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Dehydrated black olives from unfermented and alkali treated green olives

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ARTICLE INFO

Keywords: Table olives Dehydration Phenolic oxidation Hydroxytyrosol NaCl

ABSTRACT

The black dry olive is a highly regarded product that is mostly elaborated from harvested black fruits subjected to a dry-salting process. The aim of this study was to develop a new dehydrated black table olive product. Fruits of the Gordal and Hojiblanca cultivars were alkali treated and preserved in brine for several months, after which they were dehydrated at 60 °C. Among the variables assessed to avoid lactic acid fermentation of the olives (NaCl concentration, washing, temperature), only maintenance of the fruit under refrigeration (5-6 °C) succeeded in maintaining the pH of the fruit above 6 units for several months. This high pH was crucial to obtaining dark olives after the dehydration process because browning of the fruit was highly dependent on their pH level. Chemical oxidation of phenolic compounds, in particular hydroxytyrosol, was related to the first order kinetic of the darkening rate of olives. Unfermented and dried olives of the Gordal cultivar were packed and assessed by tasters that considered this new dehydrated black table olive product as acceptable for future consumers.

1. Introduction

There is an increasing worldwide interest in dehydrated foods, and particularly in dehydrated table olives. Since ancient times, black dehydrated olives have been elaborated in the Mediterranean basin from overripe fruit that are placed between layers of coarse salt for one to two months until the olives lose most of their moisture (Panagou, 2006). Additionally, the high osmotic pressure exerted by the salt gives rise to the rupture of the tissues, thereby putting the bitter compound oleuropein into contact with the enzyme polifenoloxidase, and olives become debittered after the oxidation of the phenolic compound (Ramírez, García-García, de Castro, Romero, & Brenes, 2013).

Processing oven-dried olives has been studied for green and black harvested fruit (Gambella, Piga, Agabbio, Vacca, & D'hallewin, 2000; Öngen, Sargin, Tetik, & Köse, 2005; Badaway, Abd-Elmageed, & Almoselhy, 2020; De Bruno, Piscopo, Cordopatri, Poiana, & Mafrica, 2020) along with fermented olives put directly in brine without any alkaline treatment (Aydar, 2020; De Florio-Ramírez & Lanchipa-Bergamini, 2008; Piscopo, De Bruno, Zappia, & Poiana, 2014). Moreover, olives elaborated with the Ferrandina method are very popular in the south of Italy, which consists of blanching, salting and drying harvested black olives (Lanza et al., 2014; Marsilio, Lanza, Campestre, & De Angelis, 2000). Apart of the appreciated organoleptic characteristics of the dehydrated black olives, this food product possess a very high content in bioactive substances including phenolic compounds and triterpenic acids that could contribute to the valorization and increase production of it in the future (García-Serrano et al., 2022).

On the other hand, olives that are debittered with alkali but not fermented are another type of table olives that is highly valued by consumers, although there are many different methods of elaboration including the Castelvetrano-style in Italy (Romeo Piscopo, Mincione, & Poiana, M, 2012; Ambra et al., 2017; Zinno, Guantario, Perozzi, Pastore, & Devirgiliis, 2017), Camporeal olives in Spain (Navarro, de Lorenzo, & Pérez, 2004) and the green ripe olives of the USA (Brenes & García, 2005). All these products are characterized by a mild and slightly alkaline taste and their bright green color (Berlanga-Del Pozo, Gallardo-Guerrero, & Gandul-Rojas, 2020). Under acidic conditions, the green color changes to yellowish tones due to the pheophytinization of the chlorophyll molecule and highlighting of the carotenoids color (Gandul-Rojas & Gallardo-Guerrero, 2018). In contrast, browning accounts for the main color change of these olives as they heat under non-acidic conditions (Casado, Sánchez, Rejano, & Montaño, 2007). Indeed, drving harvested or fermented green olives always leads to darkening of the fruit (Gambella et al., 2000; Öngen et al., 2005), which has been associated with chemical or enzymatic oxidation of phenolic compounds (Piscopo et al., 2014).

Taking into consideration the mild taste of unfermented olives, the aim of this work was to study the development of a new black dehydrated product based on olives treated with alkali, but not fermented, that are subsequently oven-dried. In addition, this research was carried

https://doi.org/10.1016/j.lwt.2022.114177

Received 28 July 2022; Received in revised form 24 October 2022; Accepted 15 November 2022 Available online 18 November 2022 0023-6438/© 2022 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

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out with large size olives of the Gordal and Hojiblanca cultivars due to the loss of moisture during the dehydration stage.

2. Material and methods

2.1. Processing of olives of the Gordal cultivar

Green olives of the Gordal cultivar were harvested by hand, leaves and small branches were removed from the fruits, that were then sorted by size. Olives of the biggest size (107 fruit/kg, 32.4 mm length x 23.8 mm width) were placed into eight vessels (4.7 kg olives and 2.5 L liquid) and covered with 2.0% (w/v) NaOH for 8.0 h until the alkali penetrated 2/3 the distance of the pit from the skin at 22-23 °C. Subsequently, olives were submerged in brine without prior washing of the fruit with water to remove the excess of alkali. Then, a factorial experimental design 2^2 was carried out. The variables were the concentration of NaCl (11% and 18%) and the fermentation temperature (ambient and cold). Hence, there were four treatments: A-11-Ambient, B-18-Ambient, A-11-Cold and B-18-Cold. The ambient temperature ranged between 22 and 26 °C and the refrigeration between 5 and 6 °C.

Olives (400 g) from the four treatments (A-11-Ambient, B-18-Ambient, A-11-Cold and B-18-Cold) with pH levels of 4.3, 5.4, 7.8 and 10.1 after 60 days of fermentation were dehydrated to lose half the initial weight. Dehydration was performed by infrared heating at 60 °C for 5.5 h using the equipment IRCDi3HP-V of the IRconfort Company S. L. (Mairena del Aljarafe, Seville, Spain). The evolution of the superficial color of the olives (reflectance at 700 nm) was monitored during the dehydration stage and darkening data were fixed to a first order kinetic as follows:

$Ln R_{700} = kt + b$

In addition, after 60 days of fermentation, olives from the A-11-Cold treatment were dehydrated at 60 °C to reach 47.1% moisture in the olive pulp. Subsequently, they were packed in PATE 120 TO63 jars (Juvasa, Spain) and pasteurized at 80 °C for 15 min. Physicochemical and sensory analyses of the packed olives were carried out after 30 days storage at ambient temperature. This is the time we considered necessary to check if the pasteurization treatment was effective for the control of microbial growth, in particular molds.

2.2. Processing of olives of the hojiblanca cultivar

Green olives of the Hojiblanca cultivar were mechanically harvested, and leaves and small branches were removed from the fruits. Olives of medium size (200 fruit/kg, 25 mm length x 20 mm width) were placed into six vessels (4.7 kg olives and 2.5 L liquid) and covered with 1.9% (w/v) NaOH for 7.5 h until the alkali penetrated 2/3 the distance of the pit from the skin at 22-23 °C. Brine was poured into four of the vessels at 11% (w/v) NaCl (treatment A) and 18% (w/v) NaCl (treatment B). Olives from the other two vessels were washed after the lye treatment with tap water for 10 h and, subsequently, submerged in 18% (w/v) NaCl (treatment C). The vessels were left at room temperature 22-26 °C for 100 days.

Olives from treatments A and C after 100 days of storage were dehydrated at 60 $^{\circ}$ C until loss of 40% of the initial weight, and physicochemical characterization of the fruit was performed.

2.3. Microbiological analysis

The viable and culturable populations of lactic acid bacteria (LAB), yeast and molds were determined by plating the brines and their decimal dilutions (in 0.9% NaCl) with a Spiral Plater (Don Whitley Sci. Ltd., Shipley, England). MRS agar (Oxoid) supplemented with 0.2 g/L sodium azide (Sigma-Aldrich, St. Louis, MO, US), VRBD agar (Oxoid) and oxytetracycline-glucose-yeast extract agar (Oxoid) were used for the

enumeration of LAB, Enterobacteriaceae, and yeast and molds, respectively. Enterobacteriaceae were incubated at 37 °C for 24 h, LAB and yeasts were set at 32 °C for 48 h (even five days when there was no growth), and the numbers of colony-forming units were counted with a Scan 500 colony counter (Interscience, Saint-Nom-la-Bretèche, France).

2.4. pH, NaCl, water activity and moisture

The pH value of the brines and olive paste was determined with a Crison Basis 20 pH-meter (Barcelona, Spain).

Thirty grams of olive pulp was mixed with 30 mL of distilled water and homogenized in an Ultra Turrax homogenizer. The homogenate was squeezed through cheesecloth and the concentration of NaCl in the aqueous phase was analyzed by titration with a 0.86 N silver nitrate solution, using a potassium chromate solution as indicator. The value obtained by titration was multiplied by 2 and it was expressed as the percentage of NaCl per 100 g of olive flesh (g NaCl/100 g pulp). In the case of dehydrated olives, the NaCl in the olive juice was calculated taken into account the moisture of the fruit.

The water activity (a_w) of the olives was analyzed with an AquaLab Pre apparatus (Meter Group Inc., WA, USA). Two or three pieces of olive pulp were placed in a disposable sample cup and a_w was measured in triplicate.

Olive moisture was measured by oven drying 5 g of fruit at 105 $^\circ C$ up to constant weight.

2.5. Sugars and organic acids in brine

Sugars (glucose, fructose, sucrose and mannitol) were analyzed as described by Sánchez, De Castro, Rejano, and Montaño (2000) using a Rezex RCM. Monosaccharide Ca+ (8%) column (300 \times 7.8 mm i. d., Phenomenex). The HPLC system consisted in a Waters 2690 Alliance with a pump, column heater at 85 °C and autosampler included, the detection being performed with a Waters 410 refractive index detector. Ethanol and lactic and acetic acids were also analyzed by HPLC using a Spherisorb ODS-2 column (5 μ m, 250 \times 4.6 mm, Waters Inc.) with deionized water (pH adjusted to 2.3 with phosphoric acid) as mobile phase (Sánchez et al., 2000). Flow rate was 1.2 mL/min, and the HPLC system was the same used for the carbohydrate analysis.

2.6. Color and firmness of olives

The color of olives was measured using a HunterLab ColorFlex EZ spectrophotometer, equipped with computer software to calculate the CIE L^* (lightness), a^* (redness), and b^* (yellowness) parameters. The reflectance at 700 nm was also recorded. Interference by stray light was minimized by covering samples with a box that had a matte black interior. The data from each measurement is the average of 10 olives.

The firmness of fruit was determined using a Kramer Shear Cell of one blade coupled to a Texture Analyzer TA. TX plus (Stable Microsystems, Godalming, UK). Two halves of each olive were placed facing the blade. The crosshead speed was 200 mm/min. Firmness was the mean of 10 replicate measurements and expressed as Newton/fruit.

2.7. Phenolic compounds

Phenolic compounds were extracted from the olive pulp with dimethyl sulfoxide (DMSO) according to Ramírez et al. (2013). Briefly, small pieces of pulp (<0.5 g) were cut from 20 olives up to a total of 10 g that were introduced into a solution of 30 mL of DMSO. The mixture was crushed with an Ultra-Turrax homogenizer and, after 30 min of resting contact, was centrifuged at 6000 g for 5 min, and 0.25 mL of the supernatant was diluted with 0.5 mL of DMSO plus 0.25 mL of 0.2 mM syringic acid (internal standard). Separation and quantification of each compound was carried out by HPLC by using a Spherisorb ODS-2 column, an elution gradient with acidified water and methanol, a flow rate

of 1 mL/min and a temperature of 35 °C. The mixture was filtered through a 0.22 μ m pore size nylon filter, and an aliquot (20 μ L) was injected into the HPLC chromatograph described above. Chromatograms were recorded at 280 nm (Waters 996 DAD detector).

2.8. Sensory evaluation

This was performed on dehydrated packed olives that were preserved at ambient temperature for one month. The olives were tested according to the "Method for sensory analysis of table olives" (IOC, 2011) by eight trained panelists from among the staff of the Instituto de la Grasa (Seville, Spain) in a normalized testing room. A profile sheet with a continuous scale of 10 cm ranging from 1 (absence of perception) to 11 (strongest intensity perceived) was used.

2.9. Statistical analysis

Statistical analyses were performed using Statistica 8.0 software (Statsoft, Tulsa, OK, USA). One-way analysis of variance, ANOVA (Duncan's test), was employed to compare mean values with a significant level of 95%.

3. Results and discussion

3.1. Assays with the Gordal cultivar

As expected, NaCl rapidly diffused from the brine to the flesh of the Gordal olives after the alkaline treatment (Fig. 1). However, treatments with initial 11% NaCl and 18% NaCl behaved in a different manner, with salt content equilibrium between olive flesh and brine being reached in a few days at the low salt treatment. By contrast, a surprising effect was

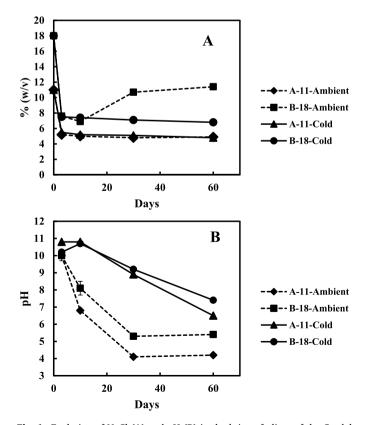


Fig. 1. Evolution of NaCl (A) and pH (B) in the brine of olives of the Gordal cultivar treated with alkali and preserved under ambient temperature or refrigeration for 60 days. Where error bars are not visible, determinations are within the size of the symbols on the graph.

observed when the initial salt content was 18%: the level of salt in the brine decreased to lower than 8% in a few days and it remained almost constant when the olives were preserved under refrigeration. In the case of the ambient temperature, the concentration of NaCl in the liquid also dropped below 8% during the first days, but started to increase after 10 days to reach around 11% after 60 days of preservation. It must be noted that olives initially covered with 18% NaCl shriveled despite the preservation temperature, so that they could be rejected by consumers but they were intended for later dehydration.

The pH of the brine is of great importance to know the ongoing status of the predictable fermentation process and its changes were strongly related to the level of NaCl in the brine along with the preservation temperature (Fig. 1). At ambient temperature, the pH dropped from values above 10 units to lower than 4.1 after 30 days of brining when a low initial salt content was used, and a similar trend was observed for the 18% salt, although in this case the pH only reached 5.2 units. By contrast, this parameter was maintained above 9 units in the refrigerated brines during the first 30 days, despite the initial salt content, although a steady decline was observed to reach around 7-8 units after 60 days of preservation. All these pH changes were strongly related to the microbial growth dynamics in the brines which is presented in Fig. 2. A population of LAB higher than 10^7 CFU/mL was reached in the brines of low initial NaCl at ambient temperature, in accordance with the low pH achieved. Low LAB population was detected in the brines with high initial NaCl content (18%) and preservation at ambient temperature, although LAB growth was even observed after 60 days under refrigeration conditions. Similar behavior was found for yeast growth. All these results were in agreement with the data of sugars and organic acids analyzed in the brines (Table 1); the lower the concentration of glucose and fructose detected in the brine after 60 days, the higher the content of

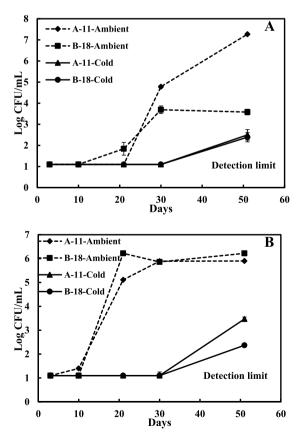


Fig. 2. Evolution of LAB (A) and yeast (B) in the brine of olives of the Gordal cultivar treated with alkali and preserved under ambient temperature or refrigeration for 60 days. Where error bars are not visible, determinations are within the size of the symbols on the graph.

Table 1

Chemical characteristics of the brine and color of the Gordal olives after 60 days of fermentation.

	Treatment	Treatment				
	A-11-Ambient	B-18-Ambient	A-11-Cold	B-18-Cold		
Brine (%, w/v))					
Lactic acid	1.34a	0.35b	0.24c	0.21c		
Acetic acid	0.16a	0.12a	0.08b	0.07b		
Ethanol	0.19a	0.12b	0.04c	0.04c		
Glucose	0.02c	0.06c	0.81a	0.67b		
Fructose	0.06c	0.14b	0.29a	0.28a		
Mannitol	0.26b	0.25b	0.31a	0.27b		
Color of olives						
L^*	38.0a	33.3b	30.7c	31.0c		
a*	3.0a	0.9b	-2,7c	-3.9d		
b*	22.2a	18.4b	15.7c	14.8d		

For each parameter, values followed with a different letter in the same row means significant difference according to Duncan's test (p < 0.05).

lactic and acetic acids found.

Processing of Spanish-style green olives includes a washing step after the alkaline treatment to facilitate lactic acid fermentation, but unwashed olives can also be fermented by LAB (Martín-Vertedor et al., 2021), in particular olives of the Gordal cultivar that are very prone to fermentation by LAB (Medina et al., 2010). These microorganisms have been found in brines of olives elaborated following the Castelvetrano method at ambient temperature (Romeo, Piscopo, Mincione, & Poiana, 2012; Zinno et al., 2017) but this is not desired at industrial level in order to maintain the green color of the olives (Berlanga-Del Pozo et al., 2020), so they are currently preserved under refrigeration. Specifically, as can be seen in Table 1, only the olives maintained at 5-6 °C with pH above 7 units presented L^* , a^* and b^* parameters that corresponded to green tones (lower values of a^* and b^*) and unlike the lactic acid fermented olives that had yellow tones (the greatest b^* parameter). Consequently, a very high initial concentration of NaCl did not avoid lactic acid fermentation nor low pH and yellow color of olives, so the only way to preserve green tones in the fruits was the refrigeration method. Obviously, these olives should be sterilized before commercialization due to their pH higher than 4.5 units.

On the other hand, the dehydration of the olives led to dark coloration on their surface, as can be seen in Table 2. The L* and *b** parameters diminished during the heating process and the *a** parameter turned to red tones along with lower values of the R₇₀₀ parameter. This browning effect has also been observed during dehydration of green olives treated with alkali (Öngen et al., 2005) and green olives fermented directly in brine (Piscopo et al., 2014). Browning of foods, and particularly olives, has been associated with phenolic compound transformation, in particular their enzymatic oxidation by the action of polyphenoloxidase and peroxidase or just their chemical oxidation alone. In our case, chemical oxidation would probably be the way the olives darkened more than enzymatic oxidation due to the alkali treatment

Table 2

Effect of dehydration at 60 $^{\circ}{\rm C}$ on the color and phenolic compounds of olives of the Gordal cultivar treated with alkali and preserved for 60 days.

	B-18-Ambient (pH 5.4)		B-18-Cold (pH 7.4)	
	Before	After	Before	After
Color				
L^*	33.4a	19.7b	32.7a	17.5b
a*	0.4b	1.9a	-3.9b	0.5a
<i>b</i> *	19.6a	2.8b	16.7a	0.1b
R ₇₀₀	15.2a	5.8b	14.2a	3.2b
Phenolic compounds				
Hydroxytyrosol (mg/kg)	3863a	3098b	2665a	66b
Tyrosol (mg/kg)	372a	406a	444a	449a

For each batch of olives, values followed with a different letter in the same row means significant difference according to Duncan's test (p < 0.05).

that the olives underwent before dehydration. Indeed, a significant reduction of hydroxytyrosol, the main o-diphenol identified in the olive pulp, occurred during the dehydration stage unlike the monophenol tyrosol (Table 2). Browning of these olives must be similar to that reported during processing of black ripe olives, where the dark color of the fruits is formed due to the oxidation of hydroxytyrosol and its further polymerization (Marsilio, Campestre, & Lanza, 2001). Likewise, the color of black ripe olives is currently monitored by reflectance at 700 nm, so this parameter was measured during the dehydration of the Gordal olives. In addition, it was found that the data fixed to a first order kinetic (Fig. 3) as also occurred during elaboration of black ripe olives (García, Brenes, Vattan, & Garrido, 1992). Then, the influence of the pH of the olives on the browning rate was studied and the results are presented in Fig. 4. As expected for the chemical oxidation of phenolic compounds (García et a., 1992), the higher the pH, the higher the browning rate achieved. It is worth noting that dehydrated black olives were obtained from unfermented Gordal olives that are available throughout the year, unlike the dry-salted black olives that are only processed during a few months of the year.

Bearing in mind this new olive product, dehydrated fruits from the A-11-Cold treatment were packed in jars, pasteurized and analyzed after one month of storage (Table 3). The pH of the olive pulp was close to neutrality, so the safety of this product must be assured by the NaCl content and a_w. The concentration of NaCl of the olives was 6.4 g/100 g olive pulp or 20.0 g/100 mL olive juice, the latter data complying with international regulations for NaCl content in the juice of dehydrated olives (>8%) (Alimentarius, 2013). Indeed, the a_w was 0.93, which is lower than the limit of 0.94 for the growth of Clostridium botulinum (Wareing & Fernandes, 2007). Likewise, the content of sodium in these olives could be reduced by using KOH instead of NaOH during the alkaline treatment as it has been proposed for the elaboration of black ripe olives (García-Serrano, Romero, García-García, & Brenes, 2020), along with KOH instead of NaCl during the fermentation stage. It must also be highlighted that the presence of molds was not visually detected on the olive surface, probably due to the pasteurization treatment.

The black color of this new product, along with its soft firmness, tried to mimic the quality characteristics of heat-dried and salt-dried black olives (Table 3). Moreover, tasters did not find negative, bitter or acid sensations, and they only found a medium salty sensation in these new table olives. This is a new product with similar characteristics than the traditional dehydrated black olives (García-Serrano et al., 2022), so these olives possess lower moisture and higher oil than the Spanish-style green and the California-style black olives. They also have higher pH than green olives and lower than oxidized black olives, and their level of salt is high in the juice but not so high in the whole fruit.

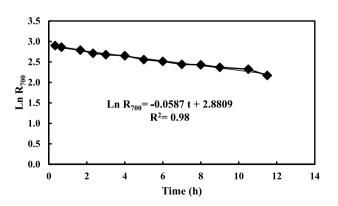


Fig. 3. Relationship between the color (Ln R_{700}) of the Gordal olives and time during the dehydration process. Fruits with pH 4.3 were dehydrated at 60 °C.

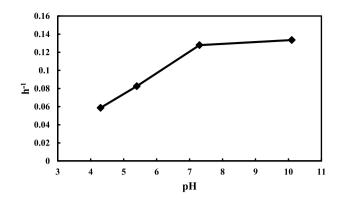


Fig. 4. Influence of the pH on the rate of olive darkening (h^{-1}) during the dehydration of the unfermented Gordal cultivar at 60 °C.

Table 3

Physico-chemical characteristics and organoleptic assessment of dehydrated black olives from unfermented Gordal cultivar. Analysis was performed one month after packing.

	Olives from A-11-Cold		
Physico-chemical characteristics			
pH	6.8		
NaCl (g/100 g)	6.4		
aw	0.93		
Moisture (g/100 g)	47.1		
Firmness (N/fruit)	112		
L	17.6		
a*	1.1		
<i>b</i> *	0.6		
Organoleptic assessment			
Negative sensations	1.9		
Salty sensation	5.0		
Bitter sensation	1.7		
Acid sensation	1.5		
Kinaesthetic sensation (hardness)	6.3		

3.2. Assays with the hojiblanca cultivar

Cold preservation was needed to avoid lactic acid fermentation of the Gordal cultivar but the Hojiblanca cultivar is currently less prone to this type of fermentation than the Gordal, so in this case the olives were fermented at ambient temperature. As occurred with the Gordal olives (Fig. 1), a rapid equilibrium of the salt content between the olive pulp and the brine was reached when 11% NaCl was initially employed (Fig. 5). Again, the initial 18% NaCl gave rise to a sharp decrease of the salt in the liquid, down to 6%, which was followed by an increase to 11–12% at equilibrium after 20 days, this behavior was observed for both washed (treatment C) and unwashed olives (treatment B). As was observed for the Gordal cultivar, the Hojiblanca olives also shriveled when using the highest level of salt although this was reduced with time.

The evolution of the pH in the brine of treatment A was similar to that observed for the Gordal cultivar (Fig. 1): a rapid decrease of the pH during the first 20 days of fermentation that led to a final value of 4.2 units at the end of the analyzed period (100 days). By contrast, the initial 18% NaCl slowed down the drop of this parameter, which was maintained at around 5.3 units for a long time in the brines of washed and unwashed olives, which was a similar behavior to that found with the Gordal cultivar fermented with 18% salt and preserved at ambient temperature (Fig. 1). Indeed, it was found that after 50 days of brining the concentrations of lactic acid in brines of treatments A, B and C were 1.12 ± 0.11 , 0.25 ± 0.10 and 0.20 ± 0.10 g/mL, respectively. It means that vigorous lactic acid fermentation was not performed in brines of treatment B and C, which is in accordance with data of pH reflected in

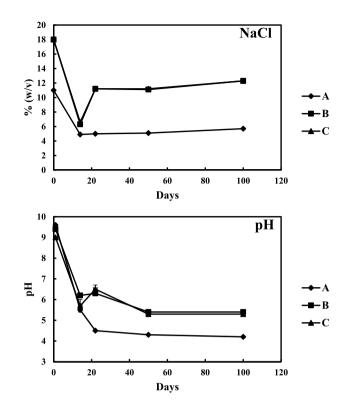


Fig. 5. Evolution of NaCl and pH in the brine of olives of the Hojiblanca cultivar treated with alkali and preserved for 100 days at ambient temperature. A, 11% NaCl after NaOH; B, 18% NaCl after NaOH; C, 18% NaCl after NaOH and washing. Where error bars are not visible, determinations are within the size of the symbols on the graph.

Fig. 5. In addition, the concentration of glucose in all the brines at this time was lower than 0.08 g/100 mL, indicating that most sugars were already consumed. Therefore, a decrease of the pH was not prevented in the brines of this cultivar even using 18% salt or washing the olives, so cold preservation must be needed to obtain lactic acid unfermented green olives.

Dehydration of fermented olives with pH in the pulp of 4.2 (treatment A) and 5.3 (treatment C) was conducted at 60 $^{\circ}$ C, and the results are presented in Table 4. Again, the heating process led to dark olives and this effect was more pronounced at a higher pH, the R₇₀₀ was 11.7 and 7.4 with olives of pH 4.2 and 5.3 respectively. Likewise, this browning effect was also related to the oxidation of hydroxytyrosol where its concentration in the olives significantly diminished during the dehydration stage (Table 4).

Table 4

Effect of dehydration at 60 $^{\circ}$ C on the color and phenolic compounds of olives of the Hojiblanca cultivar treated with alkali and preserved for 100 days.

	Treatment A (pH 4.2)		Treatment C (pH 5.3)	
	Before	After	Before	After
Color				
L^*	38.0a	26.7b	35.0a	22.4b
<i>a</i> *	2.5b	5.0a	0.4b	2.5a
<i>b</i> *	22.3a	10.3b	19.9a	4.4b
R ₇₀₀	16.5a	11.7b	16.2a	7.4b
Phenolic compounds				
Hydroxytyrosol (mg/kg)	5276a	5007b	2500a	2116b
Tyrosol (mg/kg)	463a	443a	208a	231a

For each batch of olives, values followed with a different letter in the same row means significant difference according to Duncan's test (p < 0.05).

4. Conclusions

These results indicate that the only way to avoid lactic acid fermentation and, consequently, low pH in olives was to maintain them under refrigeration. It must be noted that at ambient temperature and initial concentration of NaCl as high as 18% did not prevent a drop of pH below 6 units, regardless of any washing step after the alkaline treatment or the olive cultivar. However, these findings should be confirm with other Spanish and worldwide cultivars along with the effect of more intense washing cycles. Interestingly, olives darkened during the dehydration stage and this effect followed a first order kinetic, this browning being associated with the oxidation of the olive polyphenols, particularly the *o*-diphenol hydroxytyrosol. Finally, it is worth mentioning that tasters scored these olives as good dehydrated black olives. Hence, it has been demonstrated that dehydrated black olives can be prepared from harvested green olives, which must be treated with alkali, preserved under refrigeration and dehydrated by oven.

CRediT authorship contribution statement

M. Brenes: Conceptualization, Methodology, Writing – original draft, Writing – review & editing, Visualization. P. García-Serrano: Conceptualization, Investigation, Formal analysis. M. Brenes-Álvarez: Conceptualization, Investigation, Formal analysis. E. Medina: Conceptualization, Investigation, Formal analysis. P. García-García: Conceptualization, Methodology, Writing – original draft. C. Romero: Conceptualization, Methodology, Writing – original draft.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

This study was financed by the Spanish regional government of Junta de Andalucía and EU FEDER funds (project P18-TP-1973).

References

- Alimentarius, C. (2013). Codex standard for table olives. Codex stan. 66-1981 (Vol. 2013). revision 1987 https://www.fao.org/fao-who-codexalimentarius/es/.
- Ambra, R., Lucchetti, S., Moneta, E., Peparaio, M., Nardo, N., Baiamonte, I., et al. (2017). Effect of partial substitution of sodium with potassium chloride in the fermenting brine on organoleptic characteristics and bioactive molecules occurrence in table olives debittered using Spanish and Castelvetrano methods. *International Journal of Food Science and Technology*, 52, 662–670. https://doi.org/10.1111/jjfs.13319
- Aydar, A. Y. (2020). Quality parameters and drying kinetic of ultrasound pretreated fermented black table olives. *Latin American Applied Research*, 50, 271–276. https:// doi.org/10.52292/j.laar.2020.492
- Badaway, H. A. A., Abd-Elmageed, S. M. M., & Almoselhy, R. I. M. (2020). Effect of drying process on the quality of table olives. *Middle East Journal of Applied Sciences*, 10, 220–227. https://doi.org/10.36632/mejas/2020.10.2.22
- Berlanga-Del Pozo, M., Gallardo-Guerrero, L., & Gandul-Rojas, B. (2020). Influence of alkaline treatment on structural modifications of chlorophyll pigments in NaOHtreated table olives preserved without fermentation. *Foods*, 9, 701. https://doi.org/ 10.3390/foods9060701

- Brenes, M., & García, P. (2005). Elaboración de aceitunas denominadas "Green ripe olives" con variedades españolas. Grasas Y Aceites, 56, 188–191. http://hdl.handle. net/10261/2456.
- Casado, F. J., Sánchez, A. H., Rejano, L., & Montaño, A. (2007). Estudio de nuevos procedimientos de elaboración de aceitunas verdes tratadas con álcali, no fermentadas, conservadas mediante tratamientos térmicos. Grasas Y Aceites, 58, 275–282. http://hdl.handle.net/10261/2441.
- De Bruno, A., Piscopo, A., Cordopatri, F., Poiana, M., & Mafrica, R. (2020). Effect of agronomical and technological treatments to obtain selenium-fortified table olives. *Agriculture*, 10, 284. https://doi.org/10.3390/agriculture10070284
- De Florio-Ramírez, E., & Lanchipa-Bergamini, L. (2008). Deshidratación de aceituna negra (Olea europea L.), variedad Sevillana-Tacna. *Ciencia & Desarrollo, 12*, 45–48. https://doi.org/10.33326/26176033.2008.12.249
- Gambella, F., Piga, A., Agabbio, M., Vacca, V., & D'hallewin, G. (2000). Effect of different pre-treatments on drying of green table olives (Ascolana tenera var.). *Grasas Y Aceites*, 51, 173–176. https://doi.org/10.3989/gya.2000.v51.i3.475
- Gandul-Rojas, B., & Gallardo-Guerrero, L. (2018). Pigment changes during preservation of green table olive specialities treated with alkali and without fermentation: Effect of thermal treatments and storage conditions. Food Research International, 108, 57–67. https://doi.org/10.1016/j.foodres.2018.03.022
- García-Serrano, P., Brenes-Álvarez, M., Romero, C., Medina, E., García-García, P., & Brenes, M. (2022). Physicochemical and microbiological assessment of comercial dehydrated black olives. *Food Control*, 145, Article 109417. https://doi.org/j. foodcont.2022.109417.
- García-Serrano, P., Romero, C., García-García, P., & Brenes, M. (2020). Influence of the type of alkali on the processing of black ripe olives. *LWT–Food Science and Technology*, 126, Article 109318. https://doi.org/10.1016/j.lwt.2020.109318
- García, P., Brenes, M., Vattan, T., & Garrido, A. (1992). Kinetic study at different pH values of the oxidation process to produce ripe olives. *Journal of the Science of Food* and Agriculture, 60, 327–331. https://doi.org/10.1002/jsfa.2740600309
- IOC, International Olive Council. (2011). Method for the sensory analysis of table olives. Madrid. Spain http://www.internationaloliveoil.org.
- Lanza, B., Di Serio, M. G., Russi, F., Lannucci, E., Giansante, L., Di Loreto, G., et al. (2014). Evaluation of the nutritional value of oven-dried table olives (cv. Majatica) processed by the Ferrandina style. *Rivista Italiana delle Sostanze Grasse*, 91, 117–127. https://www.researchgate.net/publication/274265029.
- Marsilio, V., Campestre, C., & Lanza, B. (2001). Phenolic compounds change during California-style ripe olive processing. Food Chemistry, 74, 55–60. https://doi.org/ 10.1016/S0308-8146(00)00338-1
- Marsilio, V., Lanza, B., Campestre, C., & De Angelis, M. (2000). Oven-dried table olives: Textural properties as related to pectic composition. *Journal of the Science of Food and Agriculture*, 80, 1271–1276. ttps//doi.org/10.1002/1097-0010(200006)80:8<1271:: AID-JSFA635>3.0.CO;2-O.
- Martín-Vertedor, D., Schaide, T., Boselli, E., Martínez, M., Arias-Calderón, R., & Pérez-Nevado, F. (2021). Effects of different controlled temperatures on Spanish-style fermentation processes of olives. *Foods*, 10, 666. https://doi.org/10.3390/ foods10030666
- Medina, E., Gori, C., Servili, M., de Castro, A., Romero, C., & Brenes, M. (2010). Main variables affecting the lactic acid fermentation of table olives. *International Journal of Food Science and Technology*, 45, 1291–1296. https://doi.org/10.1111/j.1365-2621.2010.02274.x
- Navarro, T., de Lorenzo, C., & Pérez, R. A. (2004). SPME analysis of volatile compounds from unfermented olives subjected to thermal treatment. *Annals Bioanalytical Chemistry*, 379, 812–817. https://doi.org/10.1007/s00216-004-2552-y
- Öngen, G., Sargin, S., Tetik, D., & Köse, T. (2005). Hot air drying of green table olives. Food Technology and Biotechnology, 43, 181–187.
- Panagou, E. Z. (2006). Greek dry-salted olives: Monitoring the dry-salting process and subsequent physico-chemical and microbiological profile during storage under different packing conditions at 4 and 20°C. LWT–Food Science and Technology, 39, 322–329. https://doi.org/10.1016/j.lwt.2005.02.017
- Piscopo, A., De Bruno, A., Zappia, A., & Poiana, M. (2014). Antioxidant activity of dried green olives (Carolea cv.). LWT–Food Science and Technology, 58, 49–54. https://doi. org/10.1016/j.lwt.2014.03.013
- Ramírez, E., García-García, P., de Castro, A., Romero, C., & Brenes, M. (2013). Debittering of black dry-salted olives. *European Journal of Lipid Science and Technology*, 115, 1319–1324. https://doi.org/10.1002/ejlt.201300167
- Romeo, F. V., Piscopo, A., Mincione, A., & Poiana, M. (2012). Quality evaluation of different typical table olive preparations (cv Nocellara del Belice). *Grasas Y Aceites*, 63, 19–25. https://doi.org/10.3989/gya.058511
- Sánchez, A. H., De Castro, A., Rejano, L., & Montaño, A. (2000). Comparative study on chemical changes in olive juice and brine during green olive fermentation. *Journal of Agricultural and Food Chemistry*, 48, 5975–5980. https://doi.org/10.1021/jf000563u Wareing, P., & Fernandes, R. (2007). *Micro-facts* (6th ed.). UK: Leatherhead Food
- International Ltd (chapter 4). Zinno, P., Guantario, B., Perozzi, G., Pastore, G., & Devirgiliis, C. (2017). Impact of NaCl reduction on lactic acid bacteria during fermentation of Nocellara del Belice table
- olives. Food Microbiology, 63, 239–247. https://doi.org/10.1016/j.fm.2016.12.001