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Quality and Enhancement of Bioactive Phenolics in Cv. Napoleon Table Grapes Exposed to Different Postharvest Gaseous Treatments

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Ten different gaseous treatments were evaluated for their efficacy in the keeping quality of cv. Napoleon table grapes during 38 days of storage at 0 °C followed by 6 days of shelf life at 15 °C in air. These storage methods included modified atmosphere packaging (MAP) with and without SO_2 or natural fungicides (hexanal and hexenal), two controlled atmospheres (CA), and intermittent and continuous applications of O_3. As a control, air atmosphere during cold storage was used. Most of the treatments applied kept the postharvest quality of the grapes, although the best results were obtained by the use of a MAP with 5 kPa of O_2 plus 15 kPa of CO_2 plus 80 kPa of N_2. The total anthocyanin content at harvest was 170 ± 19 μg/g of fresh weight (fw) of grapes, which declined in most of the treatments applied and was reflected in the loss of red color. Peonidin 3-glucoside was detected at all sampling times as the major anthocyanin (always >50% from the total content). Treatments applied kept or decreased the total flavonol content from that measured at harvest (17 ± 1.4 μg/g of fw of berries). However, an increase of up to 2-fold in total stilbenoid content after shelf life for CA and O_3 treatments was observed. At all sampling times for almost every treatment piceid concentration remained unaltered or slightly changed, whereas large increases were observed after shelf life for resveratrol (1.2 ± 0.6 μg/g of fw of grapes sampled at harvest), even up to 3- and 4-fold for O_3-treated grapes and 2-fold for CA-treated ones. Therefore, improved techniques for the keeping quality of cv. Napoleon table grapes during long-term storage seem to maintain or enhance their antioxidant compound content.

KEYWORDS: Table grapes; modified atmosphere packaging; controlled atmosphere; ozone; sulfur dioxide; hexanal; hexenal; anthocyanins; flavonols; resveratrol; piceid; stilbenoids

INTRODUCTION

Table grape (*Vitis viniferera* L.) shows a nonclimacteric behavior with a low physiological activity, moderate sensitivity to weight loss mainly through the rachis tissues, and high susceptibility to fungal attack mainly due to *Botrytis cinerea* Pers. during postharvest storage. Fumigation with SO_2 is the most common method to control decay during cold storage (*1*, *2*). However, SO_2 is highly corrosive to metals and injurious to people and fresh fruits, inducing injuries to clusters if used excessively (*3*). Consequently, it is important to find alternative methods to SO_2 fumigation for table grape storage.

Some alternative techniques that have been tested included modified atmosphere packaging (MAP) (*4*, *5*), natural antifungal volatile compounds extracted from plant tissues such as hexanal and (*E*)-2-hexenal (*6*, *7*), controlled atmospheres (CA) (*8*−*10*), and the use of O_3 (*11*−*13*).

Phenolic compounds present in grapes show antioxidant and anticarcinogenic properties and are supposed to be mainly responsible for preventing cardiovascular diseases (*14*−*16*), cancer (*17*, *18*), and other degenerative disorders such as Alzheimer's disease or dementia (*19*), especially through moderate daily consumption of red wine during a long period of time. *trans*-Resveratrol (3,5,4′-trihydroxystilbene) is of interest due to its antioxidant (*20*), antiplatelet (*21*), anti-inflamatory (*22*), estrogenic (*23*), cardioprotective (*24*), and antitumor (*17*) properties, and table grapes could be a possible dietary source of stilbenoids. Resveratrol is not widely distributed in plants and has been reported in very few fruits and vegetables used for human consumption (*25*). Although concentrations of this phytoalexin in grapes are very low, it can be induced under

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stress conditions such as pathogen attack and exposure to UV-C. Piceid has properties similar to those of resveratrol in inhibiting platelet aggregation and oxidation of human low-density lipoprotein (LDL), and in a manner less active than *trans*-resveratrol, *trans*-piceid reduces the elevations of lipid levels and inhibits eicosanoid synthesis (*26*).

The aim of the present work was to evaluate the effects of 10 different gas treatments, applied during cold storage to maintain postharvest quality, on the phenolic composition of cv. Napoleon table grapes.

MATERIALS AND METHODS

Plant Material. Cv. Napoleon table grapes were harvested at 15.7 °Brix on November 20 in Abarán (Murcia), close to the Mediterranean coast of Spain. Clusters were transported ~45 km to the laboratory, where fruits were immediately forced air cooled at 0 °C. The following day, clusters were randomly selected on the basis of uniform size, color, firmness, and freedom from evident defects or diseases. Clusters were distributed into batches with five replicates per treatment and placed inside 1500 mL basket plastic packages (each basket constituted a replicate) or in 2500 mL glass jars that were stored in a cold room at 0 °C and 90% relative humidity (RH).

Treatments, Period, and Temperature Assayed. The following treatments for cold storage were applied:

(T1, MPP) Packages were thermally sealed by using macroperforated polypropylene (PP) with 18 holes of 8.8 mmϕ/dm^2 (Borden S.A.). This treatment was used as the control.

(T2, OPP) Packages were thermally sealed by using oriented PP (Borden S.A.) of 35 μm thickness and antimist treated.

(T3, OPP + 0.7 g of $Na_2S_2O_5$/kg) This treatment was the same as T2 plus a commercial two-phase generator of SO_2 (J. Pego S.L., Aspe, Alicante, Spain) with 0.35 g of $Na_2S_2O_5$ per package (0.08 g for the fast phase and 0.27 g for the slow phase) (Panreac, Montplet & Esteban S.A., Barcelona, Spain).

(T4, OPP + 8 μL of *trans*-2-hexenal) This is the same as T2 treatment plus a soaked filter paper containing 8 μL of *trans*-2-hexenal just before sealing.

(T5, OPP + 8 μL of hexanal) T5 treatment is the same as T2 plus a soaked filter paper containing 8 μL of hexenal just before sealing.

(T6, control for CA) Glass jars, each containing one cluster, were hermetically sealed and ventilated with humidified air at a flow of 20 mL/min.

[T7, CA (5 kPa of O_2 + 3 kPa of CO_2 + 92 kPa of N_2] T6 treatment was modified for ventilation with the indicated gas mixture.

[T8, CA (5 kPa of O_2 + 15 kPa of CO_2 + 80 kPa of N_2] T6 treatment was modified for ventilation with the indicated and recommended gas mixture (*9*).

(T9, MPP + 0.1 ppm of O_3) This treatment was the same as T1 but packages were placed at 0 °C and 90% RH with continuous exposure to 0.1 ppm of O_3 supplied by a generator (model Convet 20, Murcia, Spain). This equipment was used in cycles of 1 h. For the first 30 min, O_3-enriched air was applied, and for the following 30 min air was flushed into the cold room. The mean O_3 level measured in each cycle was 0.1 ppm.

(T10, shocks of 8 ppm of O_3) T6 treatment was modified to include flushing into the gastight jars of 8 ppm of O_3 for 30 min every 2.5 h.

All treatments were kept for 38 days at 0 °C (simulating cold storage and transport) followed by 6 days at 15 °C in air (simulating shelf life during marketing).

Gas Analysis. Samples of 0.5 mL were removed for gas analysis from the headspace of the packages, and changes in O_2 and CO_2 were monitored using a gas chromatograph (Perkin-Elmer Autosystem, Norwalk, CT) equipped with Porapack QS 80/100 columns (1.2 m × 3.18 mm i.d.) and with a thermal conductivity detector. Oven and injector temperatures were 35 and 115 °C, respectively; helium flow was 18.4 mL/min. Calibration of CO_2 and O_2 was done with known standards (Air Liquid, Murcia, Spain). Concentrations of O_3 were monitored by a portable detector (model A-21 ZX of Eco Sensors Inc., Santa Fe, NM).

Quality Attribute Analysis. At harvest, quality parameters of 40 grapes randomly removed from several clusters and distributed in five replicates of eight grapes each were determined. Cover color and firmness of grapes were monitored for each replicate, and then the grapes were pressed in an automatic press (Hanna Instruments, 190 MB, Singapore) to evaluate total soluble solids content (SSC), pH, and titratable acidity (TA) of the juice. After cold storage and shelf life, in another five replicates of eight grapes each, randomly removed from clusters of each treatment, color, firmness, SSC, pH, and TA were determined. Weight losses and decay were recorded after cold storage and shelf life using a scale with an accuracy of 0.01 g (Mettler, Madrid, Spain) and expressed in percentage of initial fresh weight.

Cover color was measured on three equidistant points of the equatorial zone using a compact tristimulus colorimeter (Minolta CR-300, Ramsey, NJ) with an 8 mm diameter viewing aperture and white plate reference *C* ($Y = 94.3$; $x = 0.3142$; $y = 0.3211$, standard CIE illuminant, 2° observer). Values were expressed as Hunter L^*, C^*, and H_{ab} parameters.

TA was determined by titrating a 10 mL juice sample using 0.1 N NaOH to pH 8.1 and expressed as grams of tartaric acid per 100 mL (*27*). Values of pH were recorded with a pH-meter (Crison model 501, Barcelona, Spain). SSC levels were determined with a hand refractometer (Atago N1, Tokyo, Japan) at 20 °C and expressed in degrees Brix. Firmness was recorded as the maximum mechanical resistance offered by the fruit to deformation force in newtons (*28*) in the equatorial zone with a universal testing machine (Lloyd Instrument model LR 10K, Fareham, Hants, U.K.) equipped with a rod of 6.3 mm of diameter at 25 mm/min and load cell of 5 kN.

Nine judges (six men and three women; aged 26−55 years), well trained in the comparative evaluation of table grapes, conducted a sensory evaluation. Aroma, browning of rachis, and softness were evaluated on a five-point intensity scale of damage (1, none; 2, slight; 3, moderate; 4, severe; 5, extreme) (*29*). Visual appearance, flavor, and eating texture of grapes were evaluated for intensity on a nine-point scale (1, extremely poor or soft in the case of texture; 3, poor or soft; 5, moderate; 7, good; 9, excellent) on the basis of previous reports (*29*, *30*).

Extraction of Phenolic Compounds. Control and treated grapes (3 replicates of 15 berries each) were taken at harvest, after 38 days of cold storage, and after an additional 6 days of shelf life. Grapes were peeled with a sharp knife, and the peels were stored at −80 °C until analyzed. Peels represented 9.4% (±1.5) of the total fresh weight (fw) of berries. Samples of 5 g were homogenized in an Ultraturrax T-25 (Janke and Kunkel, Ika-Labortechnick) at 24000 rpm for 1 min after the addition of 3 mL/g of methanol of HPLC grade plus 3% formic acid. The extracts were centrifuged at 5000g_n for 5 min in a Centromix centrifuge (Selecta, Barcelona, Spain), filtered through 0.45 μm, and HPLC analyzed as previously reported (*31*, *32*).

HPLC Analysis of Phenolics. The HPLC analyses were performed on an L-6200 liquid chromatograph (Merck-Hitachi, Darmstadt, Germany) equipped with a Shimadzu SPD-M6A UV diode array detector and a Licrochart RP-18 column (Merck, Darmstadt, Germany) (25 × 0.4 cm, 5 μm particle size), using as solvents water plus 5% formic acid (solvent A) and HPLC grade methanol (solvent B) at a flow rate of 1 mL/min. Elution was performed with a gradient starting with 2% B to reach 32% at 30 min, 40% B at 40 min, and 95% B at 50 min and then became isocratic for 5 min (*31*, *32*). Chromatograms were recorded at 510, 370, and 320 nm. The different phenolic compounds were identified by their UV spectra recorded with a diode array detector and by chromatographic comparisons with resveratrol (Sigma, St. Louis, MO), delphinidin 3-glucoside, cyanidin 3-glucoside, petunidin 3-glucoside, peonidin 3-glucoside, and malvidin 3-glucoside previously isolated from wine grapes (supplied by Dr. García-Viguera, CEBAS−CSIC, Murcia, Spain) and quercetin 3-glucoside, previously isolated from *Vitis* leaves (supplied by Dr. Ferreres, CEBAS−CSIC, Murcia, Spain). Anthocyanins were quantified at 510 nm as cyanidin 3-glucoside. Flavonols were quantified at 370 nm as quercetin 3-glucoside (Merck) and stilbenoids (piceid and *trans*-resveratrol) at 320 nm as *trans*-resveratrol (Sigma).

Statistical Analysis. An ANOVA with three replicates per treatment was performed. By using Statgraphics Plus (version 4.0), an LSD

Table 1. Changes in Individual (**A*i***) and Total Anthocyanin Content (Micrograms per Gram of Fresh Weight of Grapes) of Cv. Napoleon Table Grapes Sampled at Harvest, after 38 Days of Cold Storage at 0 °C (CS), and after an Additional 6 Days of Shelf Life at 15 °C (SL) under Several Gas Treatments (T*i*)[a]

	A1		A2		A3		A4		A5		A6		A7		A8		total	
treatment	CS	SL	CS	SL	CS	SL	CS	SL	CS	SL	CS	SL	CS	SL	CS	SL	CS	SL
none (at harvest)	2.82 abc ABC		12.8 a A		4.05 a A		91.4 a A		40.2 ab DEF		2.13 ab AB		3.39 ab A		13.2 a A		170 a A	
T1	2.66 bcd	4.13 A	9.72 ab	7.78 ABC	3.81 a	3.31 ABC	48.6 de	63.7 B	36.9 abc	44.6 BCD	1.81 abc	1.82 ABC	2.59 abc	3.25 AB	9.67 abc	8.27 BC	116 b	137 B
T2	1.61 def	3.02 AB	7.92 bc	5.50 BC	156 b	2.27 BCD	39.2 ef	46.2 CD	18.0 e	35.4 DEF	1.36 bc	1.78 ABC	3.33 ab	2.92 ABC	7.76 bc	11.0 ABC	81 e	108 CDE
T3	1.19 ef	0.64 E	8.02 bc	3.17 C	3.02 ab	1.28 D	42.8 ef	56.3 BC	23.2 de	28.3 GH	2.05 abc	1.96 ABC	3.30 ab	3.51 A	6.36 c	6.76 C	90 cde	102 DEF
T4	1.40 def	3.00 AB	6.53 cde	6.68 ABC	1.91 b	1.74 D	58.9 bcd	62.7 B	33.4 bc	42.4 CDE	1.39 bc	2.17 AB	2.20 bc	2.61 ABC	6.55 c	7.93 BC	112 bc	129 BCD
T5	3.42 abc	3.85 AB	6.84 bcd	6.62 ABC	2.70 ab	4.15 A	50.6 cde	65.4 B	29.5 cd	52.7 ABC	2.01 abc	2.45 A	3.37 ab	3.01 ABC	9.73 abc	12.6 A	108 bcd	151 AB
T6	0.75 f	0.98 CD	4.71 de	5.19 C	1.76 b	1.41 D	42.2 ef	38.6 D	24.6 de	21.5 H	1.34 bc	0.94 C	2.69 abc	1.60 C	7.93 bc	7.77 C	86 de	78 F
T7	4.20 a	3.93 AB	6.97 bcd	7.94 ABC	3.27 ab	4.36 A	61.0 bc	47.4 CD	35.4 bc	57.5 A	2.01 abc	1.60 ABC	2.87 abc	1.82 BC	8.35 bc	9.43 ABC	124 b	134 BC
T8	1.17 ef	2.06 BCD	3.73 e	5.58 BC	1.76 b	1.84 CD	32.5 f	39.6 D	21.2 e	33.1 EFG	1.47 bc	1.45 ABC	2.90 abc	1.79 BC	7.82 bc	8.38 BC	73 e	94 EF
T9	3.91 ab	2.03 BCD	6.35 cde	9.04 ABC	2.98 ab	2.33 BCD	56.8 bcd	45.3 CD	44.1 a	29.7 FGH	2.21 a	1.24 BC	3.97 a	2.88 ABC	11.2 ab	0.0 D	131 b	93 EF
T10	1.91 cde	3.55 AB	6.02 cde	11.7 AB	3.21 ab	3.40 AB	65.9 b	84.2 A	35.6 bc	53.5 AB	1.28 c	1.92 ABC	1.59 c	2.48 ABC	8.00 bc	12.1 AB	123 b	173 A

[a] To identify treatments, see Materials and Methods, and to identify individual anthocyanins in anthocyanin content, see Results and Discussion. Lower case letters compare significant differences between treatments and value at harvest after cold storage according to LSD multiple-range test ($p \leq 0.05$). Upper case letters compare significant differences between treatments and value at harvest after shelf life according to LSD multiple-range test ($p \leq 0.05$).

multiple-range test was conducted. Mean values sampled at harvest and after cold storage and shelf life were compared to determine significant differences among treatments.

RESULTS AND DISCUSSION

Changes in Quality Attributes. The steady state atmosphere reached for MAP treatments (T2−T5) by using OPP film was 5 kPa of O_2 + 15 kPa of CO_2 + 80 kPa of N_2, similar to that applied in one of the CA treatments (T8).

Table grapes suffered from dehydration from the moment they were harvested until the end of the experiment. These cumulative weight losses until the end of shelf life ranged between 4.3 and 5.4% for MPP packages (T10 and T1, respectively), between 1.9 and 2.3% when OPP film was used (T2−T5), and between 2.4 and 3.6% when a humidified air was introduced into tightly sealed glass jars (T6−T9). Clusters also suffered from fungal attacks mainly caused by *Botrytis cinerea* Pers.; control for CA grapes (T6) showed a severe attack (63.3% of the samples) after shelf life, whereas in the control (T1) 5% losses were obtained. These higher losses were probably due to an excessive humidification of the air used to ventilate the glass jars and may have condensed water on the cluster. Decay incidence on grapes from CA and O_3 treatments (T7−T10) ranged between 5.9% for O_3 shocks (T10) and 13% for continuous application of O_3 (T9). On the other hand, MAP treatments (T2−T5) showed the lowest fungal attacks after shelf life, without significant differences among them, ranging between 0.3% for OPP + SO_2 (T5) and 1.8% for OPP (T2).

Compared to values sampled at harvest, generally slight nonsignificant changes were monitored for all treatments at all sampling times for color parameters ($L^* = 30.4 \pm 1.4$; C^*, 5.29 ± 1.5; H_{ab}, 10.5 ± 7.8 at harvest), firmness (8−10 N), total SSC (15−17 °Brix), pH (3.7−3.9), and acidity (>0.4 g of tartaric acid/100 mL sampled at harvest). When the sensory evaluation was carried out, severe stem browning was detected for MPP conditions (T1 and T10) at both sampling times, probably due to the low RH reached in the cold room and also in clusters where hexenal was applied (T3). This suggests that this natural product used in the dose applied at 8 μL per package causes stem browning, although no color disorder was observed in the skin of grapes, confirming previous reports (*6*). MAP (without fungicide) using the OPP film (T2) was the best treatment for keeping the aroma, hydration, and color of the rachis as well as the visual appearance, flavor, and texture of grapes at harvest (5), whereas clusters under control for CA (T6) were unmarketable.

Anthocyanin Content. The major anthocyanins found in cv. Napoleon table grape skin (**Table 1**) were delphinidin 3-glucoside **(A1)**, cyanidin 3-glucoside **(A2)**, petunidin 3-glucoside **(A3)**, peonidin 3-glucoside **(A4)**, malvidin 3-glucoside **(A5)**, cyanidin 3-*p*-coumaroylglucoside **(A6)**, peonidin 3-*p*-coumaroylglucoside **(A7),** and malvidin 3-acetylglucoside plus malvidin 3-*p*-coumaroylglucoside **(A8)**, in agreement with previous results reported for the Napoleon cultivar and others (*33*, *34*). The anthocyanins found in this cultivar were similar to those found in the red seedless Reliance table grape (*35*) and in the Agiorgitiko cultivars (*36*).

Peonidin 3-glucoside was the major anthocyanin at all sampling times with 53.8% from the total content at harvest followed by malvidin 3-glucoside with 23.7%. Malvidin 3-acetylglucoside plus malvidin 3-*p*-coumaroyl-glucoside and cyanidin 3-glucoside represented at harvest 7.8 and 7.5%, respectively, whereas the rest of the anthocyanins ranged between 1.2% for cyanidin 3-*p*-coumaroylglucoside and 2.4% for peonidin 3-glucoside.

The total content of these anthocyanins found at harvest was 170 ± 19 μg/g of fw of berries (**Table 1**). Most of the treatments exhibited a decline in total anthocyanins (loss of red color) except samples analyzed after shelf life for 8 μL hexanal-treated grapes (T5) and grapes subjected to O_3 shocks during cold storage (T10), for which grape color remained unaltered.

Table 2. Changes in Total Flavonol Content, Piceid, *trans*-Resveratrol, and Total Stilbenoid Content (Micrograms per Gram of Fresh Weight of Grapes) under Several Gas Treatments (T*i*) Sampled at Harvest, after 38 Days of Cold Storage at 0 °C (CS), and after an Additional 6 Days of Shelf Life at 15 °C (SL)[a]

	flavonols		piceid		resveratrol		stilbenoids	
treatment	CS	SL	CS	SL	CS	SL	CS	SL
none (at harvest)	17.0 ab AB		1.86 ab BC		1.22 cd DE		3.08 bc CDE	
T1	19.6 a	15.3 BCD	1.88 ab	0.67 DE	1.12 cd	1.22 DE	3.00 bc	1.90 EF
T2	10.7 cd	12.2 DE	1.16 abc	1.87 BC	1.24 cd	2.56 BC	2.40 bcd	4.43 BC
T3	11.5 cd	10.0 E	0.53 c	0.39 E	0.52 d	0.91 E	1.07 e	1.33 F
T4	11.6 cd	10.6 E	0.38 c	0.45 DE	1.06 cd	1.96 CD	1.43 de	2.40 DEF
T5	14.3 bc	11.3 E	1.19 abc	1.50 BCD	1.45 c	1.82 CD	2.63 bcd	3.33 BCD
T6	17.1 ab	12.8 CDE	0.79 bc	0.52 DE	1.06 cd	2.27 BC	2.23 cde	3.07 CDE
T7	14.3 bc	15.2 BCD	1.57 abc	2.08 AB	1.47 bc	2.54 BC	2.63 bcd	4.37 BC
T8	13.5 bcd	9.60 E	0.53 c	1.84 BC	2.38 ab	2.87 B	2.93 bc	4.70 B
T9	11.9 cd	20.4 A	0.95 abc	0.81 CDE	2.71 a	2.36 BC	3.67 ab	3.17 CDE
T10	9.13 d	16.2 BC	20.5 a	3.02 A	2.81 a	3.84 A	4.87 a	6.87 A

[a] To identify treatments, see Materials and Methods. Lower case letters compare significant differences between treatments and value at harvest after cold storage according to LSD multiple-range test ($p \leq 0.05$). Upper case letters compare significant differences between treatments and value at harvest after shelf life according to LSD multiple-range test ($p \leq 0.05$).

However, these decreases were not enough to show significant changes in L^*, C^*, and H_{ab} values at all sampling times.

Changes in individual anthocyanins between values sampled at harvest and after cold storage and shelf life under the treatments assayed (**Table 1**) show that the concentration of **A4** (peonidin 3-glucoside), the major anthocyanin found in this cultivar, decreased in all treatments at all sampling times except for grapes after shelf life subjected to O_3 shocks during cold storage (T10). A similar trend was found for anthocyanins **A2**, **A3**, and **A8**, for which contents decreased in most of the treated grapes at both sampling times when compared to values found at harvest. However, no significant changes were observed in anthocyanins **A6** and **A7**, except in control for CA grapes. In addition, anthocyanin **A1** decreased its content only in SO_2-treated grapes. Values sampled after shelf life for **A5** anthocyanin show that treatments T5, T7, and T10 induced a slight increase in the content of this pigment, whereas SO_2 (T3) and control for CA (T6) treated grapes decreased this value.

Flavonol Content. Three flavonols were found in the skin of cv. Napoleon grapes showing identical UV spectra and were identified as quercetin 3-glucuronide, quercetin 3-glucoside, and quercetin 3-rutinoside (*33*). **Table 2** represents changes in total content of these compounds sampled at harvest and after cold storage and shelf life. The total flavonol content found at harvest (17 ± 1.4 μg/g of fw of berries) decreased after shelf life except for control, CA, and both O_3 treatments (T1, T7, T9, and T10, respectively), for which no significant changes were found. Control grapes showed a behavior similar to that found in previous studies (*31*), where the total flavonol content of mature and immature cv. Napoleon grapes remained quite constant during cold storage and shelf life periods assayed with ~10 μg/g of fw of berries.

Stilbenoid Content. The stilbenoids *trans*-resveratrol and piceid (*trans*-resveratrol β-D-glucoside) were also identified in grape skins. **Table 2** shows changes in the piceid and *trans*-resveratrol content expressed in micrograms per gram of fresh weight of grapes found at harvest and after cold storage and shelf life.

Piceid content sampled at harvest (1.86 ± 0.9 μg/g of fw of grapes) remained unaltered for all treatments after cold storage except for T3, T4, and T8 treatment clusters, for which it declined to 0.4−0.5 μg/g of fw. When grapes were transferred to 15 °C for shelf life, a slight decrease was found after this period for both control treatments (T1 and T6) and for SO_2- and hexenal-treated grapes (T3 and T4). This result differs from that reported by Cantos et al. (*31*), who found that this resveratrol glucoside increased 2-fold its value sampled at harvest in the control treatment. However, O_3-treated clusters under the shock technique (T10) had increased piceid content compared to that sampled at harvest, whereas in the remaining treatments no changes were observed.

Resveratrol content found at harvest (1.22 ± 0.6 μg/g of fw of grapes) kept this value after shelf life for control and SO_2-, hexenal-, and hexanal-treated grapes (T1, T3, T4, and T5, respectively). The remaining treatments increased up to 3-fold its value sampled at harvest in O_3 shock treated clusters (T10), with 3.84 ± 0.5 μg/g of fw of grapes found after shelf life, and up to 2-fold for CA treatments (T7 and T8), probably because these treatments induced a faster biosynthesis of this compound (**Figure 1**). The increases were more marked when clusters where stored at 15 °C in agreement with previous reports (*31*) where control and UV-treated cv. Napoleon table grapes increased their resveratrol content after grapes were transferred to 15 °C.

Table 2 also shows changes in the total stilbenoid content (piceid plus *trans*-resveratrol) sampled at harvest and after cold storage and shelf life. The most remarkable changes were the increases observed after shelf life in the CA and O_3 treated grapes (T8 and T10), where these compounds increased up to 2-fold its concentration found at harvest (3.08 ± 1.1 μg/g of fw of grapes).

Conclusions. Some of the alternative gaseous treatments tested in this research work should be a commercial alternative to the use of SO_2 generators for maintaining the quality of cv. Napoleon grapes for up to 38 days at 0 °C followed by a shelf life of 6 days at 15 °C in air. An MAP of 5 kPa of O_2 + 15 kPa of CO_2 + 80 kPa of N_2 is the cheapest and easiest technique. This treatment maintained the quality at harvest, avoiding browning of rachis and controlling decay without significant differences, with the same treatment plus 0.7 g of $Na_2S_2O_5$/kg (currently used treatment in Spain). The next best treatments were those using CA and O_3, which also seem to be useful for maintaining the quality of table grapes in cold storage. The natural fungicides (hexanal and hexenal), in the doses applied in this experiment, were not effective enough for commercial purposes.

From the treatments that showed a good storage potential for keeping postharvest quality, clusters subjected to 8 ppm shocks of O_3 during cold storage maintained the total anthocyanin content after shelf life, whereas a decrease was found

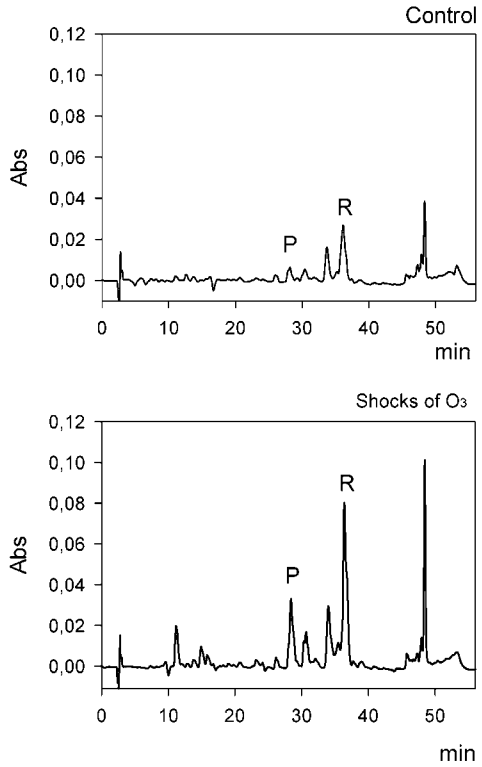

Figure 1. Control and 8 ppm of O_3 shock HPLC chromatograms (320 nm) of cv. Napoleon grape skin extracts stored for 38 days at 0 °C plus an additional 6 days of shelf life at 15 °C: (P) piceid; (R) resveratrol.

in grapes subjected to the remaining treatments. A similar trend was detected for the total flavonol content; CA (5 kPa of O_2 + 3 kPa of CO_2 + 92 kPa of N_2) and 8 ppm shocks of O_3 treatments maintained the amounts observed at harvest. An increase after shelf life was observed in total stilbenoid content for CA (5 kPa of O_2 + 15 kPa of CO_2 + 80 kPa of N_2) and 8 ppm shocks of O_3 treatments, mainly due to the important increases reached in the resveratrol content induced by these treatments. Piceid remained quite constant at all sampling times for almost every treatment except for 8 ppm shocks of O_3 treated grapes, for which a slight increase was detected.

The use of 8 ppm shocks of O_3 and CA (5 kPa of O_2 + 15 kPa of CO_2 + 80 kPa of N_2) during cold storage were the best treatments to enhance the total content of phenols for cv. Napoleon table grapes after both cold storage and shelf life periods.

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