**Relating sensory analysis with SPME-GC-MS data for Spanish-style green table
olive aroma profiling**

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Abstract

The sensory profile and volatile composition of 24 samples of Spanish-style green table olives were studied by Quantitative Descriptive Analysis and solid phase micro-extraction gas chromatography coupled to mass spectrometry (SPME-GC-MS), respectively, with the aim to characterize this type of table olive. The aroma of samples was described by the sensory panel using nine descriptors (lactic, green fruit, ripe fruit, grass, hay, musty, lupin, wine, and alcohol). A total of 133 volatile compounds were identified in the headspace of samples. Principal component analysis (PCA) applied to both datasets showed a poor separation of samples according to cultivars, but a trend to separate according to sampling time. Reliable partial least squares (PLS) regression models were developed for four sensory descriptors (lactic, lupin, wine, and alcohol) and allowed identifying the compounds both positively and negatively correlated to such odor sensations. Such models could be used to predict the intensity of the above-mentioned descriptors as a function of SPME-GC-MS data.

Keywords: green table olives, aroma, sensory profile, SPME-GC-MS, chemometrics

1. Introduction

Spanish-style green table olive is considered one of the main fermented vegetable products in western countries (Breidt, McFeeters, Perez-Diaz, & Lee, 2013). The flavor is one of the key drivers of consumers' appreciation of this type of table olive, which is closely related to both qualitative and quantitative composition of volatile and non-volatile compounds (Sabatini & Marsilio, 2008). In previous studies, using headspace solid-phase microextraction (HS-SPME) and gas chromatography coupled to mass spectrometry (GC-MS), we identified more than 100 volatile compounds in the headspace of totally fermented green table olives (Cortés-Delgado et al., 2016; Sánchez et al., 2018). Olive cultivar and production area were found to affect the volatile composition of Spanish-style green table olives (Cortés-Delgado et al., 2016). In addition, the volatile concentration of these olives was found to change as a result of post-fermentation and packing stages (Sánchez et al., 2018). Aside from the above publications, other studies concerning the volatile composition of Spanish-style green table olives have been carried out in order to evaluate the major headspace components of olive brine (Montaño, Sánchez, & Rejano, 1990), to identify the volatiles responsible for the unpleasant odor of zapatera olives (Montaño, de Castro, Rejano, & Sánchez, 1992), to screen for key odor compounds (Iraqi, Vermeulen, Benzekri, Bouseta, & Collin, 2005), to evaluate the effects of regulated deficit irrigations (Cano-Lamadrid et al., 2015), and to evaluate the effects of different plastic containers (Sánchez et al., 2017).

Sensory analysis based on a trained expert panel is still necessary for table olive classification and quality control, although it is not always feasible due to the scarcity of trained panels, the cost and the time required for analysis (Marx et al., 2017). Flavor evaluation of table olives according to the procedure described by the International

Olive Council (IOC) is based on the perception of negative sensations (abnormal fermentation, musty, rancid, cooking effect, soapy, metallic, earthy, and winey-vinegary) without taking into account any positive sensation (IOC, 2011). In fact, although the pleasant odor/taste of Spanish-style green table olives is probably the most appreciated characteristic for consumers, no study has been published concerning the description or evaluation of positive sensations in this type of table olive. A complete characterization of sensory profiles has been reported for other types of table olives such as Aloreña table olives (Galán-Soldevilla, Pérez-Cacho, & Campuzano, 2013) and black ripe olives (Lee, Kitawad, Sigal, Flynn, & Guinard, 2012). Recently, we have performed a panel study to characterize the aroma of typical samples of Spanish-style green table olives by using both positive and negative descriptors (López-López et al., unpublished results). On the basis of the frequency of citation, the following odor descriptors were selected by the panel: lactic, green fruit, ripe fruit, grass, hay, musty, lupin, wine, and alcohol. However, no investigation relating these sensory attributes to volatile components was carried out. In fact, to the best of our knowledge, no previous studies on correlations between sensory and instrumental analysis have been published in any type of table olive. On the other hand, several studies have been carried out on this topic in other foods such as wine (Vilanova et al., 2012), tea (Qin et al., 2013), fruits (Aprea et al., 2012), and olive oil (Procida, Cichelli, Lagazio, & Conte, 2016).

It is known that in general the perceived odors in foods are the result of a mixture of odorants, hence a multivariate analysis is suited to explore the relationship between sensory attributes and volatile compounds (Aprea et al., 2012). Among multivariate techniques, partial least squares (PLS) regression has been used by several researchers for determining relationships between instrumental data (X-matrix) and descriptive sensory data (Y-matrix) (Qin et al., 2013; Lee, Vázquez-Araújo, Adhikari,

Warmund, & Elmore, 2011; Xiao et al., 2014). Also, PLS has been used to develop predictive models of sensory attributes, this being interesting from a practical point of view since it might potentially reduce the need of sensory panels and avoid the several deficiencies associated with them (Aprea et al., 2012).

The objectives of the present study were: (1) to study the volatile composition and sensory attributes of different samples of Spanish-style green table olives using HS-SPME-GC-MS analysis and Quantitative Descriptive Analysis (QDA), respectively, and (2) to elucidate the relationship between volatile compounds and sensory attributes by PLS and identify the compounds that could potentially contribute to odor perception.

2. Materials and Methods

2.1. Samples

Olives from the three most popular Spanish cultivars (Manzanilla, M; Gordal, G; and Hojiblanca, H) devoted to green table olives were collected in different locations from the south of Spain (Estepa, E; Alcalá de Guadaira, Al; Utrera, U; Córdoba, C; Almendralejo, Am; and Arahál, A) at a maturity stage suitable for processing. At our laboratories, the raw olives (in total 8 samples, coded as MAI, MAm, MC, GU, GA, HE, HC, and HA, where the code denotes the cultivar followed by the location), were processed according to the Spanish style method. Initially, olives were treated with a lye solution of 1.9 g NaOH/100 mL until the lye penetrated two-thirds of the way through the flesh. Later, olives were washed with water to remove the NaOH residues. Then, the olives were covered with brine (12 g NaCl/100 mL) and allowed to spontaneously ferment for 7 months. After that, the salt level and pH value of each sample were adjusted to 9 g NaCl/100 mL and 3.9, respectively, to guarantee good preservation

during the post-fermentation stage, which lasted 4 months. Finally, after a conditioning step in water, the olives were packed in glass bottles (type “B250”, 125 g fruits plus 120 mL brine capacity) using brine acidified with lactic acid as cover liquor. Amounts of lactic acid and NaCl in cover liquor were calculated to give equilibrium values of 0.5 g/100 mL and 5 g/100 mL, respectively. Sampling was carried out at three times along the elaboration process: after fermentation (coded as 1), after post-fermentation (2), and after packing (3). Therefore, in total 24 samples of Spanish-style green table olives were analyzed. The physicochemical and microbiological characteristics of these samples are shown in Table 1S. The major end-products of fermentation are shown in Table 2S.

2.2. Chemical and microbiological analyses

The pH, titratable acidity, combined acidity, sodium chloride, total polyphenols, and microbial populations (lactic acid bacteria and yeasts) were measured following the routine procedures used in our laboratories area (Cortés-Delgado et al., 2016). The major end-products of fermentation (lactic acid, acetic acid, succinic acid, and ethanol) were analyzed by HPLC using a C18 column and deionized water (pH adjusted to 2.2 using concentrated H_3PO_4) as the mobile phase (Sánchez, de Castro, Rejano, & Montaña, 2000).

2.3. Sensory analysis

The sensory profile of samples were obtained using the QDA method performed by a trained panel, composed of 15 judges (9 males and 6 females). They were recruited because of their major role in the implementation of the Method for the Sensory Analysis of Table Olives (IOC, 2011) and their high level of training as a result of participating in the habitual sensory analysis of table olives in our department for

decades. The judges were familiarised with the QDA technique by training them 1 h twice a week for two months. The initial draft of descriptors was generated by using fermented samples from different cultivars and origins. After training with the references and once the judges agreed to be familiar with the new set of descriptors, the panel was used for the QDA. The panel performance had been evaluated previously and showed good repeatability and reproducibility (López-López et al., unpublished results). Nine odor descriptors were evaluated by the panel. Following Miller and Chambers (2013), references for the diverse descriptors were provided for each judge along with definitions/reference sheet (Table 1). Samples were served in cups coded with a 3-digit random number in individual booths under incandescent white lighting at the sensory laboratory of our department in the Instituto de la Grasa. Olives were presented in a balanced, randomized order to the judges in order to avoid any order effect. Tap water was used for mouth rinsing between each sample evaluation. Samples were analyzed in duplicate. The judges were asked to score the olives using a 10-cm unstructured scale. Anchor ratings were 1 (no perception) and 11 (extremely strong). The marks in the questionnaire were transformed into data by taking measurements (in 0.1 cm) from the left anchor. Mean scores (panel average) for each descriptor were obtained and used for further analysis.

2.4. HS-SPME-GC-MS analysis

Volatile compounds were analyzed by HS-SPME-GC-MS following the procedure described in a previous work (Sánchez et al., 2018). Approximately 200 g of olives were pitted and homogenized, and 2.5 g of pulp were inserted in a 15 mL glass vial. After the addition of a 7.5 mL of NaCl solution (300 g/L), 100 µL of 3-octanol (2 mg/L) as internal standard, and a stirring bar (for stirring at 600 rpm), the vial was

closed and placed in a water bath adjusted to 60 °C. Three replicates per each sample were prepared and analyzed. Headspace volatile compounds were extracted for 60 min on a divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) fiber (1cm, 50/30 µm; Supelco, Bellefonte, PA). Volatile compounds adsorbed on the SPME fiber were desorbed at 265 °C for 15 min in the injector port of a GC interfaced with a mass detector (internal ionization source: 70 eV) with a scan range from m/z 30 to 400 (GC model 7890A and mass detector model 5975C, Agilent Technologies, Santa Clara, CA). Separation was achieved on a VF-WAX MS capillary column (30 m x 0.25 mm x 0.25 µm film thickness) from Agilent. The initial oven temperature was 40 °C (5 min), then 40-195 °C at 3 °C/min, and then 195-240 °C at 10 °C/min and held there for 15 min. The carrier gas was helium at a constant flow of 1 mL/min. Compound identification was based on mass spectra matching with the standard NIST 08 MS library and on the comparison of retention indices (RI) sourced from NIST Standard Reference Database and from authentic reference standards when available. For the determination of the RI, a C7-C30 *n*-alkanes series was used, and the values were compared, when available, with values reported in the literature for similar chromatographic columns. The volatile compounds were quantified by comparison of peak areas in the ion extraction chromatogram (IEC), which was obtained by selecting target ions for each compound, to that of internal standard (3-octanol). These ions corresponded to base ion (m/z 100% intensity), molecular ion (M^+) or another characteristic ion for each molecule. Hence, some peaks that could be co-eluted in scan mode can be integrated with a value of resolution greater than 1.

2.5. Statistical analyses

Principal component analysis (PCA) was performed to assess the internal degree of correlation of the variables in the sensory and instrumental data. Hierarchical cluster analysis (HCA), using Euclidian distance and Ward's method as similarity criterion, was carried out to cluster the samples in homogenous groups. Both PCA and HCA were performed with XLSTAT v. 2016 (Addinsoft, New York, NY, USA). A first PLS regression was also performed with XLSTAT v. 2016 to correlate the volatile data (X-matrix) and sensory data (Y-matrix). Then, PLS was performed with SIMCA 14.1 software (Umetrics, Umea, Sweden) to model relationships between the individual sensory attributes and volatile compounds. All variables were mean-centered and normalized to unit variance before applying PLS analyses. Analysis of variance testing of cross-validated predictive residuals (CV-ANOVA) was performed to assess the reliability of PLS models. The significant variables for each sensory attribute were inspected by calculating estimated regression coefficients with 95% confidence levels derived from jack knifing. Variable Importance on Projection (VIP) values were calculated to estimate the importance of each variable in the PLS projection. Variables with $VIP > 1$ are the most relevant for explaining Y-variables (SIMCA 14.1 software).

3. Results and Discussion

3.1. Sensory evaluation results

The aroma of 24 samples of Spanish-style green table olives was described by the sensory panel using 9 different sensory descriptors. The first two principal components of the PCA applied to the sensory data accounted for 57.87 % of the total variance. As can be observed, the cultivars were poorly separated, but a trend to discriminate between samplings along the PC1 is apparent (score plot, Fig. 1a). Thus, all samples after fermentation (first sampling) were located in the right part of the plot

and were clearly separated from the packed samples (third sampling), which were located in the left part. The loading plot (Fig. 1b) showed that the attributes “lupin” (load 0.678), “hay” (0.678), “lactic” (0.664), and “wine” (0.658) had the highest positive contribution to PC1. It means that the samples taken after fermentation can be discriminated from the packed samples based on their higher “lupin”, “hay”, “lactic” and “wine” sensations. The “ripe fruit” attribute was negatively correlated with the “green fruit” odor (Pearson correlation coefficient (r) = -0.478; p = 0.018). The attributes “grass” and “green fruit” were significantly positively correlated among them (r = 0.682; p = 0.0002). However, the interpretation of correlations for the rest of variables based on Fig. 1b might be hazardous at first glance, as some information is carried on other axes. For example, one might be tempted to interpret a correlation between the variables “lupin” and “alcohol” although, in fact, there is none (r = 0.009, p = 0.966). Pearson correlation tests showed that the “lupin” descriptor was positively correlated to “hay” (r = 0.693, p = 0.0002), “green fruit” (r = 0.414, p = 0.044), and “lactic” (r = 0.538, p = 0.007) descriptors. The latter descriptor was also correlated to the “wine” attribute (r = 0.469, p = 0.021). The attribute “musty” was correlated to “wine” (r = 0.525, p = 0.008) and “alcohol” (r = 0.406, p = 0.049), the latter two attributes being highly correlated among them (r = 0.697, p = 0.0002).

3.2. Volatile compounds by SPME-GC-MS analysis

A total of 133 compounds were identified and quantified in the present study, which included 39 esters, 25 alcohols, 17 terpenes, 13 aldehydes, 10 phenols, 8 hydrocarbons, 2 sulfur compounds, 1 ketone, 1 lactone, and 5 other compounds (Table 2). All the compounds were previously identified in Spanish-style green table olives (Cortés-Delgado et al., 2016; Sánchez et al., 2018; Montañó et al., 1990, 1992; Iraqi et

al., 2005; Sabatini & Marsilio, 2008; Cano-Lamadrid et al., 2015; Sánchez et al., 2017). Similarly to what was found with the sensory attributes, a PCA applied to the volatile compounds showed a poor separation of the three cultivars, but a trend to separate according to sampling time (Fig. 2). Using HCA, 3 groups were identified which are shown in the score plot of the PCA (Fig. 2a). Group 1 was composed by all packed samples, except HA-3 and GA-3. Samples of this group were located in the negative part of PC1, mainly associated with 1,4-dimethoxybenzene (96), pseudocumene (38) and heptanoic acid (116), and the positive part of PC2 which is mainly related to octanoic acid (120), nonanal (55) and phenylacetaldehyde (84) (Fig. 2b). It is interesting to note that samples of this group are characterized by very low amount of esters. Group 2 was composed by Hojiblanca olives sampled after fermentation and post-fermentation stages, except HA-2. Samples of this group, particularly HC-1 and HE-1, were characterized by higher amount of ethanol (6), ethyl acetate (4), geraniol (109), benzyl alcohol (112), and benzaldehyde (70). In addition, samples located in the first quadrant show higher amount of esters. The samples belonging to group 3 were mostly Manzanilla and Gordal olives sampled after fermentation and post-fermentation stages, which were located in the negative part of PC2. The main compounds associated with these samples were 1-propanol (17), propanoic acid (74), methyl propanoate (5), propyl propanoate (18), propyl acetate (8), and methyl hydrocinnamate (108). In fact, these compounds along with heptanal (29), propyl benzoate (97), benzyl propanoate (102), and ethyl hydrocinnamate (113) are clustered in a well-defined group according to HCA (Fig. 1S).

3.3. Relationships between volatile compounds and sensory descriptors

To reveal the relationship between sensory descriptors and volatile compounds from Spanish-style green table olives, a first PLS analysis was applied using the whole data set. The correlation loadings of 133 volatile compounds (X-variables) and 9 sensory descriptors (Y-variables) on the first two components are shown in Fig. 3a. The percentages explained by the first two components were low, 38% of volatile compound data variation explained 36% of sensory analysis data variation. It can be seen that the attributes “lupin” and “lactic” were correlated with each other, and were associated with methyl (E)-3-hexenoate (37) and methyl hydrocinnamate (108), respectively, among other compounds. The attributes “alcohol” and “wine” were strongly correlated with each other, and were associated with methyl hexanoate (30) and benzaldehyde (70), among other compounds. The other attributes, closer to zero, were not well represented on the first two components, thereby being poorly connected with the volatile composition. Packed samples were located on the left part of the t1 vs t2 plot (Fig. 3b) and were related to hydrocarbons (e.g. p-xylene (25), o-xylene (27), toluene (15), and pseudocumene (38)), aldehydes (e.g. (E)-2-octenal (56), (E)-2-decenal (85), (E,E)-2,4-decadienal (104)) alcohols (e.g. 1-heptanol (59), 1-octanol (75), 1-nonanol (89)), fatty acids (e.g. heptanoic acid (116)), terpenes (e.g. (E)- β -ocimene (33), β -damascenone (105)), phenols (e.g. vanillin (131), p-propyl guaiacol (123)), and other compounds (e.g. 1,4-dimethoxybenzene (96)). The above-mentioned aldehydes and alcohols are typical lipid oxidation byproducts (Schaich, 2013), which could be formed during the packing stage in Spanish-style green olives (Sánchez et al., 2018).

In order to examine which compounds have greater contribution for each sensory attribute, individual PLS models (i.e. one model per each odor descriptor) were developed. Five attributes, namely, “green fruit”, “ripe fruit”, “grass”, “hay”, and “musty” gave models with a $p > 0.05$. Therefore, these attributes could not be predicted

with sufficient accuracy. Models with a $p < 0.05$, thereby being considered reliable, were obtained for “lupin”, “lactic”, “wine”, and “alcohol” (Table 3). In all these models the explained variance was higher than 50%. The PLS plots of observed vs predicted values, standardized regression coefficients and VIP values of such attributes are shown in Fig. 2S-5S.

For the “lupin” attribute, 12 compounds had significant positive regression coefficients, with ethyl propanoate (sweet, grape, winey and fermented odor), methyl (E)-3-hexenoate (fruity, green, sweet), acetic acid (sharp, pungent, sour, vinegar), methyl propanoate (fruity), and 3-methyl-2-buten-1-ol (sweet, fruity, alcoholic) showing the highest VIP values (Table 4). Although the aroma-active compounds in pickled lupine beans, which were used as reference for the “lupin” descriptor, are not known, acetic acid could be a strong contributor to the odor of this pickled vegetable as vinegar is frequently added as an ingredient. The actual concentration of this acid in our samples as measured in the olive juice by HPLC ranged between 0.11 and 2.92 g/L (Table 2S), these values being much higher than the odor threshold for acetic acid in water (0.026 g/L; Tamura, Boonbumrung, Yoshizawa, & Varanyanond, 2001). Therefore, acetic acid is likely to be an odor-active compound contributing to the odor of “lupin” in Spanish-style green table olives. On the contrary, more than 20 compounds showed significant negative coefficients, the largest VIP values being for limonene, 1,4-dimethoxybenzene, pseudocumene, 1-nonanol and 2-bornene.

For the “lactic” odor, 16 compounds showed significant positive coefficients, the largest ones corresponding to methyl propanoate, methyl hydrocinnamate (fruity, floral), methyl (E)-3-hexenoate, 1-propanol (alcoholic, fermented, musty and yeasty), and propanoic acid (pungent, acidic and dairy-like odor), whereas a similar number of compounds showed significant negative coefficients, with β -damascenone, nonanoic

acid, (E,E)-2,4-decadienal, 1-heptanol and 1-octanol having the greatest negative impact (Table 4). It is noteworthy that both propanoic acid and acetic acid were positively correlated to the intensity of the “lactic” odor. Both acids along with other volatile and non-volatile compounds (e.g. lactic acid) are responsible for flavor in yogurt (Cheng, 2010), this food being taken as reference for “lactic” descriptor in our study.

For the “wine” attribute, 16 compounds showed significant positive correlations, of which methyl hexanoate (fruity, ether), 3-methyl-3-buten-1-ol (sweet, fruity), geraniol (sweet, floral, fruity, rose, waxy, citrus), benzyl alcohol (floral, rose, phenolic, balsamic), and β -citronellol (floral, rosy, sweet, citrus) had the largest coefficients (Table 4). Geraniol and β -citronellol are regarded as having flavor/aroma significance in wines (Bakker & Clarke, 2012). On the other hand, only 7 compounds correlated negatively with “wine” odor, having toluene, o-xylene, p-xylene, 1,4-dimethoxybenzene, and 1-nonanol the largest impact.

Finally, the intensity of the “alcohol” attribute was positively correlated to 15 compounds, mainly geraniol, 1-hexanol (pungent, ethereal, fruity and alcoholic), methyl hexanoate, ethanol (alcoholic, ethereal, medical) and benzyl alcohol, and negatively correlated to 6 compounds, namely, o-xylene, p-xylene, eugenol, 1-octanol, 1-nonanol and nonanoic acid. It is noteworthy that 3 out of 5 positively correlated compounds mentioned above were alcohols, with one of them (ethanol) being the compound taken as reference for the “alcohol” descriptor. The actual concentration of ethanol as measured in the olive juice by HPLC ranged between 0.25 to 2.39 g/L after fermentation (Table 2S), which were above the odor threshold for ethanol in water (0.2 g/L; Tamura et al., 2001). Therefore, ethanol can be considered as odor-active compound in Spanish-style green table olives after fermentation. However, the concentration of ethanol found after fermentation has been reported to decrease

significantly as a result of post-fermentation stage and the subsequent packing stage (Sánchez et al., 2018), this fact being confirmed in the present study by HPLC analysis (Table 2S). As a consequence, its contribution to the aroma in case of packed product was negligible. It can be noted that some of the compounds with positive correlations were important contributors ($VIP > 1$) to different attributes, but contributing with different weights (Table 4). Thus, methyl propanoate, ethyl propanoate, and methyl (E)-3-hexenoate showed high VIP values in case of both “lupin” and “lactic” odors; methyl hexanoate was important to “lactic”, “wine”, and “alcohol” attributes; 1-hexanol, geraniol and benzyl alcohol to “wine” and “alcohol” attributes; and acetic acid to “lupin”, “lactic” and “wine” odors. These findings indicate that there may not be definite associations between a volatile compound and an odor characteristic; rather, this association changes according to the product matrix and composition (Chambers & Koppel, 2013). Similarly, various compounds with negative correlations showed VIPs > 1 in different models. For example, p-xylene and o-xylene showed high VIP values in all 4 models, whereas pseudocumene, 1-heptanol, 2-bornene, (E,E)-2,4-decadienal, and heptanoic acid were important to “lupin” and “lactic” attributes.

All in all, the above results suggest that odor sensations originate from a complex interaction among different compounds and that different mixing ratios generate different sensations (Aprea et al., 2012). The negative correlations suggest that the perception of an aromatic note is influenced not only by the presence of a few components, but also by the presence of other odorants that affect negatively in the perception of such aromatic note (Vilanova, Genisheva, Masa, & Oliveira, 2010). According to Lykomitros, Fogliano, & Capuano (2016), negative correlations could be explained by different ways: (a) some compounds could exhibit receptor antagonism, thereby decreasing the odor potency of others, (b) strong aromatic notes of some

compounds could change the overall aroma balance, making difficult for panelists to recognize a specific attribute, and (c) some compounds could be related to a chemical reaction in the sample which is responsible for creating or depleting other aroma active compounds.

The aforementioned PLS models were built using all volatile compounds identified in the present study (i.e. 133 X-variables). In order to reach the best prediction ability with the minimum number of variables, subsequent models were built following an iterative process taking into account only the volatile compounds with significant VIP values higher than 0.8. Variables with $VIP > 1$ are considered highly influential in the model, whereas variables with $0.8 < VIP < 1$ are considered moderately important for the PLS model (Lykomitros et al., 2016). The best results were obtained after 2 iterations for each sensory attribute, the quality parameters of the final PLS models being shown in Table 5. It can be seen that the new PLS models for “lupin” and “lactic” attributes, which were built using 36 and 25 volatile compounds, respectively, showed fits slightly better than the original models with 133 compounds. On the contrary, the new models for “wine” and “alcoholic” descriptors, which used 26 and 24 compounds, respectively, were slightly worse than the original ones. An observation is that the models for “wine” and “alcohol” show a similar structure, since in both models the most important contributors (with $VIPs > 1$) were almost the same. This is not surprising considering that these two descriptors showed a high correlation between them, as mentioned above.

4. Conclusions

In this study, the aroma profile and volatile composition of 24 different samples of Spanish-style green table olives were studied by Quantitative Descriptive Analysis

and SPME-GC-MS, respectively. Principal component analysis (PCA) applied to both the sensory data and the volatile compounds showed a poor separation of samples according to cultivars, but a trend to separate according to sampling time. Reliable PLS models were only obtained for four sensory descriptors (lupin, lactic, wine, and alcohol), allowing the identification of those compounds highly correlated to such descriptors. In addition, these PLS models could be used to predict the intensity of these descriptors as a function of SPME-GC-MS data.

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Supplementary material

Table 1S. Physico-chemical and microbiological characteristics of the samples analyzed in the present study.

Table 2S. Major end-products of fermentation in the samples analyzed.

Figure 1S. Dendrogram of the 133 volatile compounds measured in the headspace of the 24 samples of Spanish-style green table olives, obtained by hierarchical cluster analysis (HCA).

Fig. 2S. PLS regression model for the “lupin” attribute. (a) Standardized coefficients with jack-knife uncertainty bars (95%). Only significant coefficients are shown. (b) Plot of VIPs (sorted in descending order) with jack-knife uncertainty bars (95%). Only significant VIPs higher than 1 are shown. (c) Regression plot of observed vs. predicted values. Root Mean Square Error of Estimation (RMSEE) and Root Mean Square Error from cross-validation (RMSEcv) are listed at the bottom of plot.

Fig. 3S. PLS regression model for the “lactic” attribute. (a) Standardized coefficients with jack-knife uncertainty bars (95%). Only significant coefficients are shown. (b) Plot of VIPs (sorted in descending order) with jack-knife uncertainty bars (95%). Only significant VIPs higher than 1 are shown. (c) Regression plot of observed vs. predicted values. Root Mean Square Error of Estimation (RMSEE) and Root Mean Square Error from cross-validation (RMSEcv) are listed at the bottom of plot.

Fig. 4S. PLS regression model for the “wine” attribute. (a) Standardized coefficients with jack-knife uncertainty bars (95%). Only significant coefficients are shown. (b) Plot of VIPs (sorted in descending order) with jack-knife uncertainty bars (95%). Only

significant VIPs higher than 1 are shown. (c) Regression plot of observed vs. predicted values. Root Mean Square Error of Estimation (RMSEE) and Root Mean Square Error from cross-validation (RMSEcv) are listed at the bottom of plot.

Fig. 5S. PLS regression model for the “alcohol” attribute. (a) Standardized coefficients with jack-knife uncertainty bars (95%). Only significant coefficients are shown. (b) Plot of VIPs (sorted in descending order) with jack-knife uncertainty bars (95%). Only significant VIPs higher than 1 are shown. (c) Regression plot of observed vs. predicted values. Root Mean Square Error of Estimation (RMSEE) and Root Mean Square Error from cross-validation (RMSEcv) are listed at the bottom of plot.

FIGURE CAPTIONS

Fig. 1. (a) PCA score plot of sensory data. Abbreviations are described in text. (b) PCA loading plot of sensory data.

Fig. 2. (a) PCA score plot of GC-MS data. Abbreviations are described in text. The 3 groups identified by agglomerative hierarchical cluster analysis (AHC) are highlighted. (b) PCA loading plot of GC-MS data. Numbers indicate the volatile compounds as shown in Table 2.

Fig. 3. Partial least squares (PLS) regression of volatile compounds and sensory descriptors of Spanish-style green table olives. (a) Loading plot. Numbers indicate the volatile compounds as shown in Table 2. (b) Score plot. Abbreviations are described in text.

Table 1. Spanish-style table olive descriptors, definitions, and references

Sensory attribute	Definition	Reference
Green fruit	Odor characteristic of unripe fresh olives	Homogenized pulp of unripe fresh olives = 8.0
Ripe fruit	Odor characteristic of ripe fresh olives	Homogenized pulp of ripe fresh olives = 8.0
Grass	Odor characteristic of recently cut grass	Recently cut grass = 9.0
Hay	Odor of dried grass	Dried grass = 4.0
Lactic	Odor characteristic of pure lactic acid or yogurt	Yogurt = 5.0
Wine	Odor reminiscent of white wine	50% v/v white wine in green olive brine = 7.0
Lupin	Odor reminiscent of pickled lupine beans	Homogenized pickled lupine beans = 8.0
Musty	Odor suggestive of olives with mold	wet garden soil = 8.5
Alcohol	Odor reminiscent of ethanol	10% (v/v) solution of ethanol in water = 6.0

Table 2. Volatile composition of Spanish-style green table olive samples. Identification criteria and basic statistic parameters of the 133 volatile compounds quantified by SPME-GC-MS.

Code ^a	Compound	IEC (m/z) ^b	RI (exp.) ^c	RI (lit.) ^d	ID ^e	Mean ^f	Max ^f	Range ^f	RSD (%)
Acids									
65	Acetic acid	60	1460	1450	A	166.8	444.2	410.0	66.4
74	Propanoic acid	74	1549	1536	A	211.4	634.7	628.7	84.8
79	Isobutanoic acid	43	1581	1581	A	4.1	17.0	17.0	108.8
87	Butanoic acid	73	1640	1637	A	9.5	95.1	94.6	215.5
92	2-Methylbutanoic acid	74	1680	1655	A	30.0	91.4	88.0	68.9
111	Hexanoic acid	73	1854	1850	A	10.6	19.1	14.7	34.4
116	Heptanoic acid	73	1959	1960	A	2.3	4.6	3.9	52.5
117	(E)-3-Hexenoic acid	114	1969	1954	A	0.7	1.8	1.7	69.8
120	Octanoic acid	73	2067	2051	A	10.0	24.9	22.7	57.7
127	Nonanoic acid	73	2188	2174	A	1.4	3.4	3.4	59.0
129	Decanoic acid	73	2277	2276	A	1.5	4.2	4.1	73.4
130	Benzoic acid	105	2436	2433	A	4.6	13.4	12.6	61.2
Alcohols									
6	Ethanol	45	935	937	A	60.5	405.4	402.1	146.4
14	2-Butanol	59	1025	1019	A	16.5	63.4	63.4	108.0
17	1-Propanol	59	1039	1049	A	30.5	156.5	156.5	119.4
22	Isobutanol	43	1104	1086	A	0.9	6.2	6.2	162.5
26	1-Butanol	56	1153	1150	A	0.7	4.6	4.6	150.1
31	Isopentanol	55	1211	1217	A	25.2	116.7	113.9	117.0
35	3-Methyl-3-buten-1-ol	68	1256	1246	A	0.5	1.7	1.7	113.8
36	1-Pentanol	55	1255	1252	A	0.7	1.5	1.5	50.2
46	2-Heptanol	45	1318	1318	A	1.3	5.4	5.4	104.5
47	3-Methyl-2-buten-1-ol	71	1324	1322	A	0.9	4.3	4.3	155.3
48	3-Methyl-1-pentanol	56	1329	1313	A	0.5	1.6	1.6	73.0
52	1-Hexanol	56	1356	1360	A	11.8	38.1	34.7	74.9
53	(Z)-3-Hexen-1-ol	67	1385	1386	A	38.2	106.3	95.3	80.6
58	1-Octen-3-ol	57	1454	1452	A	8.3	19.3	15.6	39.1
59	1-Heptanol	70	1458	1467	A	8.1	19.7	17.2	53.5
63	6-Methyl-5-hepten-2-ol	95	1466	1451	A	2.6	6.1	6.1	49.9
67	2-Ethyl-1-hexanol	57	1491	1484	A	5.9	26.8	25.5	103.0
75	1-Octanol	84	1560	1553	A	11.8	27.2	22.0	57.9
82	(E)-2-Octen-1-ol	57	1613	1620	A	1.7	4.4	3.6	48.5
89	1-Nonanol	70	1661	1661	A	8.0	16.4	12.6	41.8
91	(Z)-3-Nonen-1-ol	81	1683	1682	A	0.3	1.0	1.0	117.5
107	2-Decen-1-ol	57	1817	1812	B	6.4	20.3	20.3	74.1
112	Benzyl alcohol	108	1871	1865	A	138.8	490.3	455.8	89.0

114	Phenylethyl alcohol	91	1903	1912	A	455.0	951.9	756.0	46.0
132	Homovanillyl alcohol	137	2840	2830	B	2.0	6.3	5.8	59.5
Aldehydes/ketones									
3	Methylpropenal	70	880	893	A	1.7	5.1	5.1	65.7
9	Pentanal	44	980	984	A	3.6	23.1	23.1	126.7
21	Hexanal	82	1071	1077	A	0.2	0.7	0.7	83.4
29	Heptanal	70	1177	1182	A	0.7	7.7	7.7	210.4
40	Octanal	84	1284	1280	A	2.3	3.9	3.0	31.8
41	1-Octen-3-one	70	1297	1295	A	5.8	13.3	13.3	52.0
44	(E)-2-Heptenal	83	1313	1306	A	15.4	35.2	32.0	52.1
55	Nonanal	98	1388	1390	A	1.6	3.0	3.0	42.8
56	(E)-2-Octenal	55	1420	1434	A	2.1	4.8	4.3	55.0
60	(E,E)-2,4-Heptadienal	81	1458	1461	A	4.6	8.8	8.8	42.2
70	Benzaldehyde	106	1511	1513	A	14.0	46.2	41.1	77.2
84	Phenylacetaldehyde	91	1632	1638	A	6.7	19.7	19.7	90.1
85	(E)-2-Decenal	70	1633	1631	A	14.9	42.5	38.4	67.6
104	(E,E)-2,4-Decadienal	81	1799	1800	A	1.7	7.5	7.5	110.8
Esters									
4	Ethyl acetate	43	897	896	A	37.4	261.6	260.8	159.6
5	Methyl propanoate	57	911	911	A	15.3	53.2	52.2	103.3
7	Ethyl propanoate	57	957	947	A	27.7	123.5	123.5	122.4
8	Propyl acetate	61	976	957	A	15.0	123.2	121.9	176.0
10	Methyl butanoate	87	989	989	A	1.7	9.0	8.4	101.0
12	Methyl 2-methylbutanoate	88	1010	1004	A	2.6	10.5	9.5	83.6
13	Methyl 3-methylbutanoate	74	1018	1011	A	2.0	13.8	13.8	146.4
16	Ethyl butanoate	71	1033	1026	A	3.4	58.6	58.6	356.7
18	Propyl propanoate	57	1041	1043	A	122.4	604.3	604.3	158.9
19	Ethyl 2-methylbutanoate	102	1048	1052	A	3.8	18.5	18.5	124.8
20	Ethyl 3-methylbutanoate	88	1064	1064	A	3.3	21.4	21.4	141.9
23	Isoamyl acetate	43	1118	1121	A	11.3	44.0	44.0	103.9
24	Propyl butanoate	71	1119	1123	A	4.8	23.7	23.7	145.5
30	Methyl hexanoate	74	1185	1176	A	4.4	18.0	18.0	102.7
32	Ethyl hexanoate	88	1231	1232	A	3.5	35.9	35.9	217.0
37	Methyl (E)-3-hexenoate	128	1259	1253	A	0.3	0.9	0.9	91.6
39	Hexyl acetate	56	1268	1267	A	2.0	5.6	5.6	90.2
42	Ethyl (E)-3-hexenoate	142	1301	1301	A	0.1	0.7	0.7	171.7
43	(Z)-3-Hexenyl acetate	67	1315	1313	A	10.9	28.7	28.7	70.8
45	Methyl lactate	45	1322	1314	A	3.8	10.2	10.2	65.6
50	Ethyl lactate	75	1345	1358	A	2.5	6.7	6.5	79.4
54	Methyl octanoate	74	1387	1386	A	5.7	24.4	24.4	111.9
57	Ethyl octanoate	88	1432	1436	A	8.6	65.1	64.8	187.2
76	Isoamyl lactate	45	1566	1572	A	3.5	50.6	50.6	289.5
77	Isobornyl acetate	95	1570	1568	A	3.1	9.4	9.0	73.9
80	Methyl decanoate	87	1592	1590	A	1.3	3.5	3.4	78.6
81	Methyl benzoate	105	1611	1605	A	3.0	14.7	14.7	125.9

86	Ethyl decanoate	88	1635	1635	A	2.4	13.5	13.2	152.7
88	Ethyl benzoate	105	1654	1651	A	5.5	21.5	21.5	110.6
94	Benzyl acetate	108	1721	1688	A	10.4	22.7	22.0	66.4
97	Propyl benzoate	105	1744	1745	A	2.1	17.4	17.4	214.2
98	Methyl salicylate	120	1758	1755	A	5.8	14.7	14.0	70.9
101	Ethyl phenylacetate	91	1776	1767	A	0.6	2.8	2.8	147.3
102	Benzyl propanoate	91	1783	1784	A	4.6	44.1	44.1	214.4
103	Ethyl salicylate	120	1792	1788	A	3.8	9.3	8.7	71.9
108	Methyl hydrocinnamate	104	1833	1821	A	7.8	35.1	35.1	102.5
113	Ethyl hydrocinnamate	104	1873	1872	A	10.1	72.6	72.6	186.6
121	Triacetin	145	2074	2077	A	13.0	40.6	40.6	105.7
128	Ethyl 3-cyclohexenecarboxylate	81	2185	-	C	0.4	0.9	0.9	82.4
Hydrocarbons									
2	Octane	85	807	800	A	17.7	88.3	87.2	115.7
11	Decane	57	1001	1000	A	20.8	62.5	53.4	65.6
15	Toluene	91	1034	1036	A	6.4	12.7	11.6	59.8
25	p-Xylene	91	1121	1119	A	6.3	14.0	12.8	66.1
27	o-Xylene	91	1170	1175	A	2.3	4.7	4.0	53.4
34	Styrene	104	1249	1245	A	102.7	762.1	761.7	195.7
38	Pseudocumene	105	1231	1252	A	2.3	4.1	4.1	64.6
69	2-Bornene	121	1505	-	C	36.2	88.5	82.0	61.7
Phenols									
110	o-Guaiacol	124	1854	1860	A	177.1	1251.4	1250.6	198.4
115	p-Creosol	138	1949	1960	A	935.9	1615.3	1254.2	36.2
118	Phenol	94	2006	1992	A	21.7	136.4	135.0	169.1
119	p-Ethyl guaiacol	137	2022	2033	A	6.7	14.2	12.3	51.3
122	p-Cresol	107	2083	2078	A	13.2	29.3	26.6	47.4
123	p-Propyl guaicol	137	2100	2115	A	4.2	13.7	12.7	82.3
125	Eugenol	164	2158	2167	A	1.7	4.4	3.7	49.6
126	4-Ethyl phenol	107	2175	2170	A	337.4	1744.9	1732.6	144.6
131	Vanillin	151	2541	2551	A	4.2	10.1	9.4	54.2
133	Tyrosol	107	2805	2978	A	13.3	31.5	28.7	53.9
Terpenes									
28	Limonene	93	1182	1198	A	2.4	6.5	6.5	67.1
33	(E)- β -Ocimene	93	1249	1233	A	1.6	6.1	6.1	86.9
49	6-Methyl-5-hepten-2-one	108	1334	1336	A	3.4	7.3	5.4	37.9
51	(E)-Rose oxide	94	1435	1441	A	1.4	3.2	3.2	71.3
61	Linalool oxide	139	1342	1341	A	3.0	10.0	9.5	77.2
62	(+)-Cycloisositivene	161	1463	1465	B	0.7	2.4	2.4	102.8
64	Copaene	119	1475	1465	B	13.7	36.6	35.0	84.8
68	Dihydroedulan	179	1501	1492	B	8.5	25.3	24.1	72.0
73	Linalool	93	1550	1547	A	9.2	24.0	21.3	57.4
78	Caryophyllene	133	1575	1581	A	0.1	0.5	0.5	124.4
93	α -Terpineol	93	1691	1675	A	20.0	61.2	57.9	99.6
95	α -Murolene	161	1710	1734	B	1.7	4.7	4.7	85.5
99	β -Citronellol	69	1766	1757	A	1.5	4.5	4.3	68.7

105	β -Damascenone	121	1805	1813	A	4.3	10.8	10.8	64.8
106	Isogeraniol	121	1810	1828	B	2.1	3.4	2.1	27.9
109	Geraniol	69	1847	1854	A	8.1	24.9	22.4	75.6
124	Iridomyrmecin	95	2134	-	C	4.2	9.8	9.8	62.2
Other compounds									
1	Dimethyl sulfide	62	765	760	A	17.5	42.3	38.1	51.4
66	Theaspirane A	138	1484	1487	A	19.0	52.5	49.0	62.0
71	Theaspirane B	138	1524	1522	A	20.2	55.1	51.7	60.9
72	Dimethyl sulfoxide	63	1556	1569	A	1.8	5.4	5.4	74.3
83	Butyrolactone	42	1613	1617	A	0.6	1.7	1.7	107.7
90	p-Vinylanisole	134	1668	1670	B	1.3	4.0	4.0	100.0
96	1,4-Dimethoxybenzene	123	1730	1727	A	3.6	8.5	8.5	86.7
100	Methoxyphenyl oxime	151	1781	-	C	2.4	7.8	7.8	104.9

^a Code based on assigned peak numbers in TIC ordered by increasing retention times.

^b Ion extraction chromatogram, m/z used to obtain the GC peak area of each compound.

^c Linear retention index on VF-Wax column.

^d Values of linear retention index found in literature (NIST Standard Reference Database, NIST Chemistry WebBook).

^e Identification: A, identified, mass spectrum and RI were in accordance with standards; B, tentatively identified, mass spectrum matched in the standard NIST 2008 library and RI matched with literature; C, tentatively identified, mass spectrum agreed with the standard NIST 2008.

^f Concentrations are expressed as $\mu\text{g/kg}$ of 3-octanol.

Table 3. PLS regression models relating individual odor descriptors to the 133 volatile compounds in Spanish-style green table olives

	Descriptor			
	Lupin	Lactic	Wine	Alcohol
Linear equation ^a	$y = x + 2.86 \cdot 10^{-7}$	$y = x + 3.48 \cdot 10^{-8}$	$y = x - 4.74 \cdot 10^{-9}$	$y = x + 1.62 \cdot 10^{-7}$
R ²	0.62	0.67	0.59	0.51
No. of components used by the model	1	1	1	1
p-value (CV-ANOVA)	0.0027	0.0022	0.0085	0.021
RMSEcv ^b	0.31	0.21	0.27	0.33

^a Equation of the observed values vs. the predicted values. ^b Root Mean Square Error from cross-validation.

Table 4. VIP values of volatile compounds with significant correlations based on PLS models developed for the “lupin”, “lactic”, “wine” and “alcoholic” aromas using 133 compounds as X-variables

Compound	Odor descriptor ^a	Lupin	Lactic	Wine	Alcohol
Compounds with negative regression coefficients					
methylpropenal	wild, hyacinth, foliage		0.88		
toluene	sweet	1.58	1.48	1.50	
p-xylene	sweet	1.45	1.65	1.50	1.94
o-xylene	geranium	1.56	1.60	1.50	2.00
limonene	citrus, herbal, terpene, camphor	1.93			
(E)- β -ocimene	warm, floral, herb, flower, sweet	1.26			
pseudocumene	plastic	1.61	1.25		
(E)-rose oxide	–		1.39		
nonanal	waxy, aldehydic, rose, orange, peel, fatty	1.58			
(E)-2-octenal	fresh, cucumber, fatty, herbal, banana, waxy	1.26			
1-heptanol	musty, leafy, herbal, green, sweet, woody	1.28	1.85		
theaspirane A	–	1.03			
dihydroedulan	–	1.03			
2-bornene	–	1.59	1.73		
theaspirane B	–	0.98			
linalool	citrus, floral, sweet, woody, green	1.12			
1-octanol	waxy, green, citrus, aldehydic and floral	1.51	1.79		1.45
isobornyl acetate	balsam, camphor, herbal, woody, sweet	1.55			
(E)-2-decenal	waxy, fatty, earthy, coriander, mushroom	1.58			
1-nonanol	fresh, fatty, rose, orange, dusty, wet, oily	1.59		1.30	1.41
1,4-dimethoxybenzene	sweet, green, new, hay, fennel	1.70	1.33	1.44	
(E,E)-2,4-decadienal	fatty, chicken, aldehydic, fried	1.51	1.88		
β -damascenone	apple, rose, honey, tobacco, sweet		2.00		
heptanoic acid	cheesy, waxy, sweaty, fermented, pineapple	1.51	0.95		
(E)-3-hexenoic acid	fruity, honey, acid	1.09			
octanoic acid	fatty, waxy, rancid, oily, vegetable, cheesy	0.87			
eugenol	sweet, spicy, clove, woody			1.00	1.63
nonanoic acid	waxy, dirty and cheesy		1.94	1.15	1.20
vanillin	sweet, vanilla, creamy, chocolate	1.58			

Table 5. Reduced PLS regression models relating individual odor descriptors to volatile compounds

	Descriptor			
	Lupin	Lactic	Wine	Alcohol
No. X-variables in the model	36	25	26	24
Linear equation ^a	$y = x + 2.82 \cdot 10^{-7}$	$y = x + 1.13 \cdot 10^{-7}$	$y = x - 1.97 \cdot 10^{-7}$	$y = x + 3.33 \cdot 10^{-8}$
R ²	0.76	0.70	0.52	0.47
No. of components used by the model	2	1	1	1
<i>p</i> -value (CV-ANOVA)	0.0047	0.00002	0.0033	0.0032
RMSEcv ^b	0.28	0.17	0.25	0.30

^a Equation of the observed values vs. the predicted values. ^b Root Mean Square Error from cross-validation. ^c VIP values in parenthesis.

(a)

(b)

(a)

(b)

(a)

(b)

Table 1S. Physico-chemical and microbiological characteristics of the samples analyzed in the present study.

Samples	pH	TA ^a (g L ⁻¹)	CA ^b (eq L ⁻¹)	Salt ^c (g L ⁻¹)	Total phenols ^d (g L ⁻¹)	LAB ^e (log cfu mL ⁻¹)	Y ^f (log cfu mL ⁻¹)
After fermentation (after 7 months of brining)							
MC-1	4.33	4.8	0.101	67.0	2.3	6.3	5.4
MAm-1	4.60	5.0	0.138	57.5	3.2	6.6	5.5
MAI-1	4.12	5.5	0.090	68.8	2.2	6.5	4.6
GA-1	3.93	7.8	0.097	69.3	1.6	5.9	4.4
GU-1	4.30	5.7	0.092	67.3	1.4	5.9	4.4
HA-1	4.30	5.3	0.103	68.3	2.5	6.1	5.0
HC-1	4.21	6.5	0.101	69.3	3.8	6.6	4.6
HE-1	4.06	7.6	0.109	63.8	3.4	6.0	5.1
After post-fermentation (after 11 months of brining)							
MC-2	3.99	5.8	0.095	93.6	2.4	3.7	5.2
MAM-2	3.97	7.6	0.122	94.6	2.7	3.1	5.5
MAI-2	4.19	5.0	0.089	91.8	2.1	5.8	5.3
GA-2	4.35	5.1	0.094	87.9	1.3	6.1	5.3
GU-2	4.58	3.6	0.087	95.3	1.4	6.2	5.8
HA-2	4.04	5.5	0.094	94.6	2.7	5.3	5.2
HC-2	3.99	6.1	0.093	91.9	3.9	1.0	5.2
HE-2	3.96	6.6	0.100	96.0	3.3	5.7	4.6
After packing (after 15 days of storage)							
MC-3	3.26	4.9	0.019	44.5	0.6	NA	NA
MAM-3	3.39	5.3	0.026	50.6	0.8	NA	NA
MAI-3	3.38	4.8	0.021	46.4	0.7	NA	NA
GA-3	3.35	4.9	0.021	47.2	0.5	NA	NA
GU-3	3.39	4.3	0.021	49.1	0.4	NA	NA
HA-3	3.27	4.9	0.022	53.2	0.7	NA	NA
HC-3	3.27	5.3	0.024	53.2	0.9	NA	NA
HE-3	3.21	5.4	0.022	49.3	0.9	NA	NA

^aTA, titratable acidity expressed as lactic acid. ^bCA, combined acidity expressed as equivalents of NaOH. ^cSalt expressed as NaCl. ^dTotal phenols expressed as gallic acid. ^eLAB, lactic acid bacteria. ^fY, yeasts. NA, not analyzed.

Table 2S. Major end-products of fermentation in the samples analyzed

Samples	Lactic acid (g L ⁻¹)	Acetic acid (g L ⁻¹)	Succinic acid (g L ⁻¹)	Ethanol (g L ⁻¹)
After fermentation (after 7 months of brining)				
MC-1	9.54	1.84	0.41	0.25
MAm-1	9.87	2.92	0.45	0.85
MAI-1	9.86	1.76	0.25	0.51
GA-1	14.15	1.72	0.37	0.60
GU-1	7.86	2.71	0.44	0.99
HA-1	9.34	2.20	0.33	0.64
HC-1	8.51	1.71	0.70	2.39
HE-1	12.39	1.88	0.36	1.12
After post-fermentation (after 11 months of brining)				
MC-2	11.69	0.77	0.21	0.07
MAm-2	14.34	1.49	0.24	0.11
MAI-2	8.47	1.37	0.13	0.21
GA-2	8.13	2.31	0.23	0.24
GU-2	5.67	1.79	0.19	0.16
HA-2	11.89	1.23	0.16	0.17
HC-2	10.64	0.87	0.48	1.15
HE-2	12.92	1.13	0.20	0.43
After packing (after 15 days of storage)				
MC-3	6.34	0.13	0.03	ND
MAm-3	6.80	0.24	0.04	ND
MAI-3	6.00	0.28	0.02	ND
GA-3	6.35	0.36	0.03	0.02
GU-3	5.40	0.25	0.04	0.02
HA-3	6.40	0.18	0.01	ND
HC-3	6.63	0.15	0.04	ND
HE-3	6.61	0.11	0.07	0.04
ND, not detected

Figure 1S. Dendrogram of the 133 volatile compounds measured in the headspace of the 24 samples of Spanish-style green table olives, obtained by hierarchical cluster analysis (HCA).

(c)

Fig. 2S. PLS regression model for the “lupin” attribute. (a) Standardized coefficients with jack-knife uncertainty bars (95%). Only significant coefficients are shown. (b) Plot of VIPs (sorted in descending order) with jack-knife uncertainty bars (95%). Only significant VIPs higher than 1 are shown. (c) Regression plot of observed vs. predicted values. Root Mean Square Error of Estimation (RMSEE) and Root Mean Square Error from cross-validation (RMSEcv) are listed at the bottom of plot.

Fig. 3S. PLS regression model for the “lactic” attribute. (a) Standardized coefficients with jack-knife uncertainty bars (95%). Only significant coefficients are shown. (b) Plot of VIPs (sorted in descending order) with jack-knife uncertainty bars (95%). Only significant VIPs higher than 1 are shown. (c) Regression plot of observed vs. predicted values. Root Mean Square Error of Estimation (RMSEE) and Root Mean Square Error from cross-validation (RMSEcv) are listed at the bottom of plot.

Fig. 4S. PLS regression model for the “wine” attribute. (a) Standardized coefficients with jack-knife uncertainty bars (95%). Only significant coefficients are shown. (b) Plot of VIPs (sorted in descending order) with jack-knife uncertainty bars (95%). Only significant VIPs higher than 1 are shown. (c) Regression plot of observed vs. predicted values. Root Mean Square Error of Estimation (RMSEE) and Root Mean Square Error from cross-validation (RMSECV) are listed at the bottom of plot.

Fig. 5S. PLS regression model for the “alcohol” attribute. (a) Standardized coefficients with jack-knife uncertainty bars (95%). Only significant coefficients are shown. (b) Plot of VIPs (sorted in descending order) with jack-knife uncertainty bars (95%). Only significant VIPs higher than 1 are shown. (c) Regression plot of observed vs. predicted values. Root Mean Square Error of Estimation (RMSEE) and Root Mean Square Error from cross-validation (RMSEcv) are listed at the bottom of plot.