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Fatty Acid Profile of Table Olives and Its Multivariate Characterization Using Unsupervised (PCA) and Supervised (DA) Chemometrics

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The fatty acid composition of 67 commercial presentations of table olives was determined. The most abundant fatty acids, in decreasing order of presence, were C18:1, C16:0, C18:2 n-6, and C18:0. The ranges, expressed as grams of fatty acids per 100 g of edible portion, for the different nutritional fractions were as follows: saturated fatty acids, 2.07−5.99; monounsaturated fatty acids, 5.67−19.42; polyunsaturated fatty acids, 0.52−3.87; and *trans*-fatty acids, 0.08−0.44. Principal component analysis of the matrix of the fatty acid composition led to the deduction of new factors. The first accounted for 55.10% of the total variance and was mainly related to C16:10, C18:0, C20:0, C22:0, C24:0, C18:1, C18:1t, and C20:1. The second factor accounted for 10.33% of variance and was related to C16:1 and C18:2 n-6. They did not permit differentiation among elaboration types or cultivars. However, discriminant analysis was successfully applied for this objective. The fatty acids that most contributed to discriminate among elaboration styles were C17:1, C18:1, C16:0, C17:0, and C18:0 (function 1) and C17:0, C17:1, C20:0, C16:0, C18:1, and C24:0 (function 2). In the case of cultivars, they were C20:0, C18:1, C17:1, C18:2 n-6, C18:1t, and C18:2t (function 1); C18:2 n-6, C18:1, C16:0, C20:0, C18:0, and C18:2t (function 2); and C17:0, C18:3 n-3, and C17:1 (function 3). Results from this study have shown differences among the fatty acid composition and fat content of the diverse commercial presentations of table olives, which can be applied in predictive and classification discriminant analysis.

KEYWORDS: Fatty acids; table olives; saturated fat; monounsaturated fat; polyunsaturated fat; *trans* fat; principal component analysis; discriminant analysis

INTRODUCTION

The fruits of the olive tree are mainly used for the extraction of olive oil, although about 20% of them are prepared as table olives. Table olive production reached a total of 1 600 000 tonnes in the 2003/2004 season, Spain being the main producer and exporter with about 500 000 and 250 000 tonnes, respectively, during this period (*1*). The proximate composition of this product with respect to the main compounds (total fat, total carbohydrates, fiber, etc.) is known and has shown that, after moisture, fat is the most outstanding component (*2*). However, studies related to the composition of the fat from table olives are scarce (*3*, *4*), and the comparative effect of the different processing styles or cultivars on its content has never been studied.

On the contrary, there are numerous references in the literature related to the composition of olive oil. Chemometric techniques have been used extensively in olive oil with diverse objectives (*5*−*8*). Unsupervised methods reveal relationships between oil samples and, at the same time, among analytical data, to produce a clustering of variables and samples into distinct groups. In supervised methods, a set of data describing oils of known origins is used to construct models that are then applied to classify unknown oil samples into a priori established groups, either geographically or by cultivar. Lee et al. (*9*) used the fatty acid (FA) composition in vegetable oils together with principal component analysis (PCA) and discriminant analysis (DA) to differentiate among sesame, perilla, soybean, corn germ, canola, rapeseed, olive, and coconut oils and proposed these techniques to detect adulterations.

FA analysis and chemometrics have also been used in other food or vegetable products. Abrodo et al. (*10*) studied the FA composition to differentiate between traditional and controlled cider fermentation. The use of PCA, DA, soft independent modeling of class analogy (SIMCA), and partial least squares (PLS) allowed the authors to typify fermented apple products on the basis of fermentation technology, lauric and palmitic acids being the most relevant variables for classification purposes. FAs from seeds of *Pinus pinea* L. were studied by PCA and showed that the low genetic diversity revealed by acid composi-

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tion could be explained by the anthropogenic diffusion of genetically homogeneous reproductive material (*11*).

Nutritional labeling requires the inclusion in the nutrition facts of information on total fat content (expressed as grams of triglycerides) and its different nutritional fractions: saturated fatty acids (SFA), monounsaturated fatty acids (MUFA), polyunsaturated fatty acids (PUFA), and *trans*-fatty acids (TFA). There is a consumer concern about fat, in general, and, especially, SFA and TFA contents in foods. In addition to the effects of saturated fat on health, metabolic and epidemiological studies have also pointed out the relationship between TFA intake and coronary heart disease (*12*) as well as its potential adverse effects on the metabolism of essential FAs (*13*). However, information on fat content in table olives is scarce, and no data related to the presence of TFA in this product have yet been published.

The aim of this work was (i) to study the FA composition of the different Spanish commercial presentations of table olives as well as to estimate their different nutritional fractions (SFA, MUFA, PUFA, TFA, and total fat) and (ii) to use such data for the classification and mapping of the products, using unsupervised (PCA) and supervised (DA) multivariate analysis.

MATERIALS AND METHODS

Samples. Samples belonged to the following styles, cultivars, and commercial presentations.

Green Spanish style: Gordal, plain, pitted, and seasoned; Gordal stuffed with red pepper strips, natural red pepper, almond, cucumber, onions, garlic, and jalapeño; and a blend of Gordal olives and red pepper strips called "salads"; Manzanilla, plain, pitted, sliced, anchovy flavored, and plain seasoned; Manzanilla stuffed with red pepper strips, anchovy strips, marinated anchovy strips, natural red pepper, almond, almond and red pepper, salmon strips, tuna strips, onions, capers, garlic, hazelnut, hot pepper, hot pepper strips, piquillo pepper, lemon paste, ham paste, orange strips, cheese, jalapeño strips, and garlic strips; a blend of pitted or sliced Manzanilla olives with red pepper strips called "pitted salads" and sliced "salads", respectively; a blend of Manzanilla olives with slices of carrot added called "gazpachas"; and a blend of Manzanilla olives and capers called "alcaparrado"; Carrasqueña, pitted; a blend of pitted Carrasqueña olives and red pepper strips, called "salads"; and a blend of Carrasqueña olives and capers called "alcaparrado"; Hojiblanca, plain, pitted, and sliced; and Hojiblanca olives stuffed with red pepper strips.

Directly brined olives: Gordal, broken "seasoned" turning color; Manzanilla, turning color in brine alone, "seasoned" turning color, and plain; Manzanilla olives from biologic (or ecologic) production; Hojiblanca, "seasoned" turning color; Arbequina, "seasoned" turning color; Aloreña, green "seasoned" broken, prepared from fresh fruits and from stored olives; Verdial, green "seasoned" broken.

Ripe olives (by alkaline oxidation): Gordal, plain; Manzanilla, pitted; Carrasqueña, plain and pitted; Hojiblanca, plain, pitted, and sliced; Cacereña, plain, pitted, and sliced.

Analyses were carried out in duplicate on composite samples from each commercial presentation, which were made up of three to eight units (cans, jars, or plastic pouches), depending on their sizes, and different packing dates, from one to five elaboration companies, according to their availability on market shelves. Producers kindly supplied those commercial presentations not available in the local markets. Average time from packing was ≈3 months.

Fatty Acid Analysis. Determination of FAs was accomplished through the quantification of their methyl esters (FAMEs) by GC in the extracted fat from olives. Fat was obtained by extracting 12 g of dry samples with hexane, in triplicate, for 6 h, using a Soxhlet. The solvent was removed in a rotary evaporator at 40 °C, and the residual oil was dried in an oven at 105 °C until constant weight (*14*). Methylation of the fat extracts was performed by heating the fat (100 mg) with 4 mL of 0.2 N sodium methylate in methanol plus 1 mL of internal standard solution (undecanoic acid, C11:0, 5 mg/mL), followed by heating in an acidic medium (*15*). A Hewlett-Packard 5890 series II gas chromatograph, incorporating a fused silica capillary column Select FAME (100 m × 0.25 mm, 0.25 μm film thickness) (Varian, Bellefonte, PA) and a flame ionization detector, was used for GC analysis. Hydrogen was used as the carrier gas at 1 mL/min. The injector (split 1:20) and detector temperatures were 250 °C. The operating conditions were as follows: oven temperature was held at 120 °C for 5 min and then increased by 4 °C/min to 240 °C and held for 20 min at 240 °C. Saturated and unsaturated methyl esters (C_4−C_{24}) (Sigma, St. Louis, MO) were used as reference standards as well as linoleic and linolenic acid methyl ester isomers mix, which were also purchased from Sigma.

The weights of the individual FAMEs were calculated on the basis of their integrations relative to the undecanoin internal standard and were corrected using gas chromatograph response factors for each FA (*16*). Individual FAME weights were converted to the equivalent weights of triglycerides using the appropriate conversion factors (*17*, *18*). Total fat was calculated as the sum of all FAs, expressed as triglycerides. SFA, MUFA, PUFA, and TFA were calculated following their NLEA definitions (*19*) and amendment related to TFA inclusion in nutrition labeling (*20*).

GC-MS analysis of fat samples was performed with a Fisons MD800 quadrupole mass selective detector (VG Analytical) interfaced with a CarloErba 8000 series II gas chromatograph. The column and the experimental chromatographic conditions were the same as in the GC analysis. Electron impact (EI) spectra were recorded at 70 eV. Full spectra (50−650 amu) were recorded at a scan speed of 1 spectra s^{-1} over the entire elution profile. Data were analyzed using a Masslab 1.4 version Data System from Fisons and spectra obtained for the methyl esters of interest matched with Wiley mass spectral library.

Statistical Analysis. Data from the chromatographic analyses were arranged in a 136 × 28 matrix array, where rows were cases and columns were variables (FAs plus their nutritional fractions SFA, MUFA, PUFA, TFA, and total fat). Elaboration types were coded as 1 (green Spanish style), 2 (directly brined), and 3 (ripe olives); cultivars were also coded as 1 (Gordal, G), 2 (Manzanilla, M), 3 (Carrasqueña, CR), 4 (Hojiblanca, H), 5 (Arbequina, AR), 6 (Aloreña, AL), 7 (Verdial, VRD), and 8 (Cacereña, CC).

The chemometric study was carried out using a reduced standardized matrix of data, from which SFA, MUFA, PUFA, TFA, and total fat (linear combinations of determined FAs) and the minor FAs C15:0, C21:0, C23:0, C24:1, C20:2, and C20:3 n-6 were removed. Then, data were successively studied by multiple analysis of variance (MANOVA) to test overall differences between groups across the different variables, PCA, and DA. For the selection of the number of PCs, the Kaiser criterion, as modified by Jolliffe (*21*), was followed, and only factors with eigenvalues >0.7 were retained. The DA model was built following the backward stepwise analysis option, which first includes all of the variables in the model and, then, at each step, eliminates the variable that least contributes to membership prediction. The process continues until only the important variables that contribute most to the discrimination between groups were in the model. The values of probability to enter or to remove were fixed at 0.05 and 0.1, respectively. The number of steps was fixed at 100, the minimum tolerance was fixed at 0.01, and no variable was forced to enter in any model. The prior probabilities were established proportional to the number of samples in each group.

A leave-one-out cross-validation procedure was performed for assessing the performance of the classification rule. In this last step, the sample data minus one observation was used for the estimation of the discriminant functions, and then the omitted variable was classified from them. The procedure was repeated for all samples. Consequently, each sample was classified by discriminant functions, which were estimated without its contribution (*22*). The table olive samples were plotted on the canonical axes (discriminant coordinates). These axes were determined in such a way that the ratio of the variability intergroups at the variability intragroups was maximized. These axes are orthogonal for the scalar product defined by the intragroup covariance matrix (*22*).

Table 1. Average Values (Standard Deviation in Parentheses) of the Fatty Acid Composition of Table Olives, Expressed as Grams per 100 g of Edible Portion, According to Processing Types and Cultivars:[a] Green (Spanish Style) and Ripe Olives (California Style)

	green olives				ripe olives[b]				
fatty acid	G ($n = 22$)	M ($n = 62$)	CR ($n = 6$)	H ($n = 6$)	G ($n = 2$)	M ($n = 2$)	CR ($n = 4$)	H ($n = 6$)	CC ($n = 6$)
C14:0	0.0030 (0.0011)	0.0060 (0.0072)	0.0026 (0.0004)	0.0029 (0.0002)	0.0017 (0.0001)	0.0028 (0.0001)	0.0006 (0.0013)	0.0026 (0.0026)	0.0004 (0.0010)
C15:0	0.0005 (0.0008)	0.0008 (0.0014)	0.0007 (0.0011)	0.0005 (0.0009)	0.0000	0.0000	0.0000	0.0000	0.0000
C16:0	1.17 (0.23)	2.53 (0.33)	1.94 (0.61)	2.06 (0.19)	1.22 (0.13)	2.71 (0.13)	2.91 (0.28)	1.93 (0.13)	2.02 (0.32)
C17:0	0.017 (0.003)	0.027 (0.003)	0.024 (0.006)	0.022 (0.001)	0.015 (0.002)	0.030 (0.002)	0.032 (0.004)	0.022 (0.001)	0.010 (0.004)
C18:0	0.215 (0.036)	0.398 (0.059)	0.341 (0.087)	0.305 (0.033)	0.157 (0.017)	0.439 (0.017)	0.501 (0.056)	0.315 (0.036)	0.279 (0.059)
C20:0	0.052 (0.010)	0.082 (0.013)	0.068 (0.015)	0.063 (0.007)	0.040 (0.003)	0.099 (0.003)	0.098 (0.012)	0.063 (0.007)	0.061 (0.011)
C21:0	0.0037 (0.0034)	0.0030 (0.0034)	0.0017 (0.0031)	0.0012 (0.0022)	0.0045 (0.0006)	0.0069 (0.0006)	0.0087 (0.0013)	0.0036 (0.0033)	0.0023 (0.0026)
C22:0	0.015 (0.004)	0.024 (0.005)	0.020 (0.004)	0.018 (0.002)	0.011 (0.002)	0.034 (0.002)	0.027 (0.004)	0.018 (0.004)	0.018 (0.004)
C23:0	0.0041 (0.0014)	0.0016 (0.0026)	0.0020 (0.0017)	0.0034 (0.0010)	0.0026 (0.0007)	0.0049 (0.0007)	0.0018 (0.0037)	0.0015 (0.0017)	0.0008 (0.0019)
C24:0	0.0072 (0.0028)	0.0089 (0.0021)	0.0077 (0.0018)	0.0078 (0.0013)	0.0049 (0.0004)	0.0120 (0.0004)	0.0092 (0.0018)	0.0071 (0.0007)	0.0069 (0.0011)
C16:1	0.078 (0.011)	0.165 (0.039)	0.119 (0.040)	0.101 (0.026)	0.056 (0.008)	0.192 (0.008)	0.177 (0.014)	0.090 (0.009)	0.119 (0.021)
C17:1	0.032 (0.006)	0.051 (0.006)	0.043 (0.012)	0.041 (0.002)	0.035 (0.003)	0.060 (0.003)	0.063 (0.007)	0.040 (0.003)	0.020 (0.008)
C18:1	6.91 (1.25)	10.65 (1.48)	9.01 (2.37)	9.74 (1.13)	5.54 (0.51)	12.18 (0.51)	13.77 (1.80)	9.81 (1.01)	10.26 (1.34)
C20:1	0.034 (0.006)	0.045 (0.009)	0.036 (0.008)	0.043 (0.007)	0.029 (0.002)	0.056 (0.002)	0.053 (0.007)	0.043 (0.005)	0.046 (0.005)
C24:1	0.0035 (0.0046)	0.0012 (0.0039)	0.0176 (0.0114)	0.0210 (0.0324)	0.0125 (0.0069)	0.0152 (0.0069)	0.0040 (0.0081)	0.0003 (0.0071)	0.0135 (0.0068)
C18:2 n-6	1.05 (0.55)	0.99 (0.44)	0.52 (0.17)	0.79 (0.21)	0.64 (0.05)	1.03 (0.05)	0.78 (0.07)	0.80 (0.14)	0.42 (0.08)
C18:3 n-3	0.138 (0.022)	0.126 (0.019)	0.106 (0.021)	0.011 (0.009)	0.138 (0.010)	0.127 (0.010)	0.137 (0.012)	0.137 (0.014)	0.095 (0.042)
C20:2	0.0002 (0.0010)	0.0014 (0.0023)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0006 (0.0013)	0.0000
C20:3 n-6	0.0006 (0.0020)	0.0020 (0.0024)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
C22:2 n-6	0.042 (0.017)	0.049 (0.017)	0.019 (0.004)	0.023 (0.004)	0.005 (0.003)	0.013 (0.003)	0.008 (0.002)	0.012 (0.006)	0.008 (0.004)
C18:1t	0.097 (0. 023)	0.179 (0.036)	0.122 (0.039)	0.122 (0.026)	0.072 (0.008)	0.182 (0.008)	0.187 (0.025)	0.129 (0.016)	0.133 (0.025)
C18:2t	0.012 (0.008)	0.015 (0.007)	0.020 (0.006)	0.011 (0.003)	0.005 (0.001)	0.013 (0.001)	0.007 (0.002)	0.007 (0.003)	0.004 (0.001)
C18:3t	0.012 (0.013)	0.015 (0.013)	0.008 (0.011)	0.009 (0.009)	0.003 (0.000)	0.028 (0.000)	0.022 (0.003)	0.015 (0.014)	0.002 (0.006)

[a] G, Gordal; M, Manzanilla; CR, Carrasqueña; H, Hojiblanca; CC, Cacereña. [b] Values in parentheses for groups with two commercial presentations represent the pooled standard deviation (df = 2).

The different statistical techniques used in this work were implemented using STATISTICA, release 6.0 (*23*), and SYSTAT, release 10.2 (*24*).

RESULTS AND DISCUSSION

Qualitative Fatty Acid Composition of Table Olives. The GC and GC-MS of the FAMEs from the fat of the different table olive samples permitted the identification of the following FAs: myristic acid (C14:0), pentadecanoic acid (C15:0), palmitic acid (C16:0), margaric acid (C17:0), stearic acid (C18:0), arachidic acid (20:0), heneicosanoic acid (C21:0), behenic acid (C22:0), tricosanoic acid (C23:0), lignoceric acid (C24:0), palmitoleic acid (C16:1, undifferentiated), heptadecenoic acid (C17:1), oleic acid (C18:1, including C18:1 n-9 and C18:1 n-7), eicosenoic acid (C20:1), nervonic acid (C24:1), linoleic acid (C18:2 n-6c,c), linolenic acid (C18:3 n-3c,c,c), eicosadienoic acid (C20:2 n-6c,c), eicosatrienoic acid (C20:3, undifferentiated), docosadienoic acid (C22:2), elaidic acid (C18:1t), *trans*-linoleic acid (C18:2t, including all trans forms: ct, tc, and tt), and *trans*-linolenic acid (C18:3t, including all trans forms: cct, ctc, tcc, ctt, tct, ttc, and ttt).

Quantitative Fatty Acid Composition of Table Olives. Mean values and standard deviations of the FA composition for elaboration type and cultivars are shown in **Tables 1** and **2**. The most abundant FAs were C18:1, C16:0, and C18:2 n-6. The C18:1 content ranged from 6.91 (Gordal) to 10.65 (Manzanilla) g/100 g of edible portion (ep), in green; from 5.53 (Gordal) to 13.77 (Carrasqueña) g/100 g of ep, in ripe; and from 11.38 (Verdial) to 19.20 (Arbequina) g/100 g of ep, in directly brined olives. The second most abundant FA was C16:0. Its ranges were from 1.17 (Gordal) to 2.53 (Manzanilla) g/100 g of ep in green, from 1.21 (Gordal) to 2.91 (Carrasqueña) g/100 g of ep in ripe, and from 2.14 (Hojiblanca) to 5.06 (Arbequina) g/100 g of ep in directly brined olives. The concentration of C18:2 n-6 was within the following ranges: from 0.52 (Carrasqueña) to 1.05 (Gordal) g/100 g of ep in green, from 0.42 (Cacereña) to 1.03 (Manzanilla) g/100 g of ep in ripe, and from 1.65 (Verdial) to 3.64 (Arbequina) g/100 g of ep in directly brined olives. Similarly to table olives oils, C18:1 has been reported to be the predominant FA in canola, soybean, and rapeseed oils (*9*). In sesame oils and corn germ oils the most important FA has been found to be C18:2 n-6 followed by C18:1 (*9*).

Nutritional Fractions of Fat in Table Olives. FA analysis allowed the estimation of the different nutritional fractions (SFA, MUFA, PUFA, and TFA), expressed as FAs, and total fat, expressed as triglycerides, in all of the commercial table olive presentations. Their average values, according to cultivar and commercial presentations, are shown in **Table 3**. The highest content of total fat was found in directly brined olives, especially in cv. Arbequina with >30 g/100 g of ep; Manzanilla, Hojiblanca, and Gordal had contents of ≈20 g/100 g of ep. The lowest concentration within this style was found in Aloreña. Green table olives presented relatively low concentrations, which ranged from ≈11 g/100 g of ep (Gordal) to ≈16 g/100 g of ep (Manzanilla). Ripe olives had variable concentrations of total fat; the highest content was observed in Carrasqueña, which had a total fat content close to 20 g/100 g of ep, followed by Manzanilla (≈18 g/100 g of ep). These concentrations of total fat are comparable to those reported by Ünal and Nergiz (*4*), who also found a gradation from green to naturally black olives, or by Borzillo et al. (*3*) for Oinotria table olives. The MUFA (due to the high content of oleic acid) was the main component of total fat. As in olive oil, it accounted for ≈60−80% of the fat content of the different commercial presentations of table olives. PUFA was ≈1 g/100 g of ep in most green and ripe olives, except for Carrasqueña (green), Gordal (ripe), and Cacereña (ripe), which were poorer in such fat. The contents of MUFA and PUFAs were proportionally higher in directly brined olives. SFA was, in general, fairly low, and TFA had a very limited presence; its value per U.S. serving (15 g of ep) could always be expressed as 0. To our knowledge, this is the first time that detailed information on trans fat in table olives has been published.

Table 2. Average Values (Standard Deviation in Parentheses) of the Fatty Acid Composition of Table Olives, Expressed as Grams per 100 g of Edible Portion, According to Processing Types and Cultivars:[a] Directly Brined Olives

fatty acid	G ($n = 2$)	M ($n = 6$)	H ($n = 2$)	AR ($n = 2$)	AL ($n = 4$)	VRD ($n = 2$)
C14:0	0.0050 (0.0001)	0.0050 (0.0010)	0.0035 (0.0001)	0.0060 (0.0001)	0.0044 (0.0004)	0.0057 (0.0001)
C15:0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0003 (0.0002)
C16:0	2.70 (0.09)	3.13 (0.21)	2.14 (0.09)	5.06 (0.09)	3.29 (0.02)	2.56 (0.09)
C17:0	0.027 (0.001)	0.033 (0.006)	0.023 (0.001)	0.039 (0.001)	0.010 (0.001)	0.029 (0.001)
C18:0	0.382 (0.046)	0.516 (0.108)	0.533 (0.046)	0.653 (0.046)	0.533 (0.106)	0.417 (0.046)
C20:0	0.084 (0.009)	0.100 (0.014)	0.085 (0.009)	0.157 (0.009)	0.123 (0.027)	0.099 (0.009)
C21:0	0.0000	0.0028 (0.0037)	0.0000	0.0000	0.0049 (0.0041)	0.0038 (0.0001)
C22:0	0.022 (0.005)	0.027 (0.006)	0.023 (0.005)	0.054 (0.005)	0.034 (0.016)	0.033 (0.005)
C23:0	0.0027 (0.0033)	0.0016 (0.0026)	0.0032 (0.0033)	0.0070 (0.0033)	0.0019 (0.0013)	0.0006 (0.0033)
C24:0	0.0090 (0.0031)	0.0104 (0.0015)	0.0086 (0.0031)	0.0211 (0.0031)	0.0130 (0.0043)	0.0107 (0.0031)
C16:1	0.128 (0.006)	0.218 (0.055)	0.094 (0.006)	0.010 (0.006)	0.154 (0.102)	0.116 (0.006)
C17:1	0.054 (0.003)	0.062 (0.008)	0.041 (0.003)	0.080 (0.003)	0.017 (0.001)	0.051 (0.003)
C18:1	11.68 (0.58)	12.87 (0.96)	11.70 (0.58)	19.20 (0.58)	14.31(0.90)	11.39 (0.58)
C20:1	0.060 (0.006)	0.056 (0.010)	0.059 (0.006)	0.099 (0.006)	0.076 (0.009)	0.065 (0.006)
C24:1	0.0000	0.0000	0.0000	0.0304 (0.0040)	0.0084 (0.0112)	0.0032 (0.0040)
C18:2 n-6	2.41 (0.11)	1.77 (0.88)	2.15 (0.11)	3.64 (0.11)	1.84 (0.28)	1.65 (0.11)
C18:3 n-3	0.206 (0.008)	0.184 (0.039)	0.168 (0.008)	0.183 (0.008)	0.156 (0.009)	0.176 (0.008)
C20:2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
C20:3 n-6	0.0000	0.0000	0.0000	0.0093 (0.0132)	0.0000	0.0000
C22:2 n-6	0.077 (0.008)	0.054 (0.018)	0.058 (0.008)	0.038 (0.008)	0.071 (0.022)	0.089 (0.008)
C18:1t	0.219 (0.044)	0.221 (0.031)	0.212 (0.044)	0.392 (0.044)	0.213 (0.034)	0.207 (0.044)
C18:2t	0.004 (0.006)	0.024 (0.015)	0.031 (0.006)	0.046 (0.006)	0.021 (0.005)	0.021 (0.006)
C18:3t	0.005 (0.002)	0.005 (0.001)	0.009 (0.002)	0.007 (0.002)	0.008 (0.017)	0.008 (0.002)

[a] G, Gordal; M, Manzanilla; H, Hojiblanca; AR, Arbequina; AL, Aloreña; VRD, Verdial. Values in parentheses for groups with $n = 2$ represent the pooled standard deviation (df = 4).

Table 3. Average Values (Standard Deviation in Parentheses) of the Saturated (SFA), Monounsaturated (MUFA), Polyunsaturated (PUFA), and *trans* Fat (TFA) (Expressed as Fatty Acid) as Well as Total Fat (as Triglycerides) in Table Olives, Expressed as Grams per 100 g of Edible Portion, According to Processing Types and Cultivars

processing type	cultivar[a]	SFA	MUFA	PUFA	TFA	total	PUFA/SFA	(MUFA + PUFA)/(SFA + TFA)
green olives	G ($n = 22$)	2.08 (0.28)	7.06 (1.27)	1.23 (0.55)	0.12 (0.03)	10.95 (2.11)	0.59	3.77
	M ($n = 62$)	3.08 (0.40)	10.92 (1.50)	1.17 (0.44)	0.21 (0.05)	16.08 (2.33)	0.38	3.68
	CR ($n = 6$)	2.41(0.72)	9.23 (2.43)	0.64 (0.18)	0.15 (0.05)	13.00 (3.53)	0.27	3.86
	H ($n = 6$)	2.49 (0.22)	9.94 (1.15)	0.96 (0.23)	0.15 (0.03)	14.16 (1.62)	0.39	4.13
ripe olives[b]	G ($n = 2$)	1.45 (0.14)	5.67 (0.52)	0.74 (0.06)	0.08 (0.01)	8.31 (0.76)	0.51	4.19
	M ($n = 2$)	3.34 (0.14)	12.50 (0.52)	1.18 (0.06)	0.22 (0.01)	18.03 (0.76)	0.35	3.84
	CR ($n = 4$)	3.59 (0.36)	14.07 (1.83)	0.91(0.08)	0.22 (0.03)	19.65 (2.40)	0.25	3.93
	H ($n = 6$)	2.37 (0.17)	9.99 (1.01)	0.95 (0.15)	0.15 (0.03)	14.07 (1.40)	0.40	4.34
	CC ($n = 6$)	2.40 (0.39)	10.46 (1.36)	0.52 (0.09)	0.14 (0.03)	14.14 (1.94)	0.22	4.32
directly brined olives[c]	G ($n = 2$)	3.23 (0.12)	11.93 (0.59)	2.70 (0.12)	0.26 (0.05)	18.94 (0.97)	0.84	4.19
	M ($n = 6$)	3.82 (0.31)	13.20 (0.96)	2.01 (0.92)	0.25 (0.05)	20.17 (2.09)	0.53	3.74
	H ($n = 2$)	2.82 (0.12)	11.90 (0.59)	2.38 (0.12)	0.25 (0.05)	18.14 (0.97)	0.84	4.65
	AR ($n = 2$)	5.99 (0.12)	19.42 (0.59)	3.87 (0.12)	0.44 (0.05)	31.09 (0.97)	0.65	3.62
	AL ($n = 4$)	2.40 (0.39)	10.46 (1.36)	0.52 (0.09)	0.14 (0.03)	14.14 (1.94)	0.22	4.32
	VRD ($n = 2$)	3.16 (0.12)	11.62 (0.59)	1.91 (0.12)	0.24 (0.05)	17.71 (0.97)	0.60	3.98

[a] G, Gordal; M, Manzanilla; CR, Carrasqueña; H, Hojiblanca; CC, Cacereña; AR, Arbequina; AL, Aloreña; VRD, Verdial. [b] Values in parentheses for groups with $n = 2$ represent the pooled standard deviation (df = 2). [c] Values in parentheses for groups with $n = 2$ represent the pooled standard deviation (df = 4).

The nutritional value of these products in relation to their fat composition could be deduced using well-known indices, such as the PUFA/SFA ratio or the (PUFA + MUFA)/(SFA + TFA) ratio (*25, 26*). Nutritional guidelines recommend a PUFA/SFA ratio of >0.4 (*27*). To our knowledge, a specific recommendation concerning the second ratio has not been published, but for keeping low plasma and liver cholesterol the (PUFA + MUFA)/SFA ratio has been suggested not to exceed 3 (*28*). A significantly higher PUFA/SFA ratio was found in directly brined olives (mean ± standard error, 0.61 ± 0.04) than in green (0.42 ± 0.02) or ripe olives (0.32 ± 0.02). However, the second index was significantly higher in ripe olives (4.20 ± 0.06) than in directly brined (3.94 ± 0.09) or green olives (3.75 ± 0.04), with no significant differences between the last two. Therefore, it appears that the directly brined olive is the healthiest product, that is, with the most favorable indices.

Chemometric Study of the Fatty Acid Composition of Table Olives. The MANOVA analysis of data showed that there were significant differences in FA composition among elaboration types and cultivars at $p < 0.05$. Thus, the data were appropriate to be subjected to a chemometric study.

The data matrix containing only FAs was subjected to a PCA. Basically, the extraction of the principal component (PC) amounts to a variance maximizing (varimax) rotation of the original variable space (*23*). A new set of nine orthogonal variables (axes), the PCs, was generated, and the variance contained in the starting data set was concentrated in the first PCs. Only the first PC had a high eigenvalue (9.37) and accounted for a high percentage of variance (55.10%). The second and third were at a marked distance because they had 1.76 and 1.39 eigenvalues and accounted for 10.33 and 8.19% of the variance, respectively. The following PCs progressively

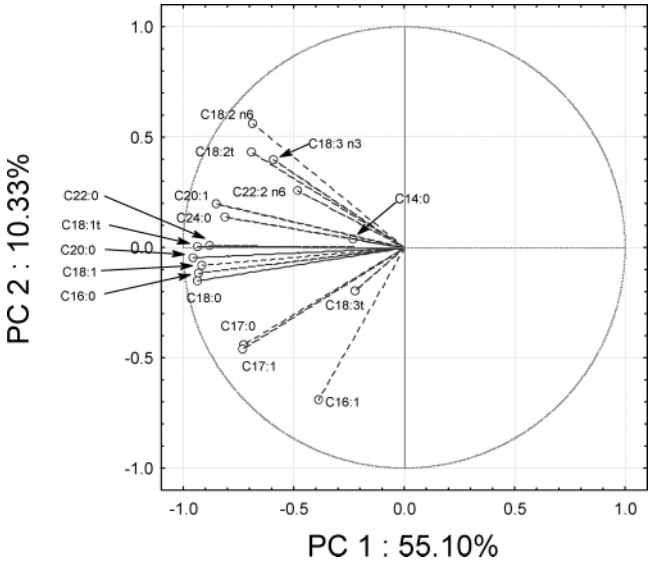

Figure 1. Projection of loadings of the variables in the first two PCs.

explained less and less variance. The projections of the variable loadings on the plane defined by the first two PCs are illustrated in **Figure 1**. These projections allowed a visualization of the position of the variables on the plane and the corresponding correlations. In this case, the correlation coefficient between two variables is the cosine of the angle of their respective vectors (90°, no correlation at all) (*29*). Thus, C18:2 n-6 had a very low correlation with C16:1, C17:1, and C17:0. Similarly, C18:3 n-3 was not correlated with C16:1. On the contrary, the following FAs had a high correlation among them: C16:0, C18:0, C18:1, C18:1t, C20:0, and C22:0. They, in turn, had a weaker relationship with C17:0, C17:1, C20:1, and C24:0. In addition, the projections (loads) of the variables on the PC1 and PC2 axes represent their contributions to them. PC1 was mainly related to the following FAs (loads in parentheses): C20:0 (−0.95), C16:0 (−0.93), C18:0 (−0.93), C18:1t (−0.93), C18:1(−0.91), C22:0 (−0.88), C20:1(−0.85), and C24:0 (−0.81). As expected, PC2 was not so strongly related to FAs, C16:1 (−0.69), C18:2 n-6 (0.56), C17:1 (−0.46), C17:0 (−0.44), and C18:2t (0.43) being those with the highest loads. When the scores for the cases were plotted as a function of PC1 versus PC2, no evident segregation between cases according to treatments and cultivars was observed (data not shown). These results indicated that PCA could hardly lead to a possible reduction of the number of variables or to a proper classification of cases.

Then, predictive DA was applied to the reduced standardized matrix of FAs with the objective of exploring its classification abilities. A back stepwise procedure led to the selection of only the following variables (in decreasing order of *F* to remove) to determine the discriminant functions: C22:2 n-6, C16:0, C18:1, C18:3 n-3, C17:0, C17:1, C18:3t, C20:0, C18:2t, C24:0, C18:2 n-6, and C18:0. The procedure led to a correct classification of 100% of the ripe, 89% of the directly brined (two classified as green), 95% of the green (five classified as ripe), and 95% overall olive samples into the appropriate groups. The jack-knifed classification (leaving out one case at a time as one form of cross-validation) showed 95, 83, 94, and 93%, respectively, correct answers. Thus, apparently, the procedure is efficient for assigning each sample to the correct elaboration type and would be useful in discriminant classification analysis to predict the type to which a future unknown sample could belong.

A canonical analysis was also carried out to study the contribution of each variable to the discrimination among groups. The first canonical function is the linear combination of variables that maximizes the differences between the means of the *k* groups in one dimension. The second canonical function represents the maximum dispersion of the means in a direction orthogonal (perpendicular) to the first direction and so on. The variables that most contributed to discrimination in function 1 were C17:1, followed by C18:1, C16:0, C17:0, and C18:0. In function 2, the most outstanding contributions were from C17:0, C17:1, C16:0, and C18:1. The nature of the discrimination for each discriminant (canonical) function can be identified by plotting (function 1 versus function 2) the individual scores of cases for the discriminant functions (**Figure 2**). It was found that the green, directly brined, and ripe olive commercial presentations were clearly clouded together in three separate

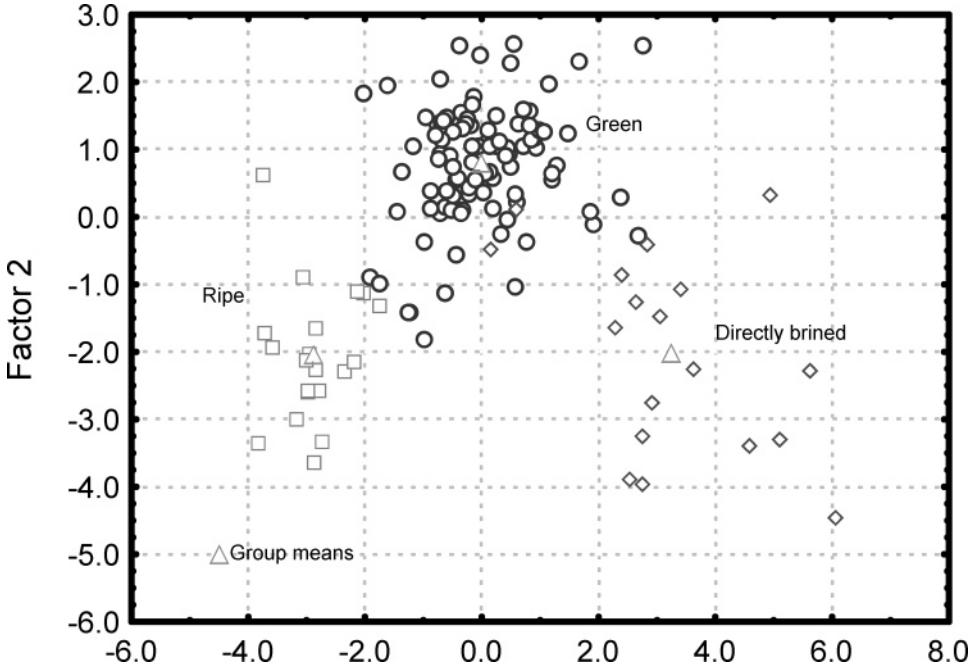

Figure 2. Plot of sample scores and group means, according to elaboration styles, as a function of the two canonical discriminant functions.

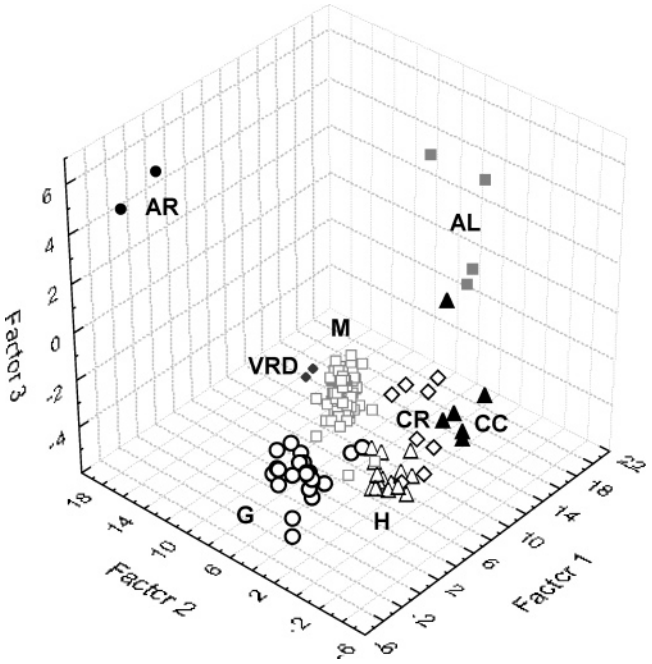

Figure 3. Plot of sample scores, according to cultivars, as a function of the three first canonical discriminant functions: (○) Gordal; (▲) Cacereña; (◆) Verdial; (■), Aloreña; (●), Arbequina; (□), Manzanilla; (◇), Carrasqueña; (△), Hojiblanca.

groups around their respective means. Directly brined olives were characterized by high scores for function 1, negative values for function 2, and a relatively wide distribution among samples (corresponding to a relatively high dispersion in their compositions). Ripe olives were related to negative values for both functions 1 and 2. Green olives had function 1 scores of around 0 and mainly positive values for function 2. These differences in FA composition that permitted discrimination among elaboration types must be due to the diverse treatments to which each of them were subjected or the maturation degree at which the fruits from each style were picked.

The FA composition was also used to discriminate among cultivars (eight). The predictive DA procedure followed was similar to that previously described for elaboration types. The variables selected in decreasing order of *F* to remove were C18:1, C18:2 n-6, C18:2t, C16:0, C18:1t, C18:3 n-3, C16:1, C20:0, and C18:0. Others with lower *F* values were C17:1, C24:0, C22:2 n-6, C22:0, and C17:0. In this case, the classification showed 94 and 99% correct answers for Hojiblanca and Manzanilla, respectively, and 100% correct answers for the rest of the cultivars, with an overall score of 99% correct answers, although one must consider the limitations derived from the reduced number of samples in some commercial presentations. The jack-knifed matrix showed 92, 94, and 88% correct answers for Gordal, Manzanilla, and Hojiblanca, respectively, and 100% correct assignations for the rest of the cultivars, with a total of 93% correct answers for all cultivars. The most outstanding contributions were due to C20:0, C18:1, C17:1, C18:2 n-6, C18:1t, and C18:2t (function 1); C18:2 n-6, C18:1, C16:0, C20:0, C18:0, and C18:2t (function 2); and C17:0, C18:3 n-3, and C17:1 (function 3). These three functions accounted for 90.4% of the total variability in FA composition among cultivars. The rest of the functions accounted for progressively decreasing percentages. The plot of the corresponding sample scores on the space defined by the first three functions allowed for the visualization of eight well-differentiated groups (cultivars) (**Figure 3**). Then, the procedure might also be useful for a discriminant classification analysis of future samples of unknown cultivars.

In summary, the present work has quantified the complete FA composition and the different nutritional fractions (SFA, MUFA, PUFA, TFA, and total fat) of the main Spanish table olive commercial presentations. This study is of general interest because most of the olives commercialized at international scale are from Spain. Results showed that there are differences among the fat compositions of table olives, according to types and cultivars. The discriminant functions deduced might be used in further discriminant classification analysis to identify elaboration styles or cultivars.

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