1}$ between Guara, Garrigues and Marcona on day 20 of the treatment.

As in the case of the GC data, a linear discriminant analysis was carried out in order to try to classify the samples in different groups according to the different almond cultivars. Again, three discriminant functions were obtained using the variable selection rule for minimizing Wilk's lambda. For day 20, the three discriminant functions account for 97.2, 2.0 and 0.8% of the total variance, respectively. The scores for the variables in the first discriminant function were −0.651, 0.533, 1.188 and −0.857 for the 3,006 $cm^{-1}$ region maximum absorbance, 1,743 $cm^{-1}$ band width, 1,743 $cm^{-1}$ band wavenumber and 967 $cm^{-1}$ region maximum absorbance, respectively. It is interesting to note that the data for the maximum absorbance at 3,468 $cm^{-1}$ is not included in the discriminant functions after the stepwise selection of variables.

Figure 4 shows the scores for the almond cultivars projected on the reduced space of the first two discriminant functions obtained after 20 days under oxidative conditions. It is very interesting to note that the Spanish cultivars showed great differences from the American cultivar. However, there is not a clear separation between the Marcona, Guara and Garrigues samples.

By using the calculated classification functions, all the samples were correctly classified into their groups except for one Guara, which was misclassified in the Marcona group.

In conclusion, the results obtained in the present work have shown that the FAME content as determined by GC and the variation in the ATR-FTIR spectra of almond oil can be used to monitor the progress of the oxidation process.

In addition, a comparison of almond oils from different cultivars can be carried out in terms of their oxidative stability. Using multivariate data treatment of the results obtained, differences between the cultivars were highlighted. In this way, the Butte cultivar proved to have a lower oxidative stability, which could, in part, be attributed

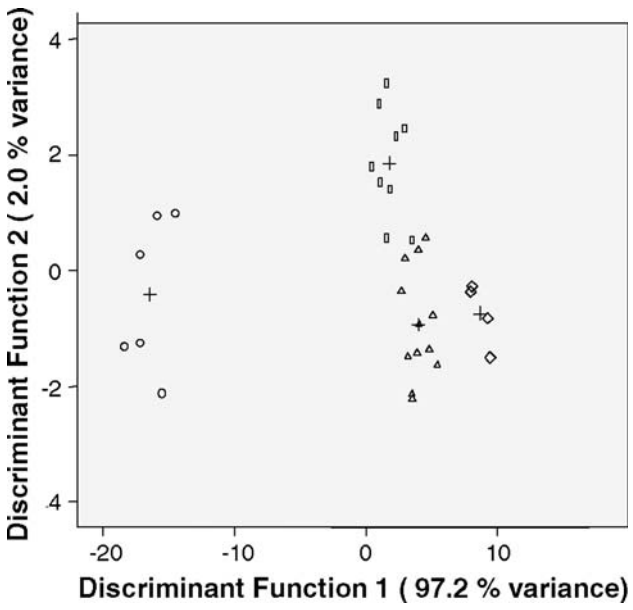


**Fig. 4** Mean scores for almond cultivars for the first two discriminant functions after 20 days under oxidative conditions. *Plus signs* Centroid, *open triangles* Marcona, *open squares* Guara, *open diamonds* Garrigues, *open circles* Butte

to the fact that it had the highest linoleic acid content at the beginning of the process. The other cultivars, Marcona, Guara and Garrigues, were similar in terms of their oxidative stability.

Finally, this work showed that similar results could be obtained using both the GC and FTIR data. However, because of the shorter amount of time required to prepare the samples, the second technique should be selected in order to monitor oil stability, as this will increase the sample throughput.

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