

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

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5 Antonio Higinio Sánchez, Antonio de Castro, Antonio López-López, Amparo Cortés-  
6 Delgado, Víctor Manuel Beato, Alfredo Montaña\*

7

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

10

11 \*Tel.: +34 95 4611550, fax: +34 95 4616790, e-mail corresponding author (A.  
12 Montaña): [amontano@cica.es](mailto:amontano@cica.es)

13 E-mail addresses for co-authors:

14 Antonio Higinio Sánchez: [ahiginio@cica.es](mailto:ahiginio@cica.es)

15 Antonio de Castro: [amillan@cica.es](mailto:amillan@cica.es)

16 Antonio López-López: [all@cica.es](mailto:all@cica.es)

17 Amparo Cortés-Delgado: [acortes@cica.es](mailto:acortes@cica.es)

18 Víctor Manuel Beato: [vmbeagal@ig.csic.es](mailto:vmbeagal@ig.csic.es)

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

21

22 **Abstract**

23

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

40

41 *Keywords:* table olives, color, volatile compounds, SPME, plastic packaging

42 **Highlights**

43

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

45 • Green olives packed in AlO<sub>x</sub>-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

## 48 **1. Introduction**

49

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

62 Since the development of the commercial pasteurization process, all pasteurized  
63 table olives have been packaged in glass or varnished can containers which do not react  
64 chemically with food components. The main function of food packaging is to achieve  
65 preservation and the safe delivery of food products until consumption (Han, 2013).  
66 However, there is an increasing interest in the use of plastic packaging by industry due  
67 to factors such as reduced weight of plastic containers, lower production costs compared  
68 to glass, less apt to shatter, transparent, flexible, and convenient to the consumer  
69 (Sajilata, Savitha, Singhal, & Kanetkar, 2007). In spite of all these advantages, plastic  
70 containers are likely to have at least a limited level of oxygen permeability. This could  
71 negatively affect the quality of pickled vegetables, which are known to be susceptible to  
72 oxidation (Zhou, McFeeters, & Fleming, 2000; Cleary & McFeeters, 2006) and reduce

73 the shelf life of products. In addition to oxidation, it must be taken into account that  
74 plastic packaging materials can absorb different compounds from the food, a  
75 phenomenon called scalping (sorption). In particular, flavor scalping is a term used to  
76 describe the loss of quality of a packaged food due either to its volatile flavors being  
77 absorbed by the package or the food absorbing undesirable flavors from the packaging  
78 material. Sorption of food aromas, particularly by plastic packaging materials, is usually  
79 perceived as a major factor contributing to the quality alteration of most foods during  
80 storage (Sajilata et al., 2007). Interactions between flavor compounds and plastic  
81 packages have been demonstrated in different food products such as orange juice  
82 (López-Gómez, Ros-Chumillas, & Belisario-Sánchez, 2009), wine (Reeves, 2009), beer  
83 (Bamforth & Krochta, 2009), milk (Kontominas, 2009), yogurt (MacBean, 2009), or  
84 vegetable oils (Piergiovanni & Limbo, 2009). However, to our knowledge, this type of  
85 study has not been carried out with any fermented vegetable.

86         The selection of proper packaging materials that are compatible with fermented  
87 olives while maintaining quality during pasteurization treatment and storage is critical  
88 to proposing a change from traditional glass containers to plastic packaging. The  
89 objective of this work was to identify differences in the color and volatile component  
90 profiles of Spanish-style green table olives pasteurized and stored at constant  
91 temperature (30 °C) in two distinct pasteurizable plastic containers in comparison with  
92 the traditional product packed in glass containers.

93

## 94 **2. Materials and Methods**

95

### 96 **2.1. Materials and chemicals**

97 Pitted Spanish-style green table olives (Manzanilla cultivar) were supplied in  
98 bulk by Angel Camacho SL (Seville, Spain). Physico-chemical characteristics of the  
99 corresponding brine were the following: pH, 3.47; titratable acidity, 0.91 g/100 mL (as  
100 lactic acid); combined acidity, 0.047 mol/L; and NaCl, 8.34 g /100 mL. Two types of  
101 plastic pouches, named as pouches A and B, were used. Both pouches were supplied by  
102 SP Group (Córdoba, Spain). Pouches A were made of PET + MDPE/EVOH  
103 (polyethylene terephthalate + medium-density polyethylene/ethylene vinyl alcohol) with  
104 oxygen permeability  $\approx 3 \text{ cm}^3/\text{m}^2/\text{d}$  at 23 °C and 50% r.h., and thickness of 106  $\mu\text{m}$ .  
105 Pouches B were made of AlO<sub>x</sub>-coated PET + MDPE (aluminium oxide coating on  
106 polyethylene terephthalate + medium-density polyethylene) with oxygen permeability  $\approx$   
107  $1 \text{ cm}^3/\text{m}^2/\text{d}$  at 23 °C and 50% r.h., and the same thickness as pouches A.

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

116

## 117 2.2. Packing of Spanish-style green table olives

118

119 Olives were packed in plastic pouches A, plastic pouches B, and glass bottles  
120 using an acidified brine as cover liquor. This acidified brine consisted of citric acid,  
121 NaCl, ascorbic acid, potassium sorbate, and sodium benzoate to give equilibrium values

122 of 0.50g/100 mL titratable acidity (expressed as lactic acid), 4.7 g /100 mL NaCl, 0.4 g  
123 L<sup>-1</sup> ascorbic acid, 0.5 g L<sup>-1</sup> sorbic acid, and 0.5 g L<sup>-1</sup> benzoic acid, respectively. Use of  
124 additives (ascorbic acid, sorbates and benzoates) was justified as it is a common practice  
125 in the olive industry, even in case of pasteurized samples. Ascorbic acid has been  
126 demonstrated to have a positive effect on fruit color (Casado, Sánchez, Rejano, de  
127 Castro, & Montaña, 2010; Casado, Sánchez, de Castro, Rejano, Beato, & Montaña,  
128 2011) whereas sorbates plus benzoates can prevent surface films of yeasts and fungi in  
129 packed table olives once the packaging has been opened (Borbolla y Alcalá, Fernández-  
130 Díez, & Cancho, 1961; Chipley, 2005).

131         In both types of pouches the drained net weight of olives was 61.5 g (17 olives)  
132 and the brine volume was 86 mL. In glass containers the drained net weight and brine  
133 volume were 96.5 g (26 olives) and 135 mL, respectively, giving the same weight-to-  
134 volume ratio (0.715) as in the plastic pouches. For the corresponding calculations, the  
135 moisture content of pitted olives was assumed to be 75 g/100 g pulp (w/w). In case of  
136 packing in glass bottles, cover brine was added hot ( $\approx 70$  °C) in order to achieve and  
137 maintain a vacuum inside the bottles. After packing (10 containers per packaging  
138 treatment), the plastic pouches and glass containers were subjected to pasteurization  
139 and then stored at 30 °C for 6.5 months in a Binder BD 720 (Tuttlingen, Germany)  
140 incubator with opaque doors and walls, natural convection and without any control of  
141 humidity. A storage temperature of 30 °C was selected to accelerate the possible  
142 reactions occurring inside the containers, and also taking into account the relatively high  
143 temperatures in our region. The pasteurization was carried out in a computer-controlled  
144 retort equipped with a water cascading system (Steriflow, SAS, Paris, France). Plastic  
145 pouches and glass containers were pasteurized separately. The process applied to both  
146 plastic bags and glass containers consisted of the following stages: (1) pre-heating from

147 the initial retort temperature (40 °C) to the final temperature (93 °C), duration 10 min;  
148 (2) pasteurization at 93 °C for 7 min; and (3) cooling with tap water at ambient  
149 temperature, duration 10 min. After the period of storage, three replicate containers  
150 (pouches or bottles) were analyzed.

151

### 152 2.3. Color parameters

153

154 Surface color of olives was measured using a Color-View Model 9000  
155 spectrophotometer (BYK-Gardner, Inc., Silver Spring, MD) with a measurement area of  
156 11 mm diameter, 45° circumferential illumination, and observation angle of 0°. All  
157 measurements were done on the CIE 1976 L\*a\*b\* scale using illuminating conditions  
158 CIE type C, 10° observer. Results were expressed as the mean of 10 replicate  
159 measurements, each made on 1 olive. In addition, from the reflectance curve supplied  
160 by the apparatus, a color index (*i*) was obtained, as described by Sánchez, Rejano, &  
161 Montaña (1985):

$$162 \quad i = (4R_{635} + R_{590} - 2R_{560})/3$$

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

167 Brine color was estimated by measuring the difference in absorbance at 440 and  
168 700 nm, ( $A_{440} - A_{700}$ ), as described by Montaña, Sánchez, & Rejano (1988). A value of  
169 0.23 absorbance unit (AU) has been proposed as acceptance limit, above which the  
170 brine color is considered unacceptable for packed green table olives.

171

172 2.4. Analysis of additives

173

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

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

187

188 2.5. Physicochemical analyses

189

190 The pH and titratable acidity of brines were measured using a Metrohm 670  
191 Titroprocessor (Herisau, Switzerland). Titratable acidity was determined by titrating to  
192 pH 8.3 with 0.2 mol/L NaOH and expressed as lactic acid. Sodium chloride was  
193 determined by titration with AgNO<sub>3</sub> (Fernández-Díez et al., 1985).

194

195 2.6. Analysis of volatile compounds

196

197 Volatile compounds in brine were analyzed by solid phase micro-extraction  
198 (SPME) and gas chromatography coupled to mass spectrometry (GC-MS) following the  
199 procedure previously reported by Cortés-Delgado, Sánchez, de Castro, López-López,  
200 Beato, & Montaña (2016) with modifications. Briefly, 2.5 g of homogenized olive pulp  
201 was placed in a 15 mL glass vial, and 7.5 mL of NaCl solution (30 g /100 mL) were  
202 added. After the addition of a stirring bar (for stirring at 600 rpm) and 100  $\mu$ L of 3-  
203 octanol (2 mg/L) used as an internal standard, the vial was closed and placed in a water  
204 bath adjusted to 40 °C. The equilibration time was 15 min at 40 °C. Headspace volatile  
205 compounds were extracted and concentrated on a  
206 divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) fiber (1cm, 50/30  
207  $\mu$ m; Supelco, Bellefonte, PA). The fiber was exposed to the brine headspace for 30 min.  
208 Volatile compounds adsorbed on the SPME fiber were desorbed at 265 °C for 15 min in  
209 the injector port of a GC interfaced with a mass detector (internal ionization source: 70  
210 eV) with a scan range from m/z 30 to 400 (GC model 7890A and mass detector model  
211 5975C, Agilent Technologies, Santa Clara, CA). Separation was achieved on a VF-  
212 WAX MS capillary column (30 m x 0.25 mm x 0.25  $\mu$ m film thickness) from Agilent.  
213 The GC oven temperature programme consisted in 40 °C for 5 min, then 40-195 °C at 3  
214 °C/min, and then 195-240 °C at 10 °C/min and held there for 15 min. The carrier gas  
215 was helium at a constant flow of 1 mL min<sup>-1</sup>. Compound identification was based on  
216 mass spectra matching with the standard NIST 08 MS library and on comparison of  
217 retention indices (RI) sourced from NIST Standard Reference Database and from  
218 authentic reference standards when available. For the determination of the RI, a C7-C30  
219 *n*-alkanes series was used, and the values were compared, when available, with values  
220 reported in the literature for similar chromatographic columns. The volatile compounds  
221 were quantified by comparison of peak areas to that of internal standard (3-octanol).

222 However, some peaks that showed interfering peaks or co-eluted in scan mode were  
223 quantified from their peak areas in the ion extraction chromatogram (IEC), which was  
224 obtained by selecting target ions for each one. These ions corresponded to base ion ( $m/z$   
225 100% intensity), molecular ion ( $M^+$ ) or another characteristic ion for each molecule.

226

## 227 2.7. Statistical data analysis

228

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

232

## 233 **3. Results and Discussion**

234

235 After 6.5 months of storage at 30 °C, packed olives were analyzed for chemical  
236 characteristics including pH, titratable acidity, salt, and content of additives in brine  
237 (Table 1). Significant differences ( $p < 0.05$ ) between packages were found for each  
238 variable. The most noticeable difference was found for ascorbic acid, which was  
239 undetected in pouches A. This can be explained by the higher oxygen permeability of  
240 this type of pouch. However, in pouches B and glass containers, the concentrations of  
241 ascorbic acid were 0.140 and 0.183 g/L, respectively, which were below the value of 0.4  
242 g/L that was set as equilibrium concentration. This can be explained by the anaerobic  
243 degradation of ascorbic acid occurring during storage time. As previously demonstrated  
244 in green olives pasteurized and stored in glass bottles, ascorbic acid was degraded at  
245 room temperature following first-order reaction kinetics (Montaño, Casado, Rejano,  
246 Sánchez, & de Castro, 2006).

247           Regarding potassium sorbate and sodium benzoate added as preservatives, it is  
248 well known that these compounds are significantly absorbed not only into the olive  
249 juice but also into the lipid phase (oil) and other tissue components of olives (Brenes,  
250 Romero, García, & Garrido, 2004). As result, contrary to other compounds like NaCl  
251 and lactic acid, the final concentrations of potassium sorbate and sodium benzoate in the  
252 cover brine were significantly lower than those expected (0.5 g/L). Despite this, the  
253 concentration of potassium sorbate by itself was above 0.2 g/L., which could be  
254 sufficient to prevent the development of surface films of yeasts and fungi once the  
255 packaging has been opened (Borbolla y Alcalá et al.,1961). Oxidation reactions could  
256 also explain the lower concentration of sorbic acid in pouches A compared to pouches B  
257 and glass bottles (Table 1). Sorbic acid is known to undergo degradation in packed  
258 foods, the overall rate of degradation being influenced by the availability of oxygen,  
259 which, in turn, is governed by the available head space in the pack and the oxygen  
260 permeability of the packaging material (Thakur, Singh, & Arya, 1994).

261           Package material also significantly affected the color parameters of both olives  
262 and cover brines (Table 2). Of the color parameters determined, L\* (lightness), b\*  
263 (yellowness) and index *i* were significantly lower, but a\* (redness) and brine color  
264 significantly higher, in pouches A compared to pouches B and glass bottles. Based on  
265 the known correlation of index *i* with a visual scale (Sánchez et al., 1985), color of  
266 olives in pouches A can be classified as very bad, whereas olives in pouches B and glass  
267 bottles can be classified as acceptable. Another useful color parameter for describing  
268 color variation is the total color difference  $\Delta E^*$ . Choi, Kim, & Lee (2002) indicated that  
269 a  $\Delta E^* > 2$  corresponds to noticeable differences in the visual perception of many  
270 products. Using the olives packed in glass bottles as reference, this parameter was just 2  
271 in pouches B indicating that visual differences between olives in pouches B and glass

272 bottles were almost imperceptible. On the contrary,  $\Delta E^*$  was 16 in pouches A,  
273 indicating a great difference in visual color. Regarding brine color, the value of the  
274 parameter  $A_{440}-A_{700}$  in pouches B and glass bottles was below the acceptance limit of  
275 0.23 AU. On the contrary,  $A_{440}-A_{700}$  was 0.35 in pouches A, which is clearly above this  
276 limit, indicating a severe browning of brine.

277 Volatile analysis data for pasteurized Spanish-style green table olives in plastic  
278 pouches A and B in comparison with glass containers at the end of storage period (6.5  
279 months) identified 43 compounds (Table 3). Apart from these compounds, two intense  
280 peaks corresponding to sorbic and benzoic acids were observed in the total ion  
281 chromatograms (TIC) of all the samples (Fig. 1). Some compounds showed a high  
282 variability between replicate containers which would explain the similarities in results  
283 when ANOVA was applied. The volatile profile of product packed in pouches B was  
284 comparable to that packed in glass containers, but 16 compounds were significantly  
285 higher in glass containers. Ayhan, Yoem, Zhang, & Min (2001), in their study of the  
286 effects of plastic packaging on flavor compounds in orange juice, noted a loss of  
287 primary aldehydes which they explained by the absorption of flavor compounds into the  
288 packaging material, the acceleration of flavor degradation due to the initial oxygen  
289 concentrations and the transmission of oxygen through the package. In the present  
290 study, volatile losses in pouches B compared to glass could be only explained by the  
291 migration of components into the plastic container (scalping), as chemical reactions due  
292 to oxygen would be ruled out due to the presence of residual ascorbic acid, as  
293 mentioned above. On the contrary, oxidation reactions appeared to occur in pouches A.  
294 Thus, five carbonyl compounds, namely, 2-butenal, 2-cyclohexen-1-one, (E,E)-3,5-  
295 heptadien-2-one, benzaldehyde, and 2-hydroxybenzaldehyde were significantly higher  
296 in pouches A than in any of the other packages. These compounds could be formed by

297 oxidation reactions involving polyphenols from olives or by oxidation of additives such  
298 as sorbic acid. Polyphenols containing an ortho-dihydroxybenzene moiety such as  
299 hydroxytyrosol, which is the major phenolic compound in the olives after fermentation  
300 (Montaño, Sánchez, López-López, de Castro, & Rejano, 2010), could be oxidized to  
301 semiquinone radicals and benzoquinone while oxygen is reduced to hydrogen peroxide,  
302 in a similar way to the mechanism proposed in the non-enzymatic oxidation of wines  
303 (Oliveira, Ferreira, de Freitas, & Silva, 2011). Hydrogen peroxide in association with  
304 ferrous ions would generate hydroxyl radicals (HO•), which is known as the Fenton  
305 reaction. Hydroxyl radical is a reduced product of oxygen and it is recognized to oxidize  
306 almost any organic molecule found in the medium (Oliveira et al., 2011). This reaction  
307 may produce many oxidation products, mainly aldehydes and ketones. Dombre, Rigou,  
308 Wirth, & Chalier (2015) found that oxidative and ageing aroma compounds appeared in  
309 higher amount in wine packed in PET than in glass bottles due to oxygen ingress  
310 through packaging. Apart from oxidation reactions involving polyphenols, sorbic acid  
311 degradation by oxygen has been reported to yield various carbonyl compounds such as  
312 2-butenal (crotonaldehyde), malonaldehyde, acetaldehyde, acrolein, formic acid, and  
313 malonic acid (Thakur et al., 1994). Benzaldehyde could be formed from  
314 phenylacetaldehyde (Chu & Yaylayan, 2008), a Strecker aldehyde which, in turn, could  
315 be formed from polyphenol-derived quinones and phenylalanine (Rizzi, 2006).  
316 However, in pouches A, benzaldehyde could also be initially present in PET (plastic  
317 material in contact with olives + brine) from the degradation of plastic additives such as  
318 plasticizer, lubricants or modifiers, and a part could migrate into the product (Ducruet,  
319 Vitrac, Saillard, Guichard, Feigenbaum, & Fournier, 2007).

320         It must be pointed out that aldehydes such as hexanal, octanal or 2-octenal did  
321 not show significant differences between packages (Table 3), indicating that lipid

322 oxidation was not important during storage in plastic pouches. These aldehydes, along  
323 with other aldehydes (e.g. pentanal, 2-hexenal, heptanal), have been used as indicators  
324 of lipid oxidation in other foods (Cleary & McFeeters, 2006).

325         Eight compounds, namely, dimethyl sulfide, ethyl acetate, ethanol, benzene, n-  
326 propyl acetate, 2-butanol, ethyl 2-methylbutanoate, and ethyl hexanoate were detected  
327 in pouches B or glass, but not in pouches A. Volatile losses in the latter pouches can be  
328 attributed to oxidation reactions and scalping. For example, dimethyl sulfide may be  
329 oxidized by hydrogen peroxide to form dimethyl sulfoxide. It is well known that, in  
330 solution, the oxidation of dimethyl sulfide by hydroperoxides leads to dimethyl  
331 sulfoxide which is, more slowly than dimethyl sulfide, further oxidized to dimethyl  
332 sulfone (Amels, Elias, & Wannowius, 1997). Ethanol could be oxidized to yield  
333 acetaldehyde (Oliveira et al., 2011). The presence of benzene in pouches B and glass  
334 can be attributed to the interaction between ascorbic acid and benzoic acid (Casado et  
335 al., 2011). However, in pouches A, the rapid oxidation of ascorbic acid would prevent  
336 the benzene formation, which appears to occur at slow rate in table olives (Casado et al.,  
337 2011). Another compound that was significantly different (lower) in pouches A  
338 compared to pouches B and glass was furfural. This compound may originate from the  
339 decomposition of ascorbic acid. Previous studies (Montaño et al., , 2006) with packed  
340 table olives showed that there was a highly significant correlation between ascorbic acid  
341 degradation and furfural formation during storage at 40 °C in glass bottles.

342

#### 343 **4. Conclusions**

344

345 The type of plastic material had a significant effect on the retention of color parameters  
346 and volatile compounds of Spanish-style green table olives pasteurized and stored in

347 plastic containers. Compared to the traditional product in glass containers, the retention  
348 of color and volatile compounds was significantly higher in plastic pouches B (AlOx-  
349 coated PET + MDPE) than in pouches A (PET + MDPE/EVOH) with higher gas  
350 permeability. Scalping could explain the loss of volatile components in pouches B,  
351 while the differences in volatile composition between pouches A and glass could be  
352 attributed to scalping and oxidation processes. These results suggest that the use of  
353 pouches made of AlOx-coated PET + MDPE could be a great alternative to the  
354 traditional package of product in glass, at least for a period of 6.5 months of storage.  
355 However, further studies are needed in order to evaluate the shelf life of product in this  
356 type of plastic container and to assess if the differences in volatile composition  
357 compared to glass affect the sensory characteristics of the final product.

358

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364

### 365 **References**

366 Amels, P., Elias, H., & Wannowius, K.J. (1997). Kinetics and mechanism of the  
367 oxidation of dimethyl sulfide by hydroperoxides in aqueous medium. Study on  
368 the potential contribution of liquid-phase oxidation of dimethyl sulfide in the  
369 atmosphere. *Journal of the Chemical Society, Faraday Transactions*, 93, 2537-  
370 2544.

371 Ayhan, Z., Yoem, H.W., Zhang, Q.H., & Min, D.B. (2001). Flavor, color, and vitamin  
372 retention of pulsed electric field processed orange juice in different packaging  
373 materials. *Journal of Agricultural and Food Chemistry*, 49, 669-674.

374 Bamforth, C.W., & Krochta, J.M. (2009). Packaging and the shelf life of beer. In G. L.  
375 Robertson (Ed.), *Food packaging and shelf life: a practical guide*, (pp 215-229).  
376 Boca Raton: CRC Press.

377 Borbolla y Alcalá, J.M.R., Fernández-Díez, M.J., & Cancho, F.G. (1961). Empleo del  
378 ácido sórbico, o sus sales, en las aceitunas aderezadas. *Grasas y Aceites*, 12, 10-  
379 15.

380 Breidt, F., Sandeep, K.P., & Arritt, F. (2010). Use of Linear Models for Thermal  
381 Processing of Acidified Foods. *Food Protection Trends*, 30, 268-272.

382 Brenes, M., Romero, C., García, P., & Garrido, A. (2004). Absorption of sorbic and  
383 benzoic acids in the flesh of table olives. *European Food Research and*  
384 *Technology*, 219, 75-79.

385 Casado, F.J., Sánchez, A.H., de Castro, A., Rejano, L., Beato, V.M., & Montañó, A.  
386 (2011). Fermented vegetables containing benzoic and sorbic acids as additives:  
387 benzene formation during storage and impact of additives on quality parameters.  
388 *Journal of Agricultural and Food Chemistry*, 59, 2403-2409.

389 Casado, F.J., Sánchez, A.H., Rejano, L., de Castro, A., & Montañó, A. (2010). Stability  
390 of sorbic and ascorbic acid in packed green table olives during long-term storage  
391 as affected by different packing conditions, and its influence on quality  
392 parameters. *Food Chemistry*, 122, 812-818.

393 Chipley, J.R. (2005). Sodium benzoate and benzoic acid. In P.M. Davidson, J.N. Sofos,  
394 & A.L. Branen (Eds.), *Antimicrobials in food*, 3<sup>rd</sup> edition (pp. 11-48). Boca  
395 Raton: CRC Press.

396 Choi, M. H., Kim, G. H., & Lee, H. S. (2002). Effects of ascorbic acid retention on juice  
397 colour and pigment stability in blood orange (*Citrus sinensis*) juice during  
398 refrigerated storage. *Food Research International*, 35, 753–759.

399 Chu, F.L. & Yaylayan, V.A. (2008). Model Studies on the oxygen-Induced Formation  
400 of Benzaldehyde from Phenylacetaldehyde Using Pyrolysis GC-MS and FTIR.  
401 *Journal of Agricultural and Food Chemistry*, 56, 10697-10704.

402 Cleary, K., & McFeeters, R.F. (2006). Effects of oxygen and turmeric on the formation  
403 of oxidative aldehydes in fresh-pack dill pickles. *Journal of Agricultural and*  
404 *Food Chemistry*, 54, 3421-3427.

405 Cortés-Delgado, A., Sánchez, A.H., de Castro, A., López-López, A., Beato, V.M., &  
406 Montaña, A. (2016). Volatile profile of Spanish-style Green table olives  
407 prepared from different cultivars grown at different locations. *Food Research*  
408 *International*, 83, 131-142.

409 Dombre, C., Rigou, P., Wirth, J., & Chalié, P. (2015). Aromatic evolution of wine  
410 packed in virgin and recycled PET bottles. *Food Chemistry*, 176, 376-387.

411 Ducruet, V., Vitrac, O., Saillard, P., Guichard, E., Feigenbaum, A., & Fournier, N.  
412 (2007). Sorption of aroma compounds in PET and PVC during the storage of a  
413 strawberry syrup. *Food Additives and Contaminants*, 24, 1306-1317.

414 Fernández-Díez, M.J., Castro, R., Fernández, A.G., Cancho, F.G., Pellissó, F.G., Vega,  
415 M.N., Moreno, A.H., Mosquera, I.M., Navarro, L.R., Quintana, M.C.D., Roldán,  
416 F.S., García, P.G., & de Castro, A. (1985). *Biotecnología de la aceituna de*  
417 *mesa*. Madrid: CSIC.

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

421 Kontominas, M.G. (2009). Packaging and the shelf life of milk. In G. L. Robertson  
422 (Ed.), *Food packaging and shelf life: a practical guide*, (pp 81-102). Boca  
423 Raton: CRC Press.

424 López, A., Montañó, A., García, P., & Garrido, A. (2005). Quantification of ascorbic  
425 acid and dehydroascorbic acid in fresh olives and in commercial presentations of  
426 table olives. *Food Science and Technology International*, 11, 199-204.

427 López-Gómez, A., Ros-Chumillas, M. and Belisario-Sánchez, Y.Y. (2009).Packaging  
428 and the shelf life of orange juice. In G. L. Robertson (Ed.), *Food packaging and*  
429 *shelf life: a practical guide*, (pp 179-198). Boca Raton: CRC Press.

430 MacBean, R.D. (2009). Packaging and the shelf life of yogurt. In G. L. Robertson (Ed.),  
431 *Food packaging and shelf life: a practical guide*, (pp 143-156). Boca Raton:  
432 CRC Press.

433 Montañó, A., Casado, F.J., Rejano, L., Sánchez, A.H., & de Castro, A. (2006).  
434 Degradation kinetics of the antioxidant additive ascorbic acid in packed table  
435 olives during storage at different temperatures. *Journal of Agricultural and Food*  
436 *Chemistry*, 54, 2206-2210.

437 Montañó, A., Sánchez, A.H., & Rejano, L. (1988). Method for determination of brine  
438 colour from green table olives. *Alimentaria*, 193, 79-83.

439 Montañó, A., Sánchez, A.H., & Rejano, L. (1995). Determination of benzoic and sorbic  
440 acids in packaged vegetable products. Comparative evaluation of methods.  
441 *Analyst*, 120, 2483-2487.

442 Montañó, A., Sánchez, A.H., López-López, A., de Castro, A., & Rejano, L. (2010).  
443 Chemical composition of fermented green olives: acidity, salt, moisture, fat,  
444 protein, ash, fiber, sugar, and polyphenol. In V.R. Preedy, & R.R. Watson

445 (Eds.), *Olives and olive oil in health and disease prevention* (pp. 291-297).  
446 Amsterdam: Elsevier Inc

447 Oliveira, C.M., Ferreira, A.C.S., de Freitas, V., & Silva, A.M.S. (2011). Oxidation  
448 mechanisms occurring in wines. *Food Research International*, *44*, 1115-1126.

449 Piergiovanni, L., & Limbo, S. (2009). Packaging and the shelf life of vegetable oils. In  
450 G. L. Robertson (Ed.), *Food packaging and shelf life: a practical guide*, (pp  
451 317-338). Boca Raton: CRC Press.

452 Reeves, M.J. (2009). Packaging and the shelf life of wine. In G. L. Robertson (Ed.),  
453 *Food packaging and shelf life: a practical guide*, (pp 231-257). Boca Raton:  
454 CRC Press.

455 Rejano, L., Montañó, A., Casado, F.J., Sánchez, A.H., & de Castro, A. (2010). Table  
456 olives: varieties and variations. In V.R. Preedy, & R.R. Watson (Eds.), *Olives  
457 and olive oil in health and disease prevention* (pp. 5-15). Amsterdam: Elsevier  
458 Inc.

459 Rizzi, G. (2006). Formation of Strecker aldehydes from polyphenol-derived quinones  
460 and  $\alpha$ -amino acids in a nonenzymic model system. *Journal of Agricultural and  
461 Food Chemistry*, *54*, 1893-1897.

462 Sajilata, M.G., Savitha, K., Singhal, R.S., & Kanetkar (2007). Scalping of flavors in  
463 packaged foods. *Comprehensive Reviews in Food Science and Food Safety*, *6*,  
464 17-35.

465 Sánchez, A.H., Rejano, L., & Montañó, A. (1985). Determinaciones del color en las  
466 aceitunas verdes aderezadas de la variedad Manzanilla. *Grasas y Aceites*, *36*,  
467 258-261.

468 Thakur, B.R., Singh, R.K., & Arya, S.S. (1994). Chemistry of sorbates: a basic  
469 perspective. *Food Reviews International*, *10*, 71-91.

470 Zhou, A., McFeeters, R.F., Fleming, H.P. (2000). Development of oxidized odor and  
471 volatile aldehydes in fermented cucumber tissue exposed to oxygen. *Journal of*  
472 *Agricultural and Food Chemistry*, 48, 193-197.

473 **Figure captions**

474

475 Fig. 1. Total ion chromatograms of the volatile profiles of Spanish-style green table  
476 olives pasteurized and stored in two distinct plastic pouches and glass bottles after 6.5  
477 months of storage at 30 °C. Peak numbers correspond to the compounds listed in Table  
478 3. IS = internal standard (3-octanol); So = sorbic acid; Bz = benzoic acid.

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 °C <sup>a</sup>

Packaging material <sup>b</sup>	pH	Titrateable acidity (g/100 mL lactic acid)	Salt (g/100 mL NaCl)	Ascorbic acid (mg/L)	Potassium sorbate (mg/L sorbic acid)	Sodium benzoate (mg/L benzoic acid)
Pouches A	3.49 ± 0.00a	0.55 ± 0.00c	5.71 ± 0.10b	0 ± 0 a	245 ± 3a	234 ± 7a
Pouches B	3.46 ± 0.00a	0.51 ± 0.01b	4.80 ± 0.05a	140 ± 12b	304 ± 7b	268 ± 7a
Glass bottles	3.66 ± 0.01b	0.43 ± 0.00a	4.80 ± 0.04a	183 ± 12b	336 ± 19b	320 ± 17b

<sup>a</sup> 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.

<sup>b</sup> Pouches A, PET + MDPE/EVOH (polyethylene terephthalate + medium-density polyethylene/ethylene vinyl alcohol) with oxygen permeability  $\approx 3 \text{ cm}^3 \text{ m}^{-2} \text{ day}^{-1}$ ; pouches B, AlO<sub>x</sub>-coated PET + MDPE (aluminium oxide coating on polyethylene terephthalate + medium-density polyethylene) with oxygen permeability  $\approx 1 \text{ cm}^3 \text{ m}^{-2} \text{ day}^{-1}$ .

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 <sup>a</sup>

Packaging material	L*	a*	b*	$\Delta E^{*b}$	Index <i>i</i>	Brine color ( $A_{440}-A_{700}$ )
Pouches A	43.2 ± 0.4a	6.2 ± 0.2c	23.5 ± 0.4a	16 ± 0.5b	20.8 ± 0.5a	0.351 ± 0.005b
Pouches B	53.6 ± 0.5b	4.4 ± 0.2b	35.9 ± 0.9b	2 ± 0.3a	26.6 ± 0.8b	0.129 ± 0.006a
Glass bottles	53.3 ± 0.6b	3.3 ± 0.1a	35.9 ± 0.3b	-	24.1 ± 0.8b	0.120 ± 0.003a

<sup>a</sup> 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. <sup>b</sup> 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)

Code	Compound	LRI <sup>b</sup>	ID <sup>c</sup>	Mean concentration <sup>a</sup>		
				Pouches A	Pouches B	Glass bottles
1	dimethyl sulfide	735	A	nda	45.25b	87.04c
2	octane	791	A	286.67a	781.64ab	1059.56c
3	ethyl acetate	881	A	nda	58.11b	172.50c
6	ethanol	925	A	nda	38.11b	58.47b
7	benzene	931	A	nda	12.74b	14.56b
8	n-propyl acetate	966	A	nda	93.46b	185.16c
4	decane	994	A	152.10	nd	nd
5	2-butenal	1029	A	219.40	nd	nd
11	hexanal	1072	A	45.21a	29.66a	62.35a
12	2-methyl-2-butenal	1084	A	93.23a	122.40a	204.27b
13	ethyl hexanoate	1228	A	nda	11.00b	14.22b
14	cyclohexanone	1269	A	3.77a	5.30a	12.55a
15	octanal	1278	A	40.43a	71.36a	163.33a
16	6-methyl -5-hepten-2-one	1328	A	7.57a	12.80a	17.67a
17	1-hexanol	1349	A	11.71a	17.26a	28.78b
18	(Z)- 3-hexen-1-ol	1378	A	95.14a	134.59a	245.94b
19	nonanal	1383	A	3.82a	6.70ab	9.98b
20	2-cyclohexen-1-one	1411	A	95.30b	8.08a	11.10a
21	(E)-2-octenal	1415	A	12.28a	36.07a	48.76a
22	furfural	1455	A	34.65a	353.54b	498.83b
23	acetic acid	1458	A	68.22a	65.22a	125.05b

24	(E,E)-3,5-heptadien-2-one	1463	C	24.64b	4.65a	6.83a
25	2-acetylfuran	1492	B	37.48b	19.17a	29.89ab
26	2-bornene	1501	C	55.91a	76.20a	125.24b
27	benzaldehyde	1504	A	71.40b	11.34a	15.38a
28	propanoic acid	1544	A	12.19a	15.26a	24.58b
29	linalool	1544	A	2.68a	3.89ab	7.46b
30	1-octanol	1552	A	22.19a	36.73ab	52.45b
31	(E)-2-decenal	1627	A	42.41a	108.54b	164.03b
32	2-hydroxybenzaldehyde	1657	A	4.26	nd	nd
33	$\alpha$ -terpineol	1683	A	16.31a	20.23ab	30.46b
34	benzyl acetate	1714	A	2.89a	3.85a	5.87b
35	methyl salicylate	1752	A	14.42a	18.44a	27.03b
36	oxime-, methoxy-phenyl	1771	C	68.73a	79.87a	124.26a
37	o-guaiacol	1845	A	39.35a	35.98a	76.85b
38	benzyl alcohol	1861	A	49.08a	64.48a	101.96b
39	phenyl ethyl alcohol	1893	A	100.41a	125.96a	201.07b
40	p-cresol	1939	A	736.70a	908.26a	1428.54b
41	phenol	1995	A	106.80b	43.82a	89.70b
42	p-cresol	2071	A	11.46a	14.82a	20.38a
43	4-ethyl phenol	2163	A	16.98a	14.49a	27.05a

<sup>a</sup> Values are means of triplicate containers (n=3). Concentrations are expressed as  $\mu\text{g}/\text{kg}$  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. <sup>b</sup> Linear retention index on VF-Wax column. <sup>c</sup> 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

