Retention of color and volatile compounds of Spanish-style green table olives pasteurized and stored in plastic containers under conditions of constant temperature

Antonio Higinio Sánchez, Antonio de Castro, Antonio López-López, Amparo Cortés-Delgado, Víctor Manuel Beato, Alfredo Montaño*

Food Biotechnology Department, Instituto de la Grasa-CSIC, Pablo Olavide University Campus, building 46, Utrera road, km 1, 41013 Seville, Spain

*Tel.: +34 95 4611550, fax: +34 95 4616790, e-mail corresponding author (A. Montaño): amontano@cica.es

E-mail addresses for co-authors:

Antonio Higinio Sánchez: ahiginio@cica.es
Antonio de Castro: amillan@cica.es
Antonio López-López: all@cica.es
Amparo Cortés-Delgado: acortes@cica.es
Víctor Manuel Beato: vmbeagal@ig.csic.es

Running title: Volatile compounds of green table olives in plastic containers
Abstract

Spanish-style green table olives pasteurized and stored in two types of pasteurizable plastic pouches and glass bottles were analyzed for color parameters and volatile components after 6.5 months of storage at 30 °C. Color parameters in pouches made of aluminium oxide coating on polyethylene terephthalate + medium-density polyethylene (AlOx-coated PET + MDPE) were acceptable and, in general, did not significantly differ from those in glass, but unacceptable values corresponding to dark visual colors of both olives and brine were found in pouches made of polyethylene terephthalate + medium-density polyethylene/ethylene vinyl alcohol (PET + MDPE/EVOH). Forty-three volatile compounds were identified and quantified in olive pulp by solid phase micro-extraction (SPME) and gas chromatography coupled to mass spectrometry (GC-MS), 36 of these compounds being significantly different between the plastic and glass treatments. The type of plastic container had an impact on the volatile composition of product. Oxidation and scalping were considered to be the most probable causes for the differences in volatile components between PET + MDPE/EVOH pouches and glass containers, but in AlOx-coated PET + MDPE pouches no oxidation process was apparent.

Keywords: table olives, color, volatile compounds, SPME, plastic packaging
Highlights

42

44 ● Plastic material significantly influenced color and volatile profile of green olives

45 ● Green olives packed in AlOx-coated PET + MDPE pouches were comparable to that

46 in glass bottles

47 ● Oxidation reactions occurred in green olives packed in PET + MDPE/EVOH pouches
1. Introduction

Fermented green olives have been consumed around the world for thousands of years. Alkali-treated green olives in brine, also known as Spanish-style green olives are the most widely distributed and investigated type of table olive. This is a fermented product whose long-term preservation is usually carried out by its own physico-chemical characteristics without the need of a pasteurization treatment if pH is sufficiently low (< 3.5) and NaCl content is 5-7 g/100 g (Rejano, Montaño, Casado, Sánchez, & de Castro, 2010). However, the progressive preference of consumers for milder levels of acidity and salt has modified such conditions and the stabilization of the final product requires the use of pasteurization. This heat treatment results in shelf stable products by killing the major spoilage microorganisms, lactic acid bacteria and yeasts, as well as by inactivating enzymes that may contribute to fruit softening (Breidt, Sandeep, & Arritt, 2010).

Since the development of the commercial pasteurization process, all pasteurized table olives have been packaged in glass or varnished can containers which do not react chemically with food components. The main function of food packaging is to achieve preservation and the safe delivery of food products until consumption (Han, 2013). However, there is an increasing interest in the use of plastic packaging by industry due to factors such as reduced weight of plastic containers, lower production costs compared to glass, less apt to shatter, transparent, flexible, and convenient to the consumer (Sajilata, Savitha, Singhal, & Kanetkar, 2007). In spite of all these advantages, plastic containers are likely to have at least a limited level of oxygen permeability. This could negatively affect the quality of pickled vegetables, which are known to be susceptible to oxidation (Zhou, McFeeters, & Fleming, 2000; Cleary & McFeeters, 2006) and reduce...
the shelf life of products. In addition to oxidation, it must be taken into account that plastic packaging materials can absorb different compounds from the food, a phenomenon called scalping (sorption). In particular, flavor scalping is a term used to describe the loss of quality of a packaged food due either to its volatile flavors being absorbed by the package or the food absorbing undesirable flavors from the packaging material. Sorption of food aromas, particularly by plastic packaging materials, is usually perceived as a major factor contributing to the quality alteration of most foods during storage (Sajilata et al., 2007). Interactions between flavor compounds and plastic packages have been demonstrated in different food products such as orange juice (López-Gómez, Ros-Chumillas, & Belisario-Sánchez, 2009), wine (Reeves, 2009), beer (Bamforth & Krochta, 2009), milk (Kontominas, 2009), yogurt (MacBean, 2009), or vegetable oils (Piergiovanni & Limbo, 2009). However, to our knowledge, this type of study has not been carried out with any fermented vegetable. The selection of proper packaging materials that are compatible with fermented olives while maintaining quality during pasteurization treatment and storage is critical to proposing a change from traditional glass containers to plastic packaging. The objective of this work was to identify differences in the color and volatile component profiles of Spanish-style green table olives pasteurized and stored at constant temperature (30 ºC) in two distinct pasteurizable plastic containers in comparison with the traditional product packed in glass containers.

2. Materials and Methods

2.1. Materials and chemicals
Pitted Spanish-style green table olives (Manzanilla cultivar) were supplied in bulk by Angel Camacho SL (Seville, Spain). Physico-chemical characteristics of the corresponding brine were the following: pH, 3.47; titratable acidity, 0.91 g/100 mL (as lactic acid); combined acidity, 0.047 mol/L; and NaCl, 8.34 g/100 mL. Two types of plastic pouches, named as pouches A and B, were used. Both pouches were supplied by SP Group (Córdoba, Spain). Pouches A were made of PET + MDPE/EVOH (polyethylene terephthalate + medium-density polyethylene/ethylene vinyl alcohol) with oxygen permeability \( \approx 3 \text{ cm}^3/\text{m}^2/\text{d} \) at 23 °C and 50% r.h., and thickness of 106 μm. Pouches B were made of AlOx-coated PET + MDPE (aluminium oxide coating on polyethylene terephthalate + medium-density polyethylene) with oxygen permeability \( \approx 1 \text{ cm}^3/\text{m}^2/\text{d} \) at 23 °C and 50% r.h., and the same thickness as pouches A.

Potassium sorbate, ascorbic acid, sodium benzoate, citric acid, sodium chloride, and all volatile compounds used as reference standards were purchased from Sigma-Aldrich (St Louis, MO). Deionised water was obtained from a Milli-Q system (Millipore, Bedford, MA). All other chemicals and solvents (orthophosphoric acid, potassium dihydrogenorthophosphate, dipotassium hydrogenorthophosphate, sodium hydroxide, silver nitrate, methanol, acetonitrile, etc.) were of analytical or chromatographic grade from various suppliers (Panreac, Barcelona, Spain; VWR, Barcelona, Spain; Merck, Darmstadt, Germany).

2.2. Packing of Spanish-style green table olives

Olives were packed in plastic pouches A, plastic pouches B, and glass bottles using an acidified brine as cover liquor. This acidified brine consisted of citric acid, NaCl, ascorbic acid, potassium sorbate, and sodium benzoate to give equilibrium values...
of 0.50g/100 mL titratable acidity (expressed as lactic acid), 4.7 g /100 mL NaCl, 0.4 g L⁻¹ ascorbic acid, 0.5 g L⁻¹ sorbic acid, and 0.5 g L⁻¹ benzoic acid, respectively. Use of additives (ascorbic acid, sorbates and benzoates) was justified as it is a common practice in the olive industry, even in case of pasteurized samples. Ascorbic acid has been demonstrated to have a positive effect on fruit color (Casado, Sánchez, Rejano, de Castro, & Montaño, 2010; Casado, Sánchez, de Castro, Rejano, Beato, & Montaño, 2011) whereas sorbates plus benzoates can prevent surface films of yeasts and fungi in packed table olives once the packaging has been opened (Borbolla y Alcalá, Fernández-Díez, & Cancho, 1961; Chipley, 2005).

In both types of pouches the drained net weight of olives was 61.5 g (17 olives) and the brine volume was 86 mL. In glass containers the drained net weight and brine volume were 96.5 g (26 olives) and 135 mL, respectively, giving the same weight-to-volume ratio (0.715) as in the plastic pouches. For the corresponding calculations, the moisture content of pitted olives was assumed to be 75 g/100 g pulp (w/w). In case of packing in glass bottles, cover brine was added hot (≈ 70 °C) in order to achieve and maintain a vacuum inside the bottles. After packing (10 containers per packaging treatment), the plastic pouches and glass containers were subjected to pasteurization and then stored at 30 °C for 6.5 months in a Binder BD 720 (Tuttlingen, Germany) incubator with opaque doors and walls, natural convection and without any control of humidity. A storage temperature of 30 °C was selected to accelerate the possible reactions occurring inside the containers, and also taking into account the relatively high temperatures in our region. The pasteurization was carried out in a computer-controlled retort equipped with a water cascading system (Steriflow, SAS, Paris, France). Plastic pouches and glass containers were pasteurized separately. The process applied to both plastic bags and glass containers consisted of the following stages: (1) pre-heating from
the initial retort temperature (40 °C) to the final temperature (93 °C), duration 10 min;
(2) pasteurization at 93 °C for 7 min; and (3) cooling with tap water at ambient
temperature, duration 10 min. After the period of storage, three replicate containers
(pouches or bottles) were analyzed.

2.3. Color parameters

Surface color of olives was measured using a Color-View Model 9000
spectrophotometer (BYK-Gardner, Inc., Silver Spring, MD) with a measurement area of
11 mm diameter, 45° circumferential illumination, and observation angle of 0°. All
measurements were done on the CIE 1976 L*a*b* scale using illuminating conditions
CIE type C, 10º observer. Results were expressed as the mean of 10 replicate
measurements, each made on 1 olive. In addition, from the reflectance curve supplied
by the apparatus, a color index ($i$) was obtained, as described by Sánchez, Rejano, &
Montaño (1985):

$$i = \frac{(4R_{635} + R_{590} - 2R_{560})}{3}$$

where $R_{635}$, $R_{590}$, and $R_{560}$ are the values of reflectance at 635, 590, and 560 nm,
respectively. Olive color can be analytically classified as excellent (30.2 < $i$ < 33.6),
good (26.8 < $i$ < 30.2), acceptable (23.7 < $i$ < 26.8), bad (21.0 < $i$ < 23.7), and very bad
($i$ < 21.0).

Brine color was estimated by measuring the difference in absorbance at 440 and
700 nm, ($A_{440} - A_{700}$), as described by Montaño, Sánchez, & Rejano (1988). A value of
0.23 absorbance unit (AU) has been proposed as acceptance limit, above which the
brine color is considered unacceptable for packed green table olives.
2.4. Analysis of additives

The ascorbic acid in brine was analyzed using an HPLC method previously used in table olives (López, Montaño, García, & Garrido, 2005). The HPLC system consisted of a Waters 2690 separations module connected to a Waters 996 photodiode array detector, controlled with Millennium 32 software (Waters, Milford, MA, USA). The separation was performed on a Luna 5 µ C18(2) (250 x 4.6 mm i.d.) column (Phenomenex, Torrance, CA, USA) using deionised water (adjusted to pH 2.3 with orthophosphoric acid) as the mobile phase at a flow rate of 1.0 mL/min at ambient temperature. Ascorbic acid was monitored at 245 nm. Its identification in samples was based on the retention time and absorption spectrum.

Sorbic and benzoic acids in brine were analyzed by HPLC using the same HPLC system and column as above mentioned for ascorbic acid, except that a phosphate buffer solution (0.03 mol/L, pH 6.7) was used as the mobile phase and detection was carried out at 230 nm (Montaño, Sánchez, & Rejano, 1995).

2.5. Physicochemical analyses

The pH and titratable acidity of brines were measured using a Metrohm 670 Titroprocessor (Herisau, Switzerland). Titratable acidity was determined by titrating to pH 8.3 with 0.2 mol/L NaOH and expressed as lactic acid. Sodium chloride was determined by titration with AgNO₃ (Fernández-Díez et al., 1985).

2.6. Analysis of volatile compounds
Volatile compounds in brine were analyzed by solid phase micro-extraction (SPME) and gas chromatography coupled to mass spectrometry (GC-MS) following the procedure previously reported by Cortés-Delgado, Sánchez, de Castro, López-López, Beato, & Montaño (2016) with modifications. Briefly, 2.5 g of homogenized olive pulp was placed in a 15 mL glass vial, and 7.5 mL of NaCl solution (30 g /100 mL) were added. After the addition of a stirring bar (for stirring at 600 rpm) and 100 µL of 3-octanol (2 mg/L) used as an internal standard, the vial was closed and placed in a water bath adjusted to 40 ºC. The equilibration time was 15 min at 40 ºC. Headspace volatile compounds were extracted and concentrated on a divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) fiber (1 cm, 50/30 µm; Supelco, Bellefonte, PA). The fiber was exposed to the brine headspace for 30 min. Volatile compounds adsorbed on the SPME fiber were desorbed at 265 ºC 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 GC oven temperature programme consisted in 40 ºC for 5 min, then 40-195 ºC at 3 ºC/min, and then 195-240 ºC at 10 ºC/min and held there for 15 min. The carrier gas was helium at a constant flow of 1 mL min⁻¹. Compound identification was based on mass spectra matching with the standard NIST 08 MS library and on 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 to that of internal standard (3-octanol).
However, some peaks that showed interfering peaks or co-eluted in scan mode were quantified from their peak areas in the ion extraction chromatogram (IEC), which was obtained by selecting target ions for each one. These ions corresponded to base ion (m/z 100% intensity), molecular ion (M⁺) or another characteristic ion for each molecule.

2.7. Statistical data analysis

Analysis of variance (ANOVA) was performed with the Statistica software (version 7, Statsoft Inc., Tulsa, OK, USA). Scheffé’s test was used for mean comparisons. Significant differences were determined at the p<0.05 level.

3. Results and Discussion

After 6.5 months of storage at 30 ºC, packed olives were analyzed for chemical characteristics including pH, titratable acidity, salt, and content of additives in brine (Table 1). Significant differences (p < 0.05) between packages were found for each variable. The most noticeable difference was found for ascorbic acid, which was undetected in pouches A. This can be explained by the higher oxygen permeability of this type of pouch. However, in pouches B and glass containers, the concentrations of ascorbic acid were 0.140 and 0.183 g/L, respectively, which were below the value of 0.4 g/L that was set as equilibrium concentration. This can be explained by the anaerobic degradation of ascorbic acid occurring during storage time. As previously demonstrated in green olives pasteurized and stored in glass bottles, ascorbic acid was degraded at room temperature following first-order reaction kinetics (Montaño, Casado, Rejano, Sánchez, & de Castro, 2006).
Regarding potassium sorbate and sodium benzoate added as preservatives, it is well known that these compounds are significantly absorbed not only into the olive juice but also into the lipid phase (oil) and other tissue components of olives (Brenes, Romero, García, & Garrido, 2004). As result, contrary to other compounds like NaCl and lactic acid, the final concentrations of potassium sorbate and sodium benzoate in the cover brine were significantly lower than those expected (0.5 g/L). Despite this, the concentration of potassium sorbate by itself was above 0.2 g/L, which could be sufficient to prevent the development of surface films of yeasts and fungi once the packaging has been opened (Borbolla y Alcalá et al., 1961). Oxidation reactions could also explain the lower concentration of sorbic acid in pouches A compared to pouches B and glass bottles (Table 1). Sorbic acid is known to undergo degradation in packed foods, the overall rate of degradation being influenced by the availability of oxygen, which, in turn, is governed by the available head space in the pack and the oxygen permeability of the packaging material (Thakur, Singh, & Arya, 1994).

Package material also significantly affected the color parameters of both olives and cover brines (Table 2). Of the color parameters determined, L* (lightness), b* (yellowness) and index i were significantly lower, but a* (redness) and brine color significantly higher, in pouches A compared to pouches B and glass bottles. Based on the known correlation of index i with a visual scale (Sánchez et al., 1985), color of olives in pouches A can be classified as very bad, whereas olives in pouches B and glass bottles can be classified as acceptable. Another useful color parameter for describing color variation is the total color difference ΔE*. Choi, Kim, & Lee (2002) indicated that a ΔE* > 2 corresponds to noticeable differences in the visual perception of many products. Using the olives packed in glass bottles as reference, this parameter was just 2 in pouches B indicating that visual differences between olives in pouches B and glass
bottles were almost imperceptible. On the contrary, ΔE* was 16 in pouches A, indicating a great difference in visual color. Regarding brine color, the value of the parameter A440-A700 in pouches B and glass bottles was below the acceptance limit of 0.23 AU. On the contrary, A440-A700 was 0.35 in pouches A, which is clearly above this limit, indicating a severe browning of brine.

Volatile analysis data for pasteurized Spanish-style green table olives in plastic pouches A and B in comparison with glass containers at the end of storage period (6.5 months) identified 43 compounds (Table 3). Apart from these compounds, two intense peaks corresponding to sorbic and benzoic acids were observed in the total ion chromatograms (TIC) of all the samples (Fig. 1). Some compounds showed a high variability between replicate containers which would explain the similarities in results when ANOVA was applied. The volatile profile of product packed in pouches B was comparable to that packed in glass containers, but 16 compounds were significantly higher in glass containers. Ayhan, Yoem, Zhang, & Min (2001), in their study of the effects of plastic packaging on flavor compounds in orange juice, noted a loss of primary aldehydes which they explained by the absorption of flavor compounds into the packaging material, the acceleration of flavor degradation due to the initial oxygen concentrations and the transmission of oxygen through the package. In the present study, volatile losses in pouches B compared to glass could be only explained by the migration of components into the plastic container (scalping), as chemical reactions due to oxygen would be ruled out due to the presence of residual ascorbic acid, as mentioned above. On the contrary, oxidation reactions appeared to occur in pouches A. Thus, five carbonyl compounds, namely, 2-butenal, 2-cyclohexen-1-one, (E,E)-3,5-heptadien-2-one, benzaldehyde, and 2-hydroxybenzaldehyde were significantly higher in pouches A than in any of the other packages. These compounds could be formed by
oxidation reactions involving polyphenols from olives or by oxidation of additives such as sorbic acid. Polyphenols containing an ortho-dihydroxybenzene moiety such as hydroxytyrosol, which is the major phenolic compound in the olives after fermentation (Montaño, Sánchez, López-López, de Castro, & Rejano, 2010), could be oxidized to semiquinone radicals and benzoquinone while oxygen is reduced to hydrogen peroxide, in a similar way to the mechanism proposed in the non-enzymatic oxidation of wines (Oliveira, Ferreira, de Freitas, & Silva, 2011). Hydrogen peroxide in association with ferrous ions would generate hydroxyl radicals (HO•), which is known as the Fenton reaction. Hydroxyl radical is a reduced product of oxygen and it is recognized to oxidize almost any organic molecule found in the medium (Oliveira et al., 2011). This reaction may produce many oxidation products, mainly aldehydes and ketones. Dombre, Rigou, Wirth, & Chalier (2015) found that oxidative and ageing aroma compounds appeared in higher amount in wine packed in PET than in glass bottles due to oxygen ingress through packaging. Apart from oxidation reactions involving polyphenols, sorbic acid degradation by oxygen has been reported to yield various carbonyl compounds such as 2-butenal (crotonaldehyde), malonaldehyde, acetaldehyde, acrolein, formic acid, and malonic acid (Thakur et al., 1994). Benzaldehyde could be formed from phenylacetaldehyde (Chu & Yaylayan, 2008), a Strecker aldehyde which, in turn, could be formed from polyphenol-derived quinones and phenylalanine (Rizzi, 2006). However, in pouches A, benzaldehyde could also be initially present in PET (plastic material in contact with olives + brine) from the degradation of plastic additives such as plasticizer, lubricants or modifiers, and a part could migrate into the product (Ducruet, Vitrac, Saillard, Guichard, Feigenbaum, & Fournier, 2007).

It must be pointed out that aldehydes such as hexanal, octanal or 2-octenal did not show significant differences between packages (Table 3), indicating that lipid
oxidation was not important during storage in plastic pouches. These aldehydes, along with other aldehydes (e.g. pentanal, 2-hexenal, heptanal), have been used as indicators of lipid oxidation in other foods (Cleary & McFeeters, 2006).

Eight compounds, namely, dimethyl sulfide, ethyl acetate, ethanol, benzene, n-propyl acetate, 2-butanol, ethyl 2-methylbutanoate, and ethyl hexanoate were detected in pouches B or glass, but not in pouches A. Volatile losses in the latter pouches can be attributed to oxidation reactions and scalping. For example, dimethyl sulfide may be oxidized by hydrogen peroxide to form dimethyl sulfoxide. It is well known that, in solution, the oxidation of dimethyl sulfide by hydroperoxides leads to dimethyl sulfoxide which is, more slowly than dimethyl sulfide, further oxidized to dimethyl sulfone (Amels, Elias, & Wannowius, 1997). Ethanol could be oxidized to yield acetaldehyde (Oliveira et al., 2011). The presence of benzene in pouches B and glass can be attributed to the interaction between ascorbic acid and benzoic acid (Casado et al., 2011). However, in pouches A, the rapid oxidation of ascorbic acid would prevent the benzene formation, which appears to occur at slow rate in table olives (Casado et al., 2011). Another compound that was significantly different (lower) in pouches A compared to pouches B and glass was furfural. This compound may originate from the decomposition of ascorbic acid. Previous studies (Montaño et al., 2006) with packed table olives showed that there was a highly significant correlation between ascorbic acid degradation and furfural formation during storage at 40 ºC in glass bottles.

4. Conclusions

The type of plastic material had a significant effect on the retention of color parameters and volatile compounds of Spanish-style green table olives pasteurized and stored in
plastic containers. Compared to the traditional product in glass containers, the retention
of color and volatile compounds was significantly higher in plastic pouches B (AlOx-
coated PET + MDPE) than in pouches A (PET + MDPE/EVOH) with higher gas
permeability. Scalping could explain the loss of volatile components in pouches B,
while the differences in volatile composition between pouches A and glass could be
attributed to scalping and oxidation processes. These results suggest that the use of
pouches made of AlOx-coated PET + MDPE could be a great alternative to the
traditional package of product in glass, at least for a period of 6.5 months of storage.
However, further studies are needed in order to evaluate the shelf life of product in this
type of plastic container and to assess if the differences in volatile composition
compared to glass affect the sensory characteristics of the final product.

Acknowledgements

This work was supported in part by the Ministry of Economy and
Competitiveness from the Spanish government through Project AGL2014-54048-R,
partially financed by the European Regional Development Fund (ERDF), and the
Andaltec R&D+I Foundation.

References

oxidation of dimethyl sulfide by hydroperoxides in aqueous medium. Study on
the potential contribution of liquid-phase oxidation of dimethyl sulfide in the
atmosphere. *Journal of the Chemical Society, Faraday Transactions, 93*, 2537-
2544.


Choi, M. H., Kim, G. H., & Lee, H. S. (2002). Effects of ascorbic acid retention on juice
colour and pigment stability in blood orange (Citrus sinensis) juice during

of Benzaldehyde from Phenylacetaldehyde Using Pyrolysis GC-MS and FTIR.
*Journal of Agricultural and Food Chemistry, 56*, 10697-10704.

of oxidative aldehydes in fresh-pack dill pickles. *Journal of Agricultural and
Food Chemistry, 54*, 3421-3427.

prepared from different cultivars grown at different locations. *Food Research
International, 83*, 131-142.


Ducruet, V., Vitrac, O., Saillard, P., Guichard, E., Feigenbaum, A., & Fournier, N.
(2007). Sorption of aroma compounds in PET and PVC during the storage of a

Fernández-Díez, M.J., Castro, R., Fernández, A.G., Cancho, F.G., Pellissó, F.G., Vega,
M.N., Moreno, A.H., Mosquera, I.M., Navarro, L.R., Quintana, M.C.D., Roldán,
mesa*. Madrid: CSIC.

Han, J.H. (2013). Emerging technologies in food packaging: overview. In S. Ebnesajjad
(Ed.), *Plastic films in food packaging: materials, technology and applications*
(pp 121-126). Amsterdam: Elsevier Inc.


**Figure captions**

Fig. 1. Total ion chromatograms of the volatile profiles of Spanish-style green table olives pasteurized and stored in two distinct plastic pouches and glass bottles after 6.5 months of storage at 30 ºC. Peak numbers correspond to the compounds listed in Table 3. IS = internal standard (3-octanol); So = sorbic acid; Bz = benzoic acid.
<table>
<thead>
<tr>
<th>Packaging material</th>
<th>pH</th>
<th>Titratable acidity (g/100 mL lactic acid)</th>
<th>Salt (g/100 mL NaCl)</th>
<th>Ascorbic acid (mg/L)</th>
<th>Potassium sorbate (mg/L sorbic acid)</th>
<th>Sodium benzoate (mg/L benzoic acid)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pouches A</td>
<td>3.49 ± 0.00a</td>
<td>0.55 ± 0.00c</td>
<td>5.71 ± 0.10b</td>
<td>0 ± 0 a</td>
<td>245 ± 3a</td>
<td>234 ± 7a</td>
</tr>
<tr>
<td>Pouches B</td>
<td>3.46 ± 0.00a</td>
<td>0.51 ± 0.01b</td>
<td>4.80 ± 0.05a</td>
<td>140 ± 12b</td>
<td>304 ± 7b</td>
<td>268 ± 7a</td>
</tr>
<tr>
<td>Glass bottles</td>
<td>3.66 ± 0.01b</td>
<td>0.43 ± 0.00a</td>
<td>4.80 ± 0.04a</td>
<td>183 ± 12b</td>
<td>336 ± 19b</td>
<td>320 ± 17b</td>
</tr>
</tbody>
</table>

Table 1. Physico-chemical characteristics and concentration of additives in Spanish-style green table olives pasteurized and stored in different packages after 6.5 months of storage at 30 ºC.

* Analyses were performed in brine. Values are means ± standard error (SE) of triplicate containers (n=3). Means within columns followed by the same letter are not significantly different at the 5% level, according to the Scheffé’s test.

* Pouches A, PET + MDPE/EVOH (polyethylene terephthalate + medium-density polyethylene/ethylene vinyl alcohol) with oxygen permeability ≈ 3 cm$^3$·m$^{-2}$·day$^{-1}$; pouches B, AlOx-coated PET + MDPE (aluminium oxide coating on polyethylene terephthalate + medium-density polyethylene) with oxygen permeability ≈ 1 cm$^3$·m$^{-2}$·day$^{-1}$. 
Table 2. Color parameters of Spanish-style green table olives pasteurized and stored in different packages after 6.5 months of storage at 30 °C.  

<table>
<thead>
<tr>
<th>Packaging material</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
<th>ΔE* b</th>
<th>Index i</th>
<th>Brine color (A440-A700)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pouches A</td>
<td>43.2± 0.4a</td>
<td>6.2 ± 0.2c</td>
<td>23.5 ± 0.4a</td>
<td>16 ± 0.5b</td>
<td>20.8 ± 0.5a</td>
<td>0.351 ± 0.005b</td>
</tr>
<tr>
<td>Pouches B</td>
<td>53.6 ± 0.5b</td>
<td>4.4 ± 0.2b</td>
<td>35.9 ± 0.9b</td>
<td>2 ± 0.3a</td>
<td>26.6 ± 0.8b</td>
<td>0.129 ± 0.006a</td>
</tr>
<tr>
<td>Glass bottles</td>
<td>53.3 ± 0.6b</td>
<td>3.3 ± 0.1a</td>
<td>35.9 ± 0.3b</td>
<td>-</td>
<td>24.1 ± 0.8b</td>
<td>0.120 ± 0.003a</td>
</tr>
</tbody>
</table>

a Values are means ± standard error (SE) of triplicate containers (n=3). Means within columns followed by the same letter are not significantly different at the 5% level, according to the Scheffé’s test. b Values of L*, a*, b* for olives packed in glass bottles were used as a reference.
Table 3. Volatile compounds in the headspace of Spanish-style green table olives packed in plastic pouches and glass bottles at the end of storage period (6.5 months)

<table>
<thead>
<tr>
<th>Code</th>
<th>Compound</th>
<th>LRI&lt;sup&gt;b&lt;/sup&gt;</th>
<th>ID&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Pouches A</th>
<th>Pouches B</th>
<th>Glass bottles</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>dimethyl sulfide</td>
<td>735</td>
<td>A</td>
<td>nda</td>
<td>45.25b</td>
<td>87.04c</td>
</tr>
<tr>
<td>2</td>
<td>octane</td>
<td>791</td>
<td>A</td>
<td>286.67a</td>
<td>781.64ab</td>
<td>1059.56c</td>
</tr>
<tr>
<td>3</td>
<td>ethyl acetate</td>
<td>881</td>
<td>A</td>
<td>nda</td>
<td>58.11b</td>
<td>172.50c</td>
</tr>
<tr>
<td>6</td>
<td>ethanol</td>
<td>925</td>
<td>A</td>
<td>nda</td>
<td>38.11b</td>
<td>58.47b</td>
</tr>
<tr>
<td>7</td>
<td>benzene</td>
<td>931</td>
<td>A</td>
<td>nda</td>
<td>12.74b</td>
<td>14.56b</td>
</tr>
<tr>
<td>8</td>
<td>n-propyl acetate</td>
<td>966</td>
<td>A</td>
<td>nda</td>
<td>93.46b</td>
<td>185.16c</td>
</tr>
<tr>
<td>4</td>
<td>decane</td>
<td>994</td>
<td>A</td>
<td>152.10</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>5</td>
<td>2-butenal</td>
<td>1029</td>
<td>A</td>
<td>219.40</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>11</td>
<td>hexanal</td>
<td>1072</td>
<td>A</td>
<td>45.21a</td>
<td>29.66a</td>
<td>62.35a</td>
</tr>
<tr>
<td>12</td>
<td>2-methyl-2-butenal</td>
<td>1084</td>
<td>A</td>
<td>93.23a</td>
<td>122.40a</td>
<td>204.27b</td>
</tr>
<tr>
<td>13</td>
<td>ethyl hexanoate</td>
<td>1228</td>
<td>A</td>
<td>nda</td>
<td>11.00b</td>
<td>14.22b</td>
</tr>
<tr>
<td>14</td>
<td>cyclohexanone</td>
<td>1269</td>
<td>A</td>
<td>3.77a</td>
<td>5.30a</td>
<td>12.55a</td>
</tr>
<tr>
<td>15</td>
<td>octanal</td>
<td>1278</td>
<td>A</td>
<td>40.43a</td>
<td>71.36a</td>
<td>163.33a</td>
</tr>
<tr>
<td>16</td>
<td>6-methyl-5-hepten-2-one</td>
<td>1328</td>
<td>A</td>
<td>7.57a</td>
<td>12.80a</td>
<td>17.67a</td>
</tr>
<tr>
<td>17</td>
<td>1-hexanol</td>
<td>1349</td>
<td>A</td>
<td>11.71a</td>
<td>17.26a</td>
<td>28.78b</td>
</tr>
<tr>
<td>18</td>
<td>(Z)-3-hexen-1-ol</td>
<td>1378</td>
<td>A</td>
<td>95.14a</td>
<td>134.59a</td>
<td>245.94b</td>
</tr>
<tr>
<td>19</td>
<td>nonanal</td>
<td>1383</td>
<td>A</td>
<td>3.82a</td>
<td>6.70ab</td>
<td>9.98b</td>
</tr>
<tr>
<td>20</td>
<td>2-cyclohexen-1-one</td>
<td>1411</td>
<td>A</td>
<td>95.30b</td>
<td>8.08a</td>
<td>11.10a</td>
</tr>
<tr>
<td>21</td>
<td>(E)-2-octenal</td>
<td>1415</td>
<td>A</td>
<td>12.28a</td>
<td>36.07a</td>
<td>48.76a</td>
</tr>
<tr>
<td>22</td>
<td>furfural</td>
<td>1455</td>
<td>A</td>
<td>34.65a</td>
<td>353.54b</td>
<td>498.83b</td>
</tr>
<tr>
<td>23</td>
<td>acetic acid</td>
<td>1458</td>
<td>A</td>
<td>68.22a</td>
<td>65.22a</td>
<td>125.05b</td>
</tr>
<tr>
<td></td>
<td>Chemical Name</td>
<td>Linear Retention Index</td>
<td>RI</td>
<td>Identification</td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>----------------------------------------</td>
<td>-------------------------</td>
<td>----------</td>
<td>-------------------------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>(E,E)-3,5-heptadien-2-one</td>
<td>1463</td>
<td>C 24.64b</td>
<td>4.65a 6.83a</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>2-acetylfuran</td>
<td>1492</td>
<td>B 37.48b</td>
<td>19.17a 29.89ab</td>
<td></td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>2-bornene</td>
<td>1501</td>
<td>C 55.91a</td>
<td>76.20a 125.24b</td>
<td></td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>benzaldehyde</td>
<td>1504</td>
<td>A 71.40b</td>
<td>11.34a 15.38a</td>
<td></td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>propanoic acid</td>
<td>1544</td>
<td>A 12.19a</td>
<td>15.26a 24.58b</td>
<td></td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>linalool</td>
<td>1544</td>
<td>A 2.68a</td>
<td>3.89ab 7.46b</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>1-octanol</td>
<td>1552</td>
<td>A 22.19a</td>
<td>36.73ab 52.45b</td>
<td></td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>(E)-2-decenal</td>
<td>1627</td>
<td>A 42.41a</td>
<td>108.54b 164.03b</td>
<td></td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>2-hydroxybenzaldehyde</td>
<td>1657</td>
<td>A 4.26</td>
<td>nd nd</td>
<td></td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>α-terpineol</td>
<td>1683</td>
<td>A 16.31a</td>
<td>20.23ab 30.46b</td>
<td></td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>benzyl acetate</td>
<td>1714</td>
<td>A 2.89a</td>
<td>3.85a 5.87b</td>
<td></td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>methyl salicylate</td>
<td>1752</td>
<td>A 14.42a</td>
<td>18.44a 27.03b</td>
<td></td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>oxime-, methoxy-phenyl</td>
<td>1771</td>
<td>C 68.73a</td>
<td>79.87a 124.26a</td>
<td></td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>o-guaiacol</td>
<td>1845</td>
<td>A 39.35a</td>
<td>35.98a 76.85b</td>
<td></td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>benzyl alcohol</td>
<td>1861</td>
<td>A 49.08a</td>
<td>64.48a 101.96b</td>
<td></td>
<td></td>
</tr>
<tr>
<td>39</td>
<td>phenyl ethyl alcohol</td>
<td>1893</td>
<td>A 100.41a</td>
<td>125.96a 201.07b</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>p-creosol</td>
<td>1939</td>
<td>A 736.70a</td>
<td>908.26a 1428.54b</td>
<td></td>
<td></td>
</tr>
<tr>
<td>41</td>
<td>phenol</td>
<td>1995</td>
<td>A 106.80b</td>
<td>43.82a 89.70b</td>
<td></td>
<td></td>
</tr>
<tr>
<td>42</td>
<td>p-cresol</td>
<td>2071</td>
<td>A 11.46a</td>
<td>14.82a 20.38a</td>
<td></td>
<td></td>
</tr>
<tr>
<td>43</td>
<td>4-ethyl phenol</td>
<td>2163</td>
<td>A 16.98a</td>
<td>14.49a 27.05a</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*aValues are means of triplicate containers (n=3). Concentrations are expressed as µg/kg of 3-octanol. nd: not detected. Means within rows followed by the same letter are not significantly different at the 5% level, according to the Scheffé’s test. b Linear retention index on VF-Wax column. c 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 the NIST Standard Reference Database (NIST Chemistry WebBook); C, tentatively identified, mass spectrum agreed with the standard NIST 2008.*
Figure 1

Pouches A

Pouches B

Glass bottles