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Aroma profile and volatile composition of black ripe olives (Manzanilla and Hojiblanca cultivars)

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Running title: Sensory/chemical relationships in black ripe olives

Abstract

The aroma profile and volatile composition of 8 samples of black ripe olives from Manzanilla and Hojiblanca cultivars were analyzed with the aim to characterize this type of table olive. The aroma of samples was described by a sensory panel using quantitative descriptive analysis (QDA), whereas the volatiles were analyzed by headspace solid-phase microextraction (HS-SPME) followed by gas chromatography-mass spectrometry (GC-MS). Eleven odor descriptors (briny, sautéed mushroom, earthy/soil-like, oak barrel, nutty, artificial fruity/floral, natural fruity/floral, vinegary, alcohol, fishy/ocean-like, and cheesy) were evaluated, of which only one descriptor (briny) showed a significant difference between cultivars. A total of 74 volatile compounds were identified in the headspace of samples, of which 12 were identified as significant volatiles contributing to the discrimination between Manzanilla and Hojiblanca black ripe olives. Partial least squares (PLS) regression was able to predict one odor descriptor (nutty) with sufficient accuracy and allowed identifying the volatiles that highly contributed to three odor descriptors of black ripe olives (nutty, natural fruity/floral, and cheesy).

Keywords: black ripe olives, aroma, volatile composition, HS-SPME/GC-MS, PLS regression

1. Introduction

Black ripe olives (or Californian-style black olives) are one of the most important types of table olives commercialized worldwide, accounting for 40-50% of all table olives exported from Spain, the world's main producer and exporter of table olives (ASEMESA, 2019). The different steps of black ripe olive processing (preservation, darkening, packing + sterilization) have been widely studied (Sánchez Gómez, García García, & Rejano Navarro, 2006). However, unlike other types of table olives such as Spanish-style or Greek-style green olives, whose volatile profiles have been characterized in recent years (Cortés-Delgado et al., 2016; De Angelis et al., 2015; de Castro, Sánchez, Cortés-Delgado, López-López, & Montaña, 2019; López-López, Sánchez, Cortés-Delgado, de Castro, & Montaña, 2018; Martorana et al., 2015; Randazzo et al., 2017; Sánchez et al., 2018), studies on the flavor characterization and volatile composition of black ripe olives have been scarce. Lee, Kitsawad, Sigal, Flynn, & Guinard (2012) found that aroma and flavor characteristics of sliced black ripe olives differed according to country of origin. Olive cultivar, grown area, and storage period have been recently demonstrated to affect the sensory profiles of black ripe olives (López-López, Sánchez-Gómez, Montaña, Cortés-Delgado, & Garrido-Fernández, 2019). Sansone-Land, Takeoka, & Shoemaker (2014) found clear differences among the volatile compositions of black ripe olives produced in different countries. The effects of each step of processing and storage period on the volatile composition of black ripe olives have been recently disclosed (López-López, Cortés-Delgado, de Castro, Sánchez, & Montaña, 2019). However, no study relating the volatile components to sensory attributes of black ripe olives has been carried out to date. This type of investigations has been previously carried out by our group in Spanish-style green table olives (López-López et al., 2018) using multivariate analysis by partial least squares (PLS) regression

to relate the data sets. As a result, reliable PLS models were obtained for four sensory descriptors (lupin, lactic, wine, and alcohol), allowing the identification of those compounds highly correlated to such descriptors. Similar studies have been carried out in other foods in the last 3 years (2017-2019). Bendini et al. (2017) investigated the sensory attributes and volatile compounds of commercial tomato sauces from Italy and Spain, and found that Spanish samples were characterized by the highest content of volatiles linked to the thermal treatment of tomatoes and to raw and sautéed garlic and onion, whereas the Italian samples were characterized by terpenic compounds typical of basil and volatiles derived from fresh tomatoes. Siebert et al. (2018) used PLS regression to assess the relationships between aroma descriptors and volatile compounds in wines having “stone fruit” aromas in order to identify the compounds responsible for this specific wine aroma attribute. These authors found that a mixture of γ -lactones, monoterpenes, and aldehydes were positively correlated to the “apricot” aroma. Wu et al. (2018) related the volatile contents in table grapes with consumer liking scores using orthogonal partial least squares (OPLS) model, and found that this model predicted liking scores of whole grape berries with high precision. Kim, Lee, Lee, & Jang (2019) determined correlations between 27 volatile compounds and 8 odor descriptors of omija (a cluster of berries mainly cultivated in East Asian countries) using multivariate analysis by principal component analysis (PCA). Among other results, it was found that the sensory attribute “ginger” was highly correlated with ethyl acetate. Saldaña et al. (2019) made an association between consumer-based sensory attributes and volatile compounds of bacon smoked with different Brazilian woods by means of multiple factor analysis (MFA). Among other results, these authors found that the sensory attributes related to the smoking process were associated with aldehydes, ketones and phenols.

The objectives of the present study were: (a) to gain knowledge about the aroma profile and volatile composition of black ripe olives from two main olive cultivars in Spain (Manzanilla and Hojiblanca cvs.), and (b) to elucidate the relationship between odor descriptors and volatile components and identify the compounds that could potentially contribute to each odor sensation.

2. Materials and Methods

2.1. Samples

Black ripe olives of the Manzanilla (M) and Hojiblanca (H) cultivars, grown in the provinces of Seville, Malaga, and Cordoba (Andalusia, Spain), and harvested in October 2017, were elaborated in our department, as previously reported (López-López et al., 2019). Overall 8 samples (coded as Mz1, Mz2, Mz3, Mz4, Hoj1, Hoj2, Hoj3, and Hoj4, where the letter denotes the cultivar) were prepared. Briefly, green olives were preserved in 35 L PVC vessels (20 kg fruits plus 15 L liquid capacity) for 3 months with an acidified solution containing 24 mL L⁻¹ of acetic acid before processing. The temperature of the sample storage room ranged between 15 and 22 °C. Then, the olives were subjected to darkening at room temperature (around 20 °C) using a lye solution (30 g L⁻¹ of NaOH), which progressively penetrated the flesh until the alkali reached the pit. Next, the lye was removed and the olives were washed with water until the pH reached 8.0. During the lye treatment and washing, air was injected through the bottom of the container. Then, a ferrous gluconate solution (1 g L⁻¹) was added to fix the black color. Finally, the olives were packed in glass bottles (145 g of olives plus 170 mL of brine capacity) and covered with a cover brine (35 g L⁻¹ of NaCl plus 0.2 g L⁻¹ of ferrous gluconate), and the bottles were subjected to sterilization for 17 min at 121 °C. The

sterilized packed olives (20 bottles per sample) were stored at room temperature until analysis. Sensory and instrumental analyses were performed after 1 month of storage. The physicochemical characteristics of the samples are shown in Table 1S.

2.2. Sensory analysis

Quantitative descriptive analysis (QDA) was carried out in a sensory panel room, equipped with individual booths under incandescent white lighting and free from any odors at ambient temperature (20 °C). A sensory panel composed of 14 members (8 men and 6 women, average age 40) from the Institute de la Grasa-CSIC was used. Eleven odor descriptors of black ripe olives, including briny, sautéed mushroom, earthy/soil-like, oak barrel, nutty, artificial fruity/floral, natural fruity/floral, vinegary, alcohol, fishy/ocean-like, and cheesy were used (Table 1), as previously reported by Lee et al. (2012). To familiarise the panelists with the QDA techniques and the black ripe table olive descriptors, they were trained for 1 h twice a week for two months. References for scoring aroma were obtained by mixing with the diverse proportions of the reference material with olives (e.g. vinegar for vinegary or red wine for oak barrel) or brines (e.g. salty anchovy for fishy). 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. Samples were served in cups coded with a 3-digit random number in a balanced, randomized order. 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 (strongest perception). 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.

2.3. Analysis of volatile compounds

Volatile compounds were analyzed by headspace-solid phase microextraction (HS-SPME) followed by gas chromatography-mass spectrometry (GC-MS), as reported in our previous study (López-López et al., 2019). Olives (approximately 150 g) were pitted and then homogenized in a blender. An aliquot (2.5 g) of homogenized pulp and 100 μL of an internal standard (3-octanol, 2 mg L^{-1}) were placed in a 15 mL glass vial containing a magnetic stirrer and 7.5 mL of NaCl solution (300 g L^{-1}). The vial was closed and thermostated at 40 °C for 15 min with constant agitation of 600 rpm. Then, a divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) StableFlex fiber (1 cm, 50/30 μm ; Supelco, Bellefonte, PA) was inserted into the headspace for 30 min at 40 °C (under stirring of 600 rpm). After extraction, the fiber was removed from the vial and immediately inserted into the injection port of the GC for desorption at 250 °C for 15 min. GC-MS conditions were the same as those used by Cortés-Delgado et al. (2016). The GC peak area of each compound was obtained from the ion extraction chromatogram (IEC) by selecting target ions for each one. These ions correspond to base ions (m/z 100% intensity), molecular ions (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. 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 the NIST Standard Reference Database and from authentic reference standards. The following chemicals were used as standards: acetic acid, benzoic acid, ethanol, isopentanol, 1-pentanol, 1-hexanol, (*Z*)-3-hexen-1-ol, 1-heptanol, 1-octanol, (*E*)-2-decen-1-ol, benzyl alcohol, phenylethyl alcohol, 2-methylbutanal, pentanal, 2-butenal, hexanal, heptanal, octanal, 2-heptenal, nonanal, (*E*)-

2-octenal, (*E,E*)-2,4-heptadienal, benzaldehyde, phenylacetaldehyde, (*E*)-2-decenal, (*E,E*)-2,4-decadienal, furfural, ethyl acetate, ethyl 2-methylbutanoate, ethyl 3-methylbutanoate, ethyl hexanoate, hexyl acetate, (*Z*)-3-hexenyl acetate, ethyl octanoate, ethyl benzoate, ethyl salicylate, octane, toluene, *p*-xylene, *o*-xylene, styrene, pseudocumene, phenol, vanillin, (*E*)- β -ocimene, 6-methyl-5-hepten-2-one, α -muurolene, β -damascenone, dimethyl sulfide, and dimethyl sulfoxide. Concentrations were expressed as $\mu\text{g kg}^{-1}$ of 3-octanol. All analyses of the volatile compounds were made in duplicate bottles, each analyzed in triplicate.

2.4. Physicochemical characteristics of packing brines

The pH, titratable acidity, combined acidity, and salt (NaCl) of samples were measured following the routine procedures used in our laboratories (Cortés-Delgado et al., 2016). The pH, titratable acidity, and combined acidity were measured using a Metrohm 670 Titroprocessor (Herisau, Switzerland). Titratable acidity was determined by titrating up to pH 8.3 with 0.2 mol L^{-1} NaOH and expressed as lactic acid. Combined acidity was determined with 2 mol L^{-1} HCl until the pH value reached 2.6 and expressed as the equivalent of NaOH per liter. Sodium chloride was determined by titration with AgNO_3 .

2.5. Statistical analyses

The Student's *t*-test was used to compare the mean values of aroma intensities of odor descriptors and concentrations of individual volatile compounds between samples from Manzanilla and Hojiblanca cultivars. Pearson's correlation tests were performed to assess the internal degree of correlation of the variables in the sensory data. The above-mentioned analyses were performed with XLSTAT v. 2016 (Addinsoft, New York, USA). Hierarchical clustering and heatmap for sensory data based on Pearson

correlation coefficient were performed with PermutMatrix software (Caraux and Pinloche, 2005). Principal component analysis (PCA) was performed for exploratory analysis of the GC-MS data. To maximize the separation among samples and to identify the volatiles responsible for the separation, orthogonal partial least squares (OPLS) was used. Partial least squares (PLS) regression was performed to model relationships between the individual odor descriptors and volatile compounds. All variables were mean-centered and normalized to unit variance before applying OPLS and PLS analyses. 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 OPLS and PLS models. The generated models were validated and the quality of the models was evaluated using diagnostic tools such as cumulative R^2X (variation explained by the models) and cumulative Q^2 (variation predicted by the model, according to the cross-validation). In addition, analysis of variance testing of cross-validated predictive residuals (CV-ANOVA, with p -value < 0.05 as a cut off) was performed to assess the reliability of the OPLS and PLS models. PCA, OPLS, and PLS analyses were performed with SIMCA 14.1 software (Umetrics, Umea, Sweden).

3. Results and Discussion

3.1. Sensory evaluation results

This study only evaluated the human olfactory responses of black ripe olives. The aroma of 8 samples of black ripe olives was described by the trained panel using 11 different odor descriptors (briny, sautéed mushroom, earthy/soil-like, oak barrel, nutty,

artificial fruity/floral, natural fruity/floral, vinegary, alcohol, fishy/ocean-like, and cheesy). Except for the “briny” descriptor, no significant differences between Manzanilla and Hojiblanca black ripe olives were observed in the aroma intensities for the above-mentioned descriptors (Figure 1). The highest intensities were found for “briny”, “sautéed mushroom”, “oak barrel”, and “natural fruity/floral” descriptors. A previous study found that sliced black ripe olives from Spain were characterized by nutty, alcohol, oak barrel, and artificial fruity/floral attributes (Lee et al, 2012). Differences with our results may be due to differences in olive cultivars and processing methods, which were unknown in the study of Lee et al. (2012), without discarding differences in the presentation forms (sliced olives vs whole olives) as well as discrepancies between sensory panels (Martin, Molimard, Spinnler, & Schlich, 2000). PCA applied to the sensory data showed a poor separation of the two cultivars (data not shown). Correlations among odor descriptors are illustrated in Figure 1S. Only a few significant correlations were found. The “sautéed mushroom” descriptor was positively correlated to “earthy/soil-like” descriptor ($r = 0.708$, $p = 0.050$) and the “vinegary” attribute was positively correlated to “fishy/ocean-like” odor ($r = 0.828$, $p = 0.011$). On the contrary, the latter two attributes exhibited high negative correlations with the “natural fruity/floral” attribute ($r = -0.810$ and -0.945 , respectively).

3.2. Volatile compounds by HS-SPME/GC-MS analysis

A total of 74 volatile compounds belonging to different chemical classes (2 acids, 10 alcohols, 21 aldehydes, 8 heterocyclic compounds, 14 esters, 6 hydrocarbons, 2 phenols, 5 terpenes, and 6 other compounds) were identified and semi-quantified in the present study (Table 2S). All the identified compounds were previously reported in black ripe olives (Sansone-Land et al., 2014; López-López et al., 2019), with the exception of

methyl cinnamate, benzyl chloride, and methoxyphenyl oxime. Among the identified compounds, furfuryl alcohol, styrene, α -muurolene, benzyl methyl ether, and (Z)-3-hexenyl methyl ether were found in Hojiblanca samples, but were not detected in Manzanilla samples. Unlike other types of table olives such as Spanish-style or Greek-style green olives, black ripe olives were characterized by the presence of several heterocyclic compounds (pyridines, furan derivatives) formed during the sterilization treatment (López-López et al., 2019). Pyridines may be formed by the condensation reaction of aldehydes, ketones, α,β -unsaturated carbonyl compounds, or various derivatives of such compounds with ammonia or amino acids (Suyama & Adachi, 1980). Furans are among the most ubiquitous heterocyclic compounds in thermally processed foods. Furfural may be formed as an intermediate product of the Maillard reaction (Martins, Jongen, & van Boekel, 2001). 2-Alkylfurans mainly result from the degradation of lipids. 2-Pentylfuran, for instance, is commonly reported as an oxidation product of linoleic acid (Adams, Bouckaert, Van Lancker, De Meulenaer, & De Kimpe, 2011). We can also speculate about the origin of benzyl chloride in black ripe olives. It is well known that benzyl chloride can be formed by free radical chlorination of toluene. Toluene is one of the hydrocarbons present in black ripe olives before packing step, as found in our previous work (López-López et al., 2019). Chlorine radicals ($\text{Cl}\cdot$) could be formed from chloride ions (Cl^-) in the sterilization step (it must be stressed that the olives were packed with a cover brine composed by 35 g L^{-1} of NaCl plus 0.2 g L^{-1} of ferrous gluconate, and subjected to sterilization for 17 min at 121°C). In aqueous solution, chloride ions would react rapidly with dissolved free radicals such as hydroxyl radicals ($\text{HO}\cdot$), which could be formed from the Fenton reaction between hydrogen peroxide and ferrous ions. In turn, hydrogen peroxide could be formed from the dissolved oxygen as the result of oxidation reactions involving polyphenols, in a similar

way to the mechanism proposed in the non-enzymatic oxidation of wines (Oliveira, Ferreira, de Freitas, & Silva, 2011). PCA was initially applied to 74 identified compounds for exploratory analyses of the GC-MS data. The first two principal components accounted for 70.5% of the variation in the data. The PCA score plot showed a trend to separate according to cultivar (Figure 2a). However, no significant differentiation was found between Manzanilla and Hojiblanca samples in the PCA model, which reflects a poor predictive capability as indicated by a Q^2 value of 0.521. In order to maximize separation between samples, OPLS, a supervised pattern recognition method, was applied to remove noncorrelated variation in X variables (volatile compounds) to Y variables (predefined classes such as cultivars under study). The OPLS score plot showed a clear separation between cultivars (Figure 2b). Compared to the PCA model, this OPLS model showed improved predictability with a Q^2 value of 0.833 (CV-ANOVA p -value was 0.049, indicating that the model was reliable). To identify the volatiles responsible for the separation, variable importance in the projection (VIP) statistics was used. A total of 23 volatiles were identified with $VIP > 1$ and $p < 0.05$ (Figure 2c), of which 12 volatiles showed significant differences between cultivars (Table 2). Typical oxidation products of fatty acids such as 1-heptanol, 1-octanol, hexanal, 2-heptenal, (*E*)-2-octenal, and (*E*)-2-decenal were found in higher amounts in the Manzanilla samples compared to Hojiblanca olives, confirming a higher susceptibility to lipid oxidation in the case of the Manzanilla cultivar (Cortés-Delgado et al., 2016). On the contrary, Hojiblanca olives showed higher amounts of 3-methylpyridine, 3-ethyl-4-methylpyridine, furfuryl alcohol, benzyl methyl ether, benzyl chloride and α -muurolene.

3.3. Relationships between volatile compounds and odor descriptors

PLS was applied to establish correlations among the odor descriptors of the black ripe olives and the volatile compounds. One PLS model per each odor descriptor was developed. The models built with the descriptors sautéed mushroom, earthy/soil-like, oak barrel, artificial fruity/floral, alcohol, and fishy/ocean-like gave poor results (the software did not extract any significant component when auto-fitting the model), indicating that these descriptors were not significantly correlated with any volatile compound (data not shown). This is likely due to the fact that the number of samples used in our study was small, which makes it difficult to associate a single compound with a single descriptor. However, the models for the remaining descriptors (briny, vinegary, natural fruity/floral, cheesy, and nutty) were auto-fitted by the software and their quality parameters are reported in Table 3. As can be seen, two PLS models per each of these descriptors were developed: the first model was built using all volatiles identified (i.e. 74 X-variables) while the second one was built using the volatiles with significant VIP values in the first model. Only one model was considered reliable according to the *p*-value (< 0.05) obtained by CV-ANOVA, namely, the model for “nutty” odor developed using 17 volatile compounds. This model explained 92% of variance (calculated by cross-validation) with a RMSECV (which represents one standard deviation in the metric of the Y variable) of 0.041. Therefore, this sensory attribute could be predicted with sufficient accuracy. The relationship between the “nutty” descriptor and the 17 volatiles are summarized in Figure 3a. Significant positive correlations were found for 3-ethyl-4-methylpyridine (regression coefficient: 0.164), 4-ethylbenzaldehyde (0.156), copaene (0.152), pyridine (0.138), benzyl chloride (0.135), 3-ethylpyridine (0.112), methyl acetate (0.094), benzyl alcohol (0.089), benzoic acid (0.081), isopentanol (0.065), and 3-methylbutanal (0.050). It must be pointed out that the largest VIPs corresponded to 3-ethyl-4-methylpyridine, 4-ethylbenzaldehyde,

pyridine, 3-ethylpyridine, and benzyl alcohol (Figure 3b), indicating that these compounds were the main contributors to the “nutty” model. Interestingly, pyridines are among the volatiles reported in a variety of foods (Maga, 1981); for example, in peanuts, which was taken as reference for “nutty” descriptor in our study. The above-mentioned compounds have a variety of aroma characteristics associated with them. The odor of 3-ethyl-4-methylpyridine has been reported as sweet-woody, herbaceous and slightly spicy-earthly (Arctander, 1969). For the remaining compounds, the following odor descriptions (in parenthesis) are reported in the Perflavory website (<http://www.perflavory.com>): pyridine (sour, smoky, warm, burnt, coffee, putrid, fishy, amine), 3-ethylpyridine (tobacco, oakmoss, leather), 4-ethylbenzaldehyde (bitter, almond, sweet, anise), and benzyl alcohol (floral, rose, phenolic, balsamic). This appears to indicate that “nutty” odor in black ripe olives originates from an interaction among different volatile compounds, which produces an odor sensation different to that of the individual compounds, as suggested for other odor sensations in Spanish-style green table olives (López-López et al., 2018).

Of the remaining descriptors shown in Table 3, the models for “natural fruity/floral” and “cheesy” showed some interesting correlations with volatile compounds, although none of them were adequate for accurate predictions. The model using 22 volatiles for the “natural fruity/floral” descriptor presented a significant positive correlation with benzyl alcohol (regression coefficient: 0.120), phenol (0.111), and dimethyl sulfoxide (0.108) (Figure 2S). Therefore, benzyl alcohol (floral odor) appears to be the main contributor to this odor sensation in black ripe olives. For the “cheesy” descriptor, the PLS model using 17 volatiles showed 15 compounds with significant positive coefficients, the largest ones corresponded to 1-pentanol (0.058), ethyl benzoate (0.054), methyl cinnamate (0.053), ethanol (0.052), and ethyl 2-methylbutanoate

(0.051) (Figure 3S). The odor types reported in the Perflavory website for these compounds were: fermented, minty, balsamic, alcoholic, and fruity, respectively. Both 1-pentanol and ethanol have been identified in Feta cheese, the reference used for the cheesy odor in the present study, the latter compound being the major alcohol in this food (Kondyli, Pappa, & Vlachou, 2012). According to Horwood, Lloyd, & Stark (1981), 1-pentanol greatly contributes to the aroma of Greek Feta cheese.

4. Conclusions

The aroma profile and volatile composition of different samples of black ripe olives from Manzanilla and Hojiblanca cultivars were studied by QDA and HS-SPME/GC-MS, respectively. The aroma profile of these samples was found highly similar. However, clear differences in the volatile profiles of Manzanilla and Hojiblanca samples were found, as evidenced by application of OPLS to the GC-MS data. A reliable PLS model was only obtained for the “nutty” descriptor. Pyridine and two pyridine derivatives (3-ethyl-4-methylpyridine and 3-ethylpyridine), which showed a high correlation between them, along with 4-ethylbenzaldehyde and benzyl alcohol were found to be associated with “nutty” odor. Furthermore, the latter volatile compound (i.e. benzyl alcohol with a floral odor) was found to be a major contributor to “natural fruity/floral” odor, while 1-pentanol along with ethanol and some esters were found to contribute to “cheesy” odor in black ripe olives. In summary, the data obtained have shown that with the analytical procedures used and a relatively small number of samples, it has been possible to determine associations of volatile compounds with three odor descriptors of black ripe olives. In order to improve this study, it may be necessary to analyze a greater number of samples of different cultivars, grown areas and storage periods that influence the volatile composition of black ripe olives. In addition, further

research using recombinates is needed to prove the positive or negative effect of individual compounds on certain aroma descriptors.

Authors' contributions

Antonio H. Sánchez: Elaboration of products (packing and sterilization treatments) and analysis of physicochemical characteristics of samples.

Antonio López-López: Elaboration of products (darkening and packing stages), sensory panel leader, and analysis of sensory data.

Amparo Cortés-Delgado: Sample preparations for HS-SPME/GC-MS and analysis of GC-MS data.

Antonio de Castro: Elaboration of products, microbiological analysis during the preservation stage, and revision of the final version of manuscript.

Alfredo Montaña: Design and supervision of the research project, statistical data analysis, and writing of the manuscript.

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Supplementary material

Table 1S. Physico-chemical characteristics of packing brines from Manzanilla and Hojiblanca black ripe olives analyzed in the present study.

Table 2S. Volatile composition of the black ripe olive samples analyzed in the present study.

Fig. 1S. Pearson's correlation between the odor descriptors of black ripe olives. The colors of the scale bar denote the nature of the correlation, with 1 indicating a perfectly positive correlation (red) and -1 indicating a perfectly negative correlation (green) between two descriptors.

Fig. 2S. PLS coefficients plot for the "natural fruity/floral" attribute developed using 22 volatile compounds as X-variables. Error bars denote jack-knife uncertainty bars (95%).

Fig. 3S. PLS coefficients plot for the "cheesy" attribute developed using 17 volatile compounds as X-variables. Error bars denote jack-knife uncertainty bars (95%).

FIGURE CAPTIONS

Fig.1. Spider plot for sensory data of black ripe olives. Values represent mean scores. Asterisk denotes significant difference between samples ($p < 0.05$).

Fig.2. (a) PCA score plot, computed from the first two PCs, derived from GC-MS data, (b) OPLS score plot derived from GC-MS data. (c) VIP plot for the OPLS model.

Fig. 3. (a) PLS coefficients plot and (b) VIP plot for the “nutty” odor developed using 17 volatile compounds as X-variables. Error bars denote jack-knife uncertainty bars (95%).

Table 1. Aroma descriptors used for the sensory evaluation of black ripe olives from Manzanilla and Hojiblanca cultivars (Adapted from Lee et al., 2012)

Aroma descriptor	Definition
Briny	Aroma of pickling salt
Sautéed mushroom	Aroma of sautéed and cooked mushrooms
Earthy/Soil-like	Aroma of natural wet soil
Oak barrel	Aroma of wood
Nutty	Aroma of peanut
Artificial fruity/Floral	Scent of artificial fruit flavor (e.g. raspberry)
Natural fruity/Floral	Mild scent of natural fruit/flower (e.g. chrysanthemum)
Vinegary	Aroma of fermented vegetables and vinegar
Alcohol	Aroma of ethanol
Fishy/Ocean-like	Aromas of the ocean and of dried anchovy
Cheesy	Aroma of Feta cheese

Table 2. Significant volatile compounds contributing to the differences in the Manzanilla and Hojiblanca black ripe olives

Compound	Manzanilla samples ^a	Hojiblanca samples ^a	<i>p</i> -value ^b	FC ^c
1-Heptanol	3.2	0.3	0.032	10.7
1-Octanol	3.8	0.9	0.024	4.0
Hexanal	5.8	1.3	0.049	4.4
2-Heptenal	17.7	2.7	0.001	6.5
(<i>E</i>)-2-Octenal	4.0	0.5	0.002	7.7
(<i>E</i>)-2-Decenal	20.8	2.2	0.003	9.5
3-Methylpyridine	6.5	33.4	0.038	0.2
3-Ethyl-4-methylpyridine	13.9	27.1	0.033	0.5
Furfuryl alcohol	ND	1.9		
Benzyl methyl ether	ND	3.7		
Benzyl chloride	2.4	14.0	0.000	0.2
α -Muurolene	ND	1.2		

^a Mean values expressed as $\mu\text{g kg}^{-1}$ of 3-octanol. ND = not detected. ^b *p*-value according to ANOVA. ^c Fold change (value of the average concentration of Manzanilla/Hojiblanca).

Table 3. Quality parameters of the PLS models relating sensory descriptors with volatile compounds

Sensory attribute	no. X ^a	no. PC ^b	Regression line ^c	R ² X ^d	R ² Y ^e	RMSEE ^f	Q ² Y ^g	RMSECV ^h	p-value (CV-ANOVA) ⁱ
Briny	74	2	$y = x + 4.69 * 10^{-8}$	0.679	0.793	0.183	0.424	0.249	0.535
	17	2	$y = x + 4.92 * 10^{-7}$	0.839	0.791	0.184	0.562	0.206	0.279
Vinegary	74	4	$y = x + 5.98 * 10^{-8}$	0.932	0.990	0.049	0.876	0.230	0.880
	18	4	$y = x - 1.18 * 10^{-8}$	0.975	0.998	0.022	0.976	0.106	0.279
Natural fruity/floral	74	3	$y = x - 4.30 * 10^{-8}$	0.750	0.952	0.066	0.677	0.168	0.749
	22	2	$y = x - 3.51 * 10^{-7}$	0.759	0.861	0.102	0.653	0.131	0.224
Cheesy	74	1	$y = x + 3.60 * 10^{-7}$	0.435	0.583	0.051	0.183	0.062	0.602
	17	1	$y = x + 1.39 * 10^{-7}$	0.830	0.591	0.051	0.522	0.047	0.157
Nutty	74	2	$y = x - 4.38 * 10^{-7}$	0.685	0.963	0.039	0.755	0.086	0.130
	17	2	$y = x + 4.69 * 10^{-7}$	0.623	0.973	0.033	0.922	0.041	0.007
^a Number of X variables in the model. ^b Number of principal components in the model. ^c Linear equation of the observed values vs. the predicted values. ^d The fraction of the variation of the X variables explained by the model. ^e The fraction of the variation of the Y variables explained by the model. ^f Root mean square error of estimation. ^g The fraction of the variation of the Y variables predicted by the model. ^h Root mean square error from cross-validation. ⁱ p-value obtained by analysis of variance testing of cross-validated predictive residuals.

Figure 1

(a) component PCA model, R2X(cum): 0.880, Q2: 0.521

(b) OPLS model, 1+1+0 components, R2X(cum): 0.701, Q2: 0.833

(c)

Figure 2

Figure 3

Table 1S. Physico-chemical characteristics of packing brines from Manzanilla and Hojiblanca black ripe olives analyzed in the present study^a

Sample	pH	Titrateable acidity (g L ⁻¹ of lactic acid)	Combined acidity (eq L ⁻¹)	Salt (g L ⁻¹ of NaCl)
M1	6.78±0.09	0.2±0.0	0.038±0.003	19.9±1.0
M2	5.55±0.40	3.1±0.6	0.038±0.007	16.3±0.7
M3	6.12±0.05	0.5±0.0	0.037±0.002	19.9±0.7
M4	4.92±0.27	2.8±0.3	0.037±0.001	17.5±0.8
H1	6.71±0.02	0.3±0.1	0.054±0.002	18.8±0.6
H2	6.13±0.19	0.8±0.2	0.061±0.007	16.3±0.3
H3	6.66±0.06	0.4±0.0	0.056±0.004	19.2±0.8
H4	5.71±0.19	1.5±0.4	0.063±0.003	17.2±0.4

^a Values are means ± SD of three replicate bottles

Table 2S. Volatile composition of the black ripe olive samples analyzed in the present study.

				Samples ^a							
	Code	IEC (<i>m/z</i>) ^b	ID ^c	M1	M2	M3	M4	H1	H2	H3	H4
Acids											
acetic acid	1	60	1	n.d. ^d	n.d.	n.d.	50.2±17.6	n.d.	n.d.	n.d.	5.5±3.0
benzoic acid	2	105	1	5.5±1.6	11.4±3.6	n.d.	n.d.	6.3±0.9	6.0±0.9	4.8±1.5	7.2±1.6
Alcohols											
ethanol	3	45	1	67.2±16.7	93.7±37.9	12.7±2.5	32.7±9.9	19.3±6.2	34.5±5.6	20.6±5.6	34.9±6.6
isopentanol	4	55	1	3.8±1.1	6.6±2.4	n.d.	n.d.	n.d.	2.5±0.5	1.7±0.6	4.7±0.9
1-pentanol	5	55	1	5.0±1.3	6.0±1.6	n.d.	n.d.	0.8±0.3	2.6±0.7	0.8±0.2	2.8±0.6
1-hexanol	6	56	1	10.4±2.5	16.3±5.6	1.8±0.1	6.1±2.0	1.0±0.2	2.4±0.5	2.2±0.6	4.3±0.8
(<i>Z</i>)-3-hexen-1-ol	7	67	1	8.2±1.7	14.5±4.6	2.2±0.4	7.3±2.7	1.6±0.4	2.4±0.5	2.9±0.7	6.2±1.1
1-heptanol	8	70	1	2.6±0.9	5.7±2.1	0.9±0.1	3.7±0.9	n.d.	1.2±0.3	n.d.	n.d.
1-octanol	9	84	1	3.3±1.0	5.9±1.9	1.5±0.2	4.4±1.0	0.9±0.2	1.2±0.2	0.6±0.2	1.1±0.3
(<i>E</i>)-2-decen-1-ol	10	57	1	2.1±0.7	2.7±0.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
benzyl alcohol	11	108	1	2.1±0.3	4.0±1.4	0.6±0.1	2.8±0.9	1.1±0.3	2.4±0.5	1.4±0.3	2.9±0.5
phenylethyl alcohol	12	91	1	23.8±3.2	4.8±1.7	1.6±0.2	6.7±2.2	1.7±0.4	3.6±0.7	2.2±0.6	4.0±0.9

Aldehydes											
2-methylpropanal	13	72	2	n.d.	n.d.	10.2±2.1	44.4±15.2	4.1±1.7	19.7±4.2	11.8±4.1	26.2±5.6
2-methylbutanal	14	57	1	80.7±19.5	240.5±98.6	67.6±9.6	309.2±97.5	30.0±5.9	126.6±35.4	66.9±18.6	162.9±38.8
3-methylbutanal	15	44	2	113.4±27.9	278.6±115.4	103.0±17.8	467.7±141.0	52.8±11.7	176.0±56.1	101.8±32.1	241.3±59.9
pentanal	16	44	1	33.6±13.4	96.0±36.5	12.5±2.6	52.4±15.7	11.9±3.1	27.6±6.5	12.8±3.3	28.6±8.4
2-butenal	17	70	1	10.8±2.9	8.3±3.6	39.1±5.1	48.7±11.9	7.6±1.8	21.5±5.8	14.2±3.6	9.2±2.0
hexanal	18	82	1	4.2±1.8	9.9±4.8	1.7±0.3	7.6±2.2	0.9±0.3	1.7±0.5	0.7±0.1	2.0±0.5
2-ethyl-2-butenal	19	98	2	7.4±1.2	17.7±7.3	8.8±1.5	35.3±3.0	7.8±2.1	20.3±5.8	13.3±3.2	30.9±6.5
heptanal	20	70	1	7.7±3.5	27.3±11.0	1.7±0.4	6.2±1.7	1.0±0.3	1.8±0.5	0.7±0.1	1.7±0.3
2-vinyl-2-butenal	21	67	2	5.4±1.8	n.d.	109.1±15.9	47.9±12.4	n.d.	n.d.	5.0±1.4	2.1±0.8
octanal	22	84	1	10.8±4.7	29.0±12.7	4.5±0.7	9.4±2.9	2.7±1.0	2.7±0.6	1.8±0.4	2.0±0.4
2-heptenal	23	83	1	18.9±7.9	21.6±8.1	11.4±2.6	19.1±4.9	5.2±1.6	5.7±2.4	n.d.	n.d.
nonanal	24	98	1	10.4±3.1	20.2±7.7	2.1±0.2	6.4±1.4	1.7±0.4	2.5±0.6	1.3±0.3	1.5±0.4
(<i>E</i>)-2-octenal	25	55	1	3.9±1.6	4.9±1.8	2.3±0.4	4.8±0.8	1.0±0.3	0.6±0.2	0.5±0.1	n.d.
(<i>E,E</i>)-2,4-heptadienal	26	81	1	8.0±2.4	3.3±1.4	3.5±0.4	4.7±1.2	3.4±1.0	n.d.	n.d.	n.d.
benzaldehyde	27	106	1	81.1±21.3	202.7±78.5	205.4±30.8	736.7±237.7	336.8±88.5	648.2±125.5	645.8±150.5	1162.7±213.4
phenylacetaldehyde	28	91	1	35.3±11.9	20.5±6.0	36.7±4.1	52.3±18.3	n.d.	n.d.	18.5±6.1	17.0±5.0

(<i>E</i>)-2-decenal	29	70	1	18.4±5.7	25.3±7.5	11.2±1.6	28.2±7.5	2.6±0.5	2.4±0.7	1.8±0.6	1.9±0.4
4-ethylbenzaldehyde	30	134	3	1.9±0.5	3.1±0.9	0.9±0.2	3.0±1.0	3.1±0.7	4.6±0.9	2.8±0.7	3.6±0.8
(<i>E,E</i>)-2,4-decadienal	31	81	1	5.2±1.4	9.0±2.8	1.6±0.3	4.9±1.1	2.7±0.8	2.6±0.5	1.7±0.4	1.6±0.5
(<i>E</i>)-cinnamaldehyde	32	131	3	1.9±0.6	2.1±0.8	0.8±0.1	2.4±0.9	2.7±0.6	2.5±0.5	3.0±0.7	3.0±0.8
2-phenyl-2-butenal	33	146	2	n.d.	45.1±14.3	n.d.	2.5±0.7	n.d.	3.2±1.0	0.4±0.1	3.8±1.1
Heterocyclic compounds											
pyridine	34	79	2	5.9±1.7	11.8±5.1	n.d.	n.d.	5.6±1.2	12.3±3.0	10.2±2.2	16.5±2.7
3-methylpyridine	35	93	2	7.6±2.6	18.4±6.4	n.d.	n.d.	14.9±4.7	45.3±11.2	20.8±4.7	52.5±10.0
3-ethylpyridine	36	107	2	41.0±8.9	47.7±19.2	15.9±1.9	25.9±9.6	25.5±6.0	34.9±8.7	35.5±8.2	41.8±5.2
3-vinylpyridine	37	105	3	41.9±9.0	62.7±21.4	33.0±5.5	77.1±25.7	41.4±9.7	64.1±13.6	109.9±28.2	149.9±24.3
3-ethyl-4-methylpyridine	38	106	3	15.4±3.5	20.9±8.4	6.8±0.7	12.3±4.5	17.4±3.8	28.7±5.6	26.6±6.4	35.8±4.4
furfural	39	96	1	24.4±5.7	16.7±5.3	18.6±2.3	44.2±10.1	15.6±3.4	13.7±3.4	19.7±6.0	19.8±4.5
furfuryl alcohol	40	98	2	n.d.	n.d.	n.d.	n.d.	0.8±0.2	2.7±0.5	1.0±0.2	3.0±0.5
2-pentylfuran	41	81	2	5.6±1.7	4.2±1.8	n.d.	n.d.	n.d.	1.5±0.3	n.d.	n.d.
Esters											
methyl acetate	42	74	2	14.8±5.8	48.3±17.8	11.6±3.4	69.1±21.3	14.4±6.7	36.1±7.4	22.4±6.7	50.5±9.9
ethyl acetate	43	43	1	606.9±207.5	1474.5±518.9	124.4±33.8	742.8±220.9	154.2±57.8	396.7±91.4	172.5±57.6	403.4±122.1

ethyl 2-methylbutanoate	44	102	1	9.2±2.1	20.0±6.3	1.0±0.2	3.5±1.0	n.d.	2.4±0.7	1.1±0.3	2.6±0.7
ethyl 3-methylbutanoate	45	88	1	8.9±2.2	22.3±7.9	1.3±0.3	4.7±1.4	n.d.	1.6±0.5	1.0±0.3	2.1±0.6
ethyl hexanoate	46	88	1	2.1±0.3	3.2±1.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
hexyl acetate	47	56	1	1.8±0.3	n.d.	n.d.	n.d.	0.8±0.1	1.4±0.4	3.1±0.7	5.0±1.2
(Z)-3-hexenyl acetate	48	67	1	n.d.	n.d.	10.0±2.4	n.d.	5.7±1.6	10.5±1.7	19.7±4.8	33.9±6.4
ethyl octanoate	49	88	1	3.1±0.6	5.0±1.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
ethyl benzoate	50	105	1	2.5±0.5	4.5±1.6	n.d.	n.d.	n.d.	n.d.	1.1±0.2	1.5±0.4
methyl nicotinate	51	106	2	4.4±1.3	7.5±2.8	3.3±0.5	11.1±3.5	1.1±0.3	1.7±0.5	1.5±0.5	2.5±0.7
ethyl salicylate	52	120	1	1.2±0.2	2.5±0.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
methyl cinnamate	53	162	2	0.5±0.1	0.8±0.2	n.d.	n.d.	n.d.	n.d.	0.3±0.1	0.4±0.1
ethyl cinnamate	54	131	2	2.0±0.5	4.5±1.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
methyl 2-formylbenzoate	55	133	3	5.5±1.7	4.4±1.4	13.9±1.5	33.7±8.9	5.5±1.9	3.5±0.7	10.3±3.3	7.8±2.8
Hydrocarbons											
octane	56	85	1	498.7±183.6	1508.6±554.0	126.9±30.3	765.2±217.9	7.9±2.0	48.9±18.0	6.7±2.0	22.2±7.3
toluene	57	91	1	15.0±3.6	32.6±11.9	5.3±0.9	24.2±4.7	5.8±0.7	5.6±0.9	2.4±0.5	6.7±2.1
<i>p</i> -xylene	58	91	1	9.1±2.2	21.3±7.2	2.5±0.6	10.8±2.3	4.4±1.1	13.4±4.7	1.8±0.4	4.7±1.4
<i>o</i> -xylene	59	91	1	4.7±1.0	11.5±4.0	1.8±0.5	5.4±1.6	3.1±0.6	8.1±1.6	1.1±0.2	2.7±0.9

styrene	60	104	1	n.d.	n.d.	n.d.	n.d.	1.8±0.3	6.7±2.1	0.4±0.0	1.0±0.3
pseudocumene	61	105	1	n.d.	n.d.	n.d.	n.d.	2.4±0.4	5.2±1.3	n.d.	n.d.
Phenols											
phenol	62	94	1	3.9±1.1	8.4±2.0	2.1±0.3	8.2±2.5	3.7±0.8	3.4±0.7	3.4±0.8	3.9±0.7
vanillin	63	151	1	0.8±0.2	6.3±2.2	1.2±0.3	14.7±4.7	1.2±0.4	3.9±0.8	1.5±0.5	4.2±1.4
Terpenes											
(<i>E</i>)- β -ocimene	64	93	1	1.4±0.2	3.5±1.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6-methyl-5-hepten-2-one	65	108	1	7.8±3.3	23.3±8.7	4.1±0.6	8.4±1.3	2.5±0.9	2.6±0.6	1.8±0.5	2.7±0.8
copaene	66	119	2	1.5±0.6	2.8±0.8	3.0±0.4	12.0±4.1	8.5±1.5	12.5±2.6	16.2±5.4	22.7±6.3
α -muurolene	67	161	1	n.d.	n.d.	n.d.	n.d.	0.8±0.1	0.9±0.2	1.4±0.4	1.9±0.5
β -damascenone	68	121	1	2.7±0.4	4.7±1.2	0.8±0.1	2.6±0.8	1.7±0.3	2.7±0.6	1.6±0.5	2.2±0.5
Miscellaneous compounds											
dimethyl sulfide	69	62	1	314.0±79.6	537.7±214.8	200.8±28.1	782.3±286.1	85.0±21.0	279.4±79.5	202.3±74.3	391.8±91.7
benzyl methyl ether	70	121	2	n.d.	n.d.	n.d.	n.d.	1.4±0.3	3.7±0.9	3.8±0.9	5.9±1.2
benzyl chloride	71	91	2	n.d.	2.5±0.8	2.4±0.9	4.5±1.4	10.9±3.2	16.4±3.0	14.0±3.7	14.6±4.8
dimethyl sulfoxide	72	63	1	8.2±2.0	12.2±2.4	5.6±0.9	13.0±3.3	6.1±1.4	8.5±2.6	7.9±2.2	9.0±2.2
methoxyphenyl oxime	73	151	2	n.d.	6.4±2.1	n.d.	n.d.	13.1±2.4	3.3±0.6	n.d.	n.d.

(Z)-3-hexenyl methyl ether	74	82	2	n.d.	n.d.	n.d.	n.d.	3.5±0.8	11.0±3.4	12.0±3.3	26.9±8.0
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^a Concentrations are expressed as $\mu\text{g kg}^{-1}$ of 3-octanol. Values are means $\pm$ SD of duplicate bottles, each analyzed in triplicate.

^b m/z used in ion extraction chromatogram (IEC) to obtain the GC peak area of each compound.

^c Identification: 1, identified, mass spectrum and RI were in accordance with standards; 2, tentatively identified, mass spectrum matched in the standard NIST 2008 library and RI matched with literature; 3, tentatively identified, mass spectrum agreed with the standard NIST 2008.

^d n.d. = not detected.

Fig. 1S. Pearson's correlation between the aroma descriptors of black ripe olives. The colors of the scale bar denote the nature of the correlation, with 1 indicating a perfectly positive correlation (red) and -1 indicating a perfectly negative correlation (green) between two descriptors.

Fig. 2S. PLS coefficients plot for the “natural fruity/floral” attribute developed using 22 volatile compounds as X-variables. Error bars denote jack-knife uncertainty bars (95%).

Fig. 3S. PLS coefficients plot for the “cheesy” attribute developed using 17 volatile compounds as X-variables. Error bars denote jack-knife uncertainty bars (95%).