Effect of Postharvest Ultraviolet Irradiation on Resveratrol and Other Phenolics of Cv. Napoleon Table Grapes

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In the skin of cv. Napoleon table grapes, the anthocyanins malvidin 3-glucoside (and its acetyl and *p*-coumaroyl derivatives), cyanidin 3-glucoside, peonidin 3-glucoside, cyanidin 3-glucoside, petunidin 3-glucoside, and delphinidin 3-glucoside were identified by HPLC-DAD-MS. In addition, quercetin 3-glucoside and 3-glucuronide, caffeoyltartaric, piceid, and resveratrol were also detected. The content of most phenolics remained quite constant during postharvest refrigerated storage (10 days at 0 °C) while the resveratrol derivatives increased 2-fold. Postharvest treatments of grapes with UVC and UVB light induced a large increase in resveratrol derivatives (3- and 2-fold, respectively). This means that a serving of mature Napoleon grapes (200 g) provides ∼1 mg of resveratrol, which is in the range of the amount supplied by a glass of red wine. This can be increased to 2 or 3 mg of resveratrol per serving in grapes that have been irradiated with UVB or UVC, respectively. These results show that refrigerated storage and UV irradiation of table grapes can be beneficial in terms of increasing the content of potentially health-promoting phenolics.

Keywords: *Table grapes; phenolics; UV irradiation; postharvest storage; resveratrol; stilbenoids; anthocyanins; flavonoids; postharvest storage*

INTRODUCTION

In the past few years, epidemiological, clinical, and in vitro studies have shown the role of wine, especially red wine, in preventing cardiovascular disease mortality (Cao et al., 1998; Frankel et al., 1993; Kinsella et al., 1993; Renaud and De Lorgeril, 1992). Antioxidant and anticarcinogenic phenolic compounds present in grapes and red wine seem to be responsible for these activities.

Irradiation of plant tissues with UV light has some important effects on phenolic metabolism. UVB light irradiation seems to be associated with an increase in the enzymes responsible of flavonoid biosynthesis, as these compounds can act as UV screens preventing the UV-induced damage in the genetic material of plant cells. UV light also produces an abiotic stress in plant tissues and affects plant phenolic metabolites in different ways. It can induce postharvest anthocyanin biosynthesis in apples (Dong et al., 1995) and cherries (Arakawa, 1993; Kataoka et al., 1996). UVB is associated with flavonoid biosynthesis in parsley (Eckeykaltenbach et al., 1993) and with the protection of UVB-induced damage in apple (Kootstra, 1994) and maize (Stapleton and Walbot, 1994). In addition, it has been demonstrated that *Arabidopsis mutans* lacking phenolic sunscreens exhibit an enhanced UVB-induced injury and oxidative damage (Landry et al., 1995; Lois and Buchanan, 1994).

Previous works have reported the induction of resveratrol and viniferins in grapevines by UV irradiation (Langcake and Pryce, 1977). Other works, however, have reported that UV irradiation of grape skins induces resveratrol degradation (Roggero and García-Parrilla, 1995).

The purpose of this work is evaluate the effect of postharvest UVB and UVC irradiation on the phenolic metabolism and phenolic composition of red grapes and the changes observed during refrigerated storage.

MATERIALS AND METHODS

Grapes and UV Irradiation Treatments. Red cv. Napoleon grapes were harvested in October 1999 in Blanca (Murcia, Spain) and transported to the laboratory, where they were treated the same day. Two groups of grapes were harvested depending on the pigmentation. One group comprised fully pigmented grapes (color values in the range $L^* = 26 \pm 1.5$; $a^* = 4 \pm 2.0$; $b^* = 0.5 \pm 1.0$) (mature grapes), and another group comprised grapes in which the pigmentation had not been fully developed yet (color values in the range $L^* = 30 \pm 2.5$; $a^* = 8.5 \pm 2.0$; $b^* = 1.5 \pm 1.0$) (immature grapes).

The grape berries were separated from the cluster with the help of a sharp knife by cutting the peduncle, which remained attached to the berry to avoid dehydration and decay susceptibility. Grapes were placed on plastic wells and irradiated with UV light for 30 min. UVB irradiation was performed with a UVB lamp VL-340-E (240 W) (Viber Lourmat, Marne le Valle, France) (peak output at 340 nm) equipped with three lamps of 80 W T-40 M. A similar treatment was performed for UVC irradiation, using three Sylvania germicidal lamps (G30T8) (peak output at 254 nm). Treatments of 30 min at room temperature (1780−2300 μW/cm^2) were achieved. The grapes were then stored at 0 °C for 10 days and then transferred to 15 °C for 5 days to simulate the commercialization period. Samples were stored in perforated plastic bags and at a relative humidity of 90−95% to avoid dehydration and grape decay.

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Color Measurement. A tristimulus color spectrophotometer Minolta CM-508i (Osaka, Japan), that has an 8 mm diameter measuring area and uses a diffuse illumination, 8° viewing angle geometry and observation beam width of 7.4° (geometry *d*/8 and also *d*/2 and *t*/0) was used to obtain the absorption spectra from each grape berry sample. Analyses were performed by reflectance, in which only the light reflected perpendicular to the surface was collected by the optical fiber cable for color analysis. *L**, *a**, and *b** values were calculated using illuminant D65 and a 10° observer according to the CIELAB 76 convention (McLaren, 1980). Data were recorded and processed on a Minolta Software ChromaControl S, PC-based colorimetric data system. Three different zones of each grape were measured to obtain a representative overall color of the individual fruits. The mean values of each batch (control and UVC- and UVB-irradiated grapes) were compared.

Extraction of Phenolic Compounds. Control (nonirradiated) and UVC- and UVB-treated samples (three replicates of four grapes) were taken at 0 days and after 5 and 10 days of storage at 0 °C and after 10 days storage at 0 °C plus 5 additional days at 15 °C (15 days in total). Grapes were peeled with the help of a sharp knife, and the peels were stored at −20 °C until analyzed. Peels were 13.1% (±1.5) of the total weight of the grapes. Samples (between 2 and 3 g) were homogenized in Ultraturrax T-25 equipment (Janke and Kunkel, Ika-Labortechnick) at 24000 rpm for 1 min after the addition of 3 mL g^{-1} of methanol of HPLC grade plus 3% formic acid. The extracts were centrifuged at 5000*g* for 5 min in a Centromix centrifuge (Selecta, Barcelona, Spain), filtered through 0.45 μm, and HPLC analyzed.

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^{-1}. Elution was performed with a gradient starting with 2% B to reach 32% B at 30 min, 40% B at 40 min, and 95% B at 50 min and then became isocratic for 5 min (conditions used for the chromatograms in Figures 1 and 6). Chromatograms were recorded at 510, 320, and 290 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 C. García-Viguera), and quercetin 3-glucoside, previously isolated from *Vitis* leaves (marker supplied by Dr. F. Ferreres, Murcia, Spain). Anthocyanins were quantified at 510 nm as cyanidin 3-glucoside previously isolated and identified from pigmented lettuce (Ferreres et al., 1998), flavonols at 320 nm as quercetin 3-rutinoside (Merck), stilbenoids at 320 nm as resveratrol (Sigma), and the hydroxycinnamic acid derivatives at 320 nm as chlorogenic acid (Sigma).

Enzyme Hydrolysis. The methanol extracts (1 mL) were taken to dryness under reduced pressure (40 °C) and dissolved in 1 mL of 0.1 N acetate buffer, pH 5.5. β-D-Glucosidase (Sigma) (5 mg) was added to the extract dissolved in buffer and left for 4 h at 37 °C. After this time, the extract was filtered through 0.45 μm and HPLC analyzed.

HPLC-MS. The HPLC-MS analyses were carried out using HPLC Hewlett-Packard 1100 equipment, provided with a quaternary pump and a photodiode array detector (DAD) (Hewlett-Packard, Waldbronn, Germany). The column was a Spherisorb S3 ODS2 (4.6 × 150 mm), 3 μm (Waters, Wexford, Ireland), and solvents were (A) acetic acid 2.5%, (B) acetic acid 2.5%/acetonitrile (90:10), and (C) acetonitrile. A gradient was established from 0 to 100% B in A for 5 min, from 0 to 15% C in B for 25 min, from 15 to 50% C in B for 5 min, and 50% C isocratically for 5 min, at a flow rate of 0.5 mL/min. The injection volume was 100 μL. A first detection was made using the photodiode detector selecting 280 nm as a preferred wavelength, followed by a second detection in the mass spectrometer (MS).

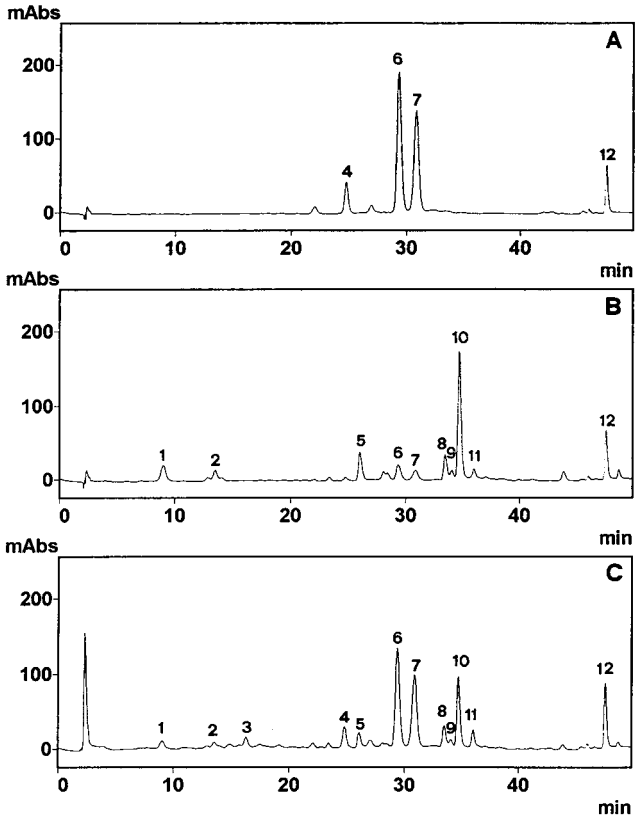

Figure 1. HPLC chromatograms of skin extracts of mature grapes: (A) 510 nm; (B) 320 nm; (C) 290 nm. Peaks: (1) caffeic acid derivative; (2) caffeoyltartaric; (3) procyanidin B1; (4) cyanidin 3-glucoside; (5) *trans*-piceid; (6) peonidin 3-glucoside; (7) malvidin 3-glucoside; (8) quercetin 3-glucuronide; (9) quercetin 3-glucoside; (10) *trans*-resveratrol; (11) *cis*-resveratrol; (12) malvidin 3-acetylglucoside + malvidin 3-*p*-coumaroylglucoside.

Mass spectrometry was performed using a Finnigan LCQ (Finnigan Corp., San Jose, CA) equipped with an API source, using a chemical ionization (APCI) interface; data treatment was carried out with Navigator 1.1 (Finnigan Corp.). The HPLC system was connected to the probe of the mass spectrometer via the UV cell outlet, using PEEK tubing. Both the auxiliary and the sheath gas were a mixture of nitrogen and helium. APCI conditions were optimized using a malvidin 3-glucoside standard. The capillary temperature was 150 °C and the vaporizer temperature 450 °C, using a capillary voltage of 4 V. The MS was programmed to do a series of three scans: a full mass, a zoom scan of the most abundant ion in the first scan, and an MS-MS of the most abundant ion using a collision energy of 20.

RESULTS

HPLC-DAD-MS Analysis of Cv. Napoleon Grape Phenolics. The methanol extracts of Napoleon grape skins were analyzed by HPLC, and the characteristic chromatograms are shown in Figure 1. The chromatogram at 510 nm shows that this grape cultivar has four main anthocyanins and two minor compounds. The major compounds were identified as peonidin 3-glucoside (**6**), malvidin 3-glucoside (**7**), and cyanidin 3-glucoside (**4**). In addition, another anthocyanin peak with a larger retention time was detected (**12**), showing a UV−vis spectrum characteristic of an anthocyanin acylated with a hydroxycinnamic acid (maximum at ∼315 nm). In addition, traces of delphinidin 3-glucoside

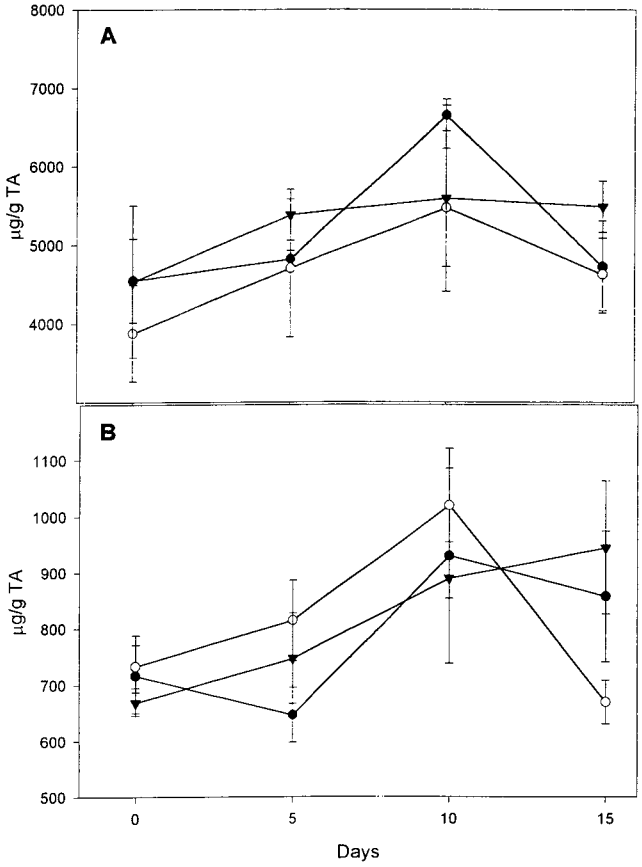

Figure 2. Changes in total anthocyanins (TA) of mature (A) and immature (B) grape skins during refrigerated storage and effect of UV irradiation: (●) control; (○) UVC irradiated; (▼) UVB irradiated.

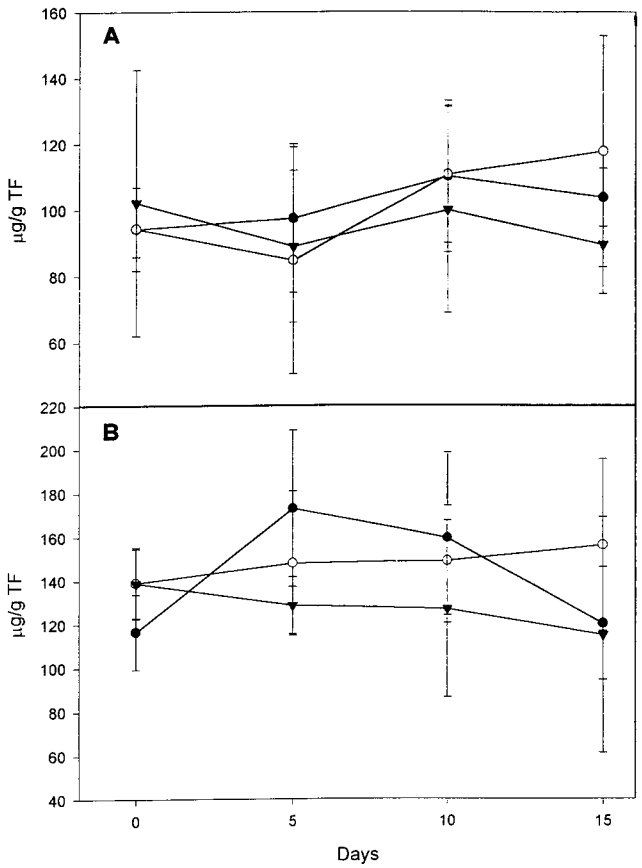

Figure 3. Changes in total flavonols (TF) of mature (A) and immature (B) grape skins during refrigerated storage and effect of UV irradiation: (●) control; (○) UVC irradiated; (▼) UVB irradiated.

Table 1. HPLC-DAD-MS Analysis of Napoleon Grape Skin Phenolics

compd no.	structure	molecular ion *m/z*	fragment *m/z*
2	caffeoyl tartaric	333	182
3	procyanidin B1	579	289
4	cyanidin 3-glucoside	449	287
5	*trans*-resveratrol-*β*-D-glucoside (*trans*-piceid)	391	228
6	peonidin-3-glucoside	479	303
7	malvidin-3-glucoside	493	331
8	quercetin-3-glucuronide	479	303
9	quercetin-3-glucoside	465	303
10	*trans*-resveratrol	229	
11	*cis*-resveratrol	229	
12	malvidin-3-acetylglucoside	535	331
12	malvidin-3-*p*-coumaroylglucoside	639	331

and petunidin 3-glucoside were also detected. The HPLC-MS analysis confirmed the identity of cyanidin 3-glucoside, peonidin 3-glucoside, and malvidin 3-glucoside (Table 1). In addition, this analysis showed that under the peak of the acylated anthocyanin, a mixture of malvidin 3-acetyl-glucoside and malvidin 3-*p*-coumaroylglucoside was also present. The minor compound (the acetyl derivative) was much better ionized than the major *p*-coumaroyl derivative and gave a better MS spectrum.

In addition, two caffeic acid derivatives were detected (**1** and **2**) by their characteristic UV spectrum, and the HPLC-MS analysis showed that compound **2** was caffeoyltartaric acid ($M = 332$) (Table 1). The ionization of compound **1** was very poor and prevented its identification. Two flavonols were also detected (compounds **8** and **9**), showing identical UV spectra. Compound **8** was identified as quercetin 3-glucuronide and compound **9** as quercetin 3-glucoside by chromatographic comparisons with authentic markers and by their MS spectra (Table 1).

In grape skins the stilbenoids of *trans*-resveratrol (**10**), *cis*-resveratrol (**11**), and *trans*-resveratrol *β*-D-glucoside (piceid) (**5**) were identified (Figure 1). The occurrence of *cis* and *trans*-resveratrol was demonstrated by their UV spectra (Roggero and García-Parrilla, 1995), their HPLC-MS spectra (Table 1), and chromatographic comparisons with an authentic marker. Another compound with the same UV spectrum as *trans*-resveratrol and a shorter retention time was identified as *trans*-resveratrol *β*-D-glucoside, as it showed an HPLC-MS spectrum corresponding to a resveratrol hexoside and, after hydrolysis with *β*-D-glucosidase, *trans*-resveratrol was obtained.

In addition, the HPLC-MS analysis detected the presence of traces of catechin, procyanidin B1, and gallocatechin derivatives, which were not quantified due to the small amount detected.

Effect of Irradiation on Color and Anthocyanin Content. Changes in L^*, a^*, and b^* values of the surface of immature and mature grapes were measured immediately after harvest and during the storage period. Some slight changes were observed in the mature grape color, although they were not significant. The values remained even more constant in the immature grapes.

Grape pigmentation is associated with the anthocyanin content, and by this reason the individual antho-

Table 2. Effect of UV Treatments on the Content of Individual Anthocyanins in Napoleon Grape Skins[a]

anthocyanin	days: initial	5 days at 0 °C	10 days at 0 °C	10 days at 0 °C + 5 days at 15 °C
Mature Grapes				
control				
delphinidin 3-glucoside	96 (15)	97 (11)	115 (55)	87 (25)
cyanidin 3-glucoside	284 (63)	252 (5)	434 (71)	239 (39)
petunidin 3-glucoside	116 (15)	114 (8)	143 (44)	97 (38)
peonidin 3-glucoside	1836 (615)	1993 (63)	2997 (361)	2168 (291)
malvidin 3-glucoside	1710 (18)	2006 (148)	2149 (504)	1888 (568)
malvidin 3-glucoside acylated	413 (70)	359 (11)	459 (50)	364 (22)
UVB treatment				
delphinidin 3-glucoside	70 (39)	91 (7)	106 (30)	112 (23)
cyanidin 3-glucoside	137 (48)	263 (26)	209 (53)	321 (46)
petunidin 3-glucoside	76 (44)	103 (8)	104 (47)	119 (27)
peonidin 3-glucoside	2113 (465)	2460 (278)	2868 (573)	2588 (286)
malvidin 3-glucoside	1405 (262)	2170 (250)	2067 (482)	2171 (286)
malvidin 3-glucoside acylated	293 (136)	449 (58)	418 (37)	492 (30)
UVC treatment				
delphinidin 3-glucoside	66 (16)	78 (24)	126 (38)	102 (26)
cyanidin 3-glucoside	242 (71)	241 (49)	349 (88)	320 (56)
petunidin 3-glucoside	82 (16)	109 (54)	113 (13)	105 (23)
peonidin 3-glucoside	1710 (267)	1930 (414)	2456 (497)	2054 (312)
malvidin 3-glucoside	1441 (208)	1689 (350)	2038 (171)	1630 (77)
malvidin 3-glucoside acylated	336 (43)	414 (72)	419 (25)	415 (7)
Immature Grapes				
control				
peonidin 3-glucoside	356 (65)	387 (33)	490 (123)	492 (19)
malvidin 3-glucoside	216 (44)	191 (26)	327 (69)	273 (86)
malvidin 3-glucoside acylated	78 (15)	67 (11)	112 (22)	92 (21)
UVB treatment				
peonidin 3-glucoside	394 (119)	495 (132)	509 (72)	611 (112)
malvidin 3-glucoside	199 (53)	256 (44)	288 (29)	307 (58)
malvidin 3-glucoside acylated	75 (21)	83 (11)	90 (13)	198 (21)
UVC treatment				
peonidin 3-glucoside	425 (41)	421 (76)	551 (34)	465 (157)
malvidin 3-glucoside	226 (4)	295 (15)	342 (53)	270 (99)
malvidin 3-glucoside acylated	82 (5)	99 (5)	110 (9)	85 (25)

[a] Values are expressed as mg/kg of fresh weight of grape skins. Standard deviation in parentheses ($n = 3$).

cyanins were also analyzed by HPLC to confirm that the UV treatments had no effect on grape color and pigmentation. The anthocyanins are present only in the skin of this cultivar; they are not detected in the flesh. When the grape skin anthocyanins were analyzed by HPLC, a remarkable difference was observed between mature and immature grapes. The mature grape skins had anthocyanins in the range of 4000−4500 mg/kg of fresh weight (fw) of skin, whereas the immature peels had values <1000 mg/kg. A slight increase was observed in mature grapes during the storage at 0 °C for 10 days (from 4500 to 6000 mg/kg of peel fresh weight). The anthocyanin content, however, decreased to initial levels after the 5 additional days of storage at 15 °C (to simulate commercialization) (Figure 2A). Similar results were observed in the case of immature grapes, although in this case the changes were less marked (Figure 2B). The observed changes did not correlate with any change in the objective physical color (L^*, a^*, b^* values) (data not shown). When the individual anthocyanins were evaluated (Table 2), a similar behavior was observed for the different anthocyanin glycosides, with some differences in the case of the acylated derivatives that remained more stable during the commercialization period. The anthocyanins delphinidin 3-glucoside, cyanidin 3-glucoside, and petunidin 3-glucoside were detected in quite small amounts in the immature grapes, which prevented their quantification in the samples.

As a general rule the UVC-treated grapes had a more reduced anthocyanin content than the control grapes, but these differences were statistically nonsignificant (Table 2). These results show that UVB or UVC irradiation of grapes has no effect on either anthocyanins or color of grapes.

Effect of Irradiation on Flavonols and Hydroxycinnamic Acid Derivatives. As in the case of the anthocyanins, flavonols were present only in the peel. Immature grapes had higher flavonol content (130 mg/kg of fw of skins) than the corresponding mature grapes (95 mg/kg), following a pattern opposite to what was found for the anthocyanins. Quercetin 3-glucuronide (**8**) and 3-glucoside (**9**) were detected in the grape skins. Myricetin and kaempferol derivatives, which had previously been described in other grape cultivars, were not detected in this case. Two hydroxycinnamic acid derivatives were also detected in small amounts (**1** and **2**). The structure of **1** was not established, but its UV spectrum recorded by HPLC-DAD showed that it was a caffeic acid derivative. Compound **2** was identified as caffeoyl tartaric.

The flavonol content of grape skins remained quite constant during the storage period of mature and immature grapes at both temperatures (Figure 3). UV irradiation did not induce any significant change in the content of these compounds in the grape skins (Figure 3). Similar results were observed for the hydroxycinnamic acid derivatives (data not shown).

Effect of UV Irradiation on Stilbenoids (Resveratrol and Piceid). The skin of mature grapes also contained piceid (10 mg/kg of fw). This resveratrol glucoside increased 2-fold during refrigerated storage and the following commercialization period (Figure 4).

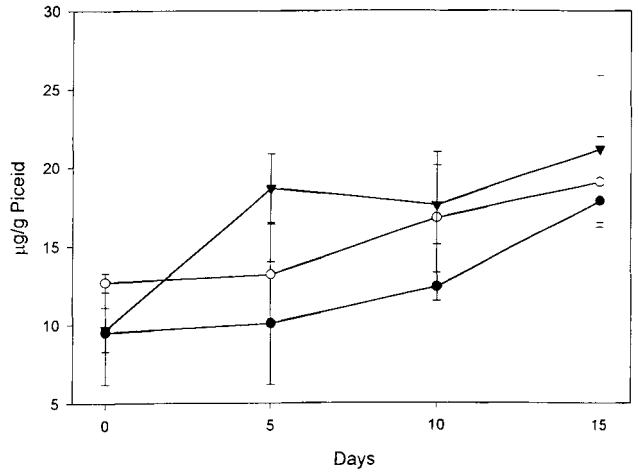

Figure 4. Changes in piceid (*trans*-resveratrol glucoside) content of mature grape skins during storage and effect of UV irradation: (●) control; (○) UVC irradiated; (▼) UVB irradiated.

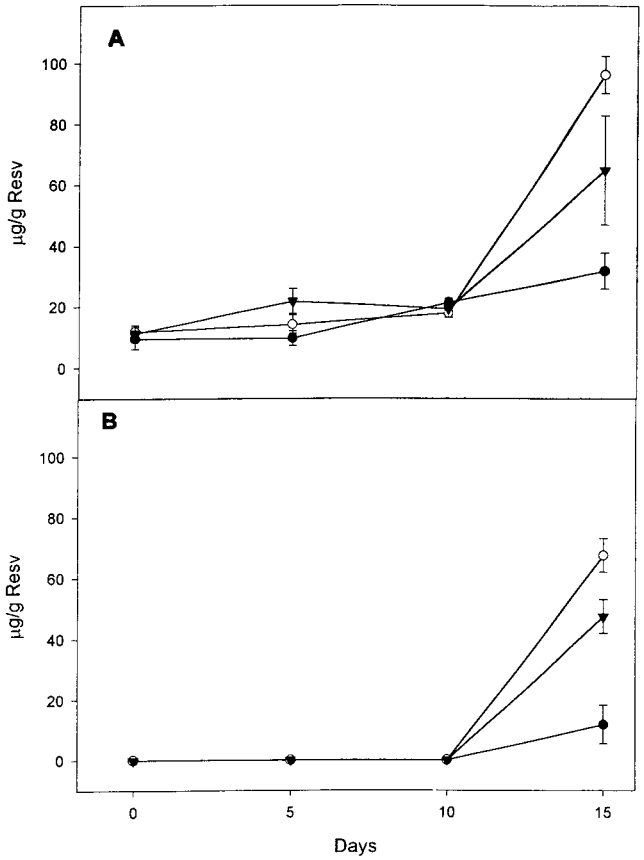

Figure 5. Changes in *trans*-resveratrol content of mature (A) and immature (B) grape skins during refrigerated storage and effect of UV irradiation: (●) control; (○) UVC irradiated; (▼) UVB irradiated.

In this case the UVB irradiation induced a faster biosynthesis of this compound during the first 5 days of refrigerated storage, but the differences of UV-treated grapes with the control were not significant after the commercialization period (Figure 4).

The skin of mature grapes contained ~10 mg/kg of fw of *trans*-resveratrol, whereas this compound was not detected in the immature grape skins. Nevertheless, the irradiation treatments increased the *trans*-resveratrol content of mature and inmature grapes (Figure 5). In previous studies on UV irradiation of grape skins, it was

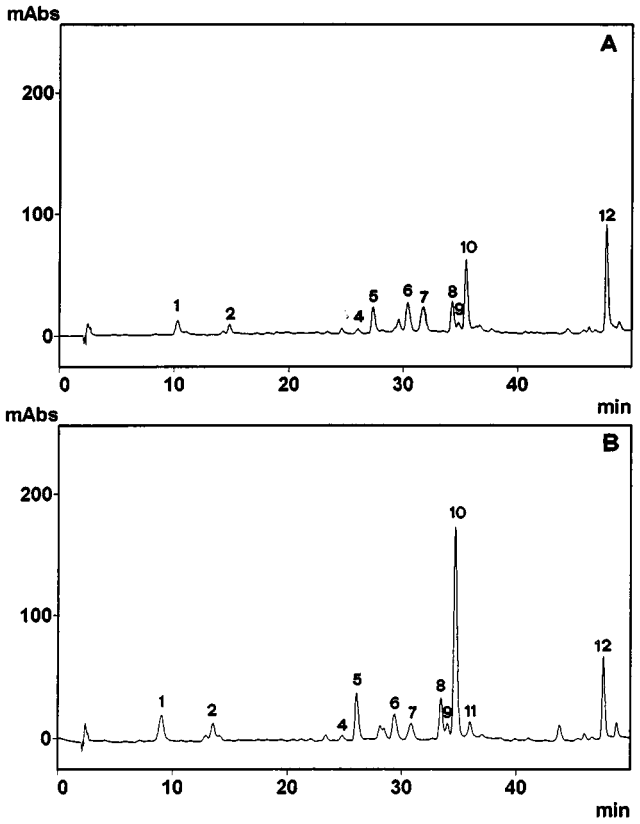

Figure 6. HPLC chromatograms of skin extracts of mature grapes stored for 10 days at 0 °C and for an additional 5 days at 15 °C: (A) control grapes; (B) UVC irradiated grapes. Peaks: (1) caffeic acid derivative; (2) caffeoyltartaric; (3) procyanidin B1; (4) cyanidin 3-glucoside; (5) *trans*-piceid; (6) peonidin 3-glucoside; (7) malvidin 3-glucoside; (8) quercetin 3-glucuronide; (9) quercetin 3-glucoside; (10) *trans*-resveratrol; (11) *cis*-resveratrol; (12) malvidin 3-acetylglucoside + malvidin 3-*p*-coumaroylglucoside.

reported that the irradiation destroyed resveratrol (Roggero and García-Parrilla, 1995). The irradiation conditions used in the present work (10 times less than the dose applied in the previous work) induced an increase in resveratrol content during the refrigerated storage.

The content of *trans*-resveratrol increased during refrigerated storage (0 °C for 10 days) to reach ~20 mg/kg of fw without significant differences between the control and UV-treated grapes. This increase was more marked when grapes were transferred to 15 °C to simulate the commercialization period (5 days), at the end of which the skins of control grapes contained close to 30 mg/kg (Figure 5A). During the storage at 15 °C significant differences were observed between the control grapes and those irradiated. UVC irradiation produced higher increases in resveratrol (close to 100 mg/kg) than UVB irradiation (65 mg/kg) (Figure 5A), and both treatments induced higher levels of this compound than the control grapes. In Figure 6, the HPLC chromatograms of skin extracts from mature control grapes and UVC-treated grapes after the 15 °C storage period are shown. The chromatograms clearly show that *trans*-resveratrol and *cis*-resveratrol are the main peaks affected by UV irradiation, whereas no significant differences were found in the other phenolic constituents.

In immature grapes, no increase in resveratrol was observed during the storage at 0 °C, but after the

Table 3. Effect of UV Irradiation on the Phenolic Compound Content of Harvested Mature and Immature Grapes[a]

	days			
phenolic compound	initial	5 days at 0 °C	10 days at 0 °C	10 days at 0 °C + 5 days at 15 °C
		Mature Grapes		
control				
stilbenes	2.4 (0.4)	2.6 (0.8)	4.4 (0.3)	6.4 (0.8)
flavonols	21.6 (16.3)	12.7 (3.2)	19.6 (9.3)	13.5 (1.5)
anthocyanins	591.2 (69.4)	626.8 (13.7)	864.4 (26.6)	614.0 (76.2)
hydroxycinnamics	3.8 (0.7)	1.8 (0.4)	3.0 (0.5)	2.9 (1.0)
UVB treatment				
stilbenes	2.7 (0.4)	5.2 (0.8)	4.8 (0.7)	11.2 (2.9)
flavonols	14.1 (8.0)	11.6 (3.1)	13.0 (4.0)	11.7 (4.1)
anthocyanins	589.4 (125.3)	700.0 (42.2)	726.7 (154.1)	713.6 (15.0)
hydroxycinnamics	4.3 (0.4)	5.9 (1.6)	4.0 (0.4)	5.3 (0.7)
UVC treatment				
stilbenes	3.2 (0.4)	3.5 (0.8)	4.5 (0.7)	15.0 (1.2)
flavonols	11.1 (3.1)	11.0 (4.5)	14.4 (3.2)	15.3 (4.6)
anthocyanins	504.0 (79.4)	611.5 (113.9)	726.6 (154.1)	601.4 (60.0)
hydroxycinnamics	4.6 (0.9)	4.4 (0.7)	4.6 (0.6)	4.2 (0.3)
		Immature Grapes		
control				
stilbenes				1.5 (0.8)
flavonols	23.9 (10.1)	21.3 (5.7)	20.7 (5.3)	14.3 (2.8)
anthocyanins	93.2 (9.2)	84.0 (6.3)	120.8 (24.8)	111.4 (15.1)
hydroxycinnamics	5.2 (0.8)	4.3 (0.6)	5.7 (1.1)	6.3 (1.9)
UVB treatment				
stilbenes				6.1 (0.7)
flavonols	22.8 (7.0)	21.3 (9.3)	16.5 (5.3)	13.6 (6.7)
anthocyanins	87.0 (2.4)	97.1 (10.4)	115.6 (4.7)	133.3 (24.7)
hydroxycinnamics	6.2 (0.8)	6.3 (0.2)	5.9 (0.3)	7.2 (3.8)
UVC treatment				
stilbenes				8.8 (0.7)
flavonols	17.0 (3.4)	19.2 (4.3)	19.4 (3.3)	20.3 (5.2)
anthocyanins	95.3 (5.0)	105.6 (9.3)	132.5 (8.6)	87.0 (5.1)
hydroxycinnamics	5.0 (0.9)	7.3 (0.9)	5.9 (0.6)	5.7 (0.9)

[a] Values are mg/kg of fresh weight of grapes. Standard deviations in parentheses.

transfer to 15 °C, a slight increase was observed in the skin of control grapes (<10 mg/kg), whereas the UV treatments induced higher levels of these compounds (Figure 5B). In this case, as observed for mature grapes, UVC irradiation induced higher resveratrol levels (65 mg/kg) than UVB irradiation (45 mg/kg).

cis-Resveratrol was also detected in trace amounts in mature grapes. This compound increased slightly during storage. This increment was more marked on those grapes irradiated with UVC than on the ones treated with UVB light (data not shown). As this compound was present only as traces, its quantification was not possible.

DISCUSSION

The biological activity of resveratrol as an anticarcinogenic and an antioxidant has been reported (Jang et al., 1997; Soleas et al., 1997). There have been a number of works dealing with the identification and quantification of resveratrol in wines from different origins, due to its potential health-promoting properties. Previous works reported that the content of resveratrol in red Californian wines was <1 mg/L (Lamuela-Raventós and Waterhouse, 1993), whereas the mean content of Spanish red wines was 5.6 mg/L (Lamuela-Raventós et al., 1995). Similar results (1−5 mg/L) were found in other red wines (McMurtrey et al., 1994); the resveratrol contents of rosé (2 mg/L) (Romero-Pérez et al., 1996a) and white (0.1−2 mg/L) wines (Romero-Pérez et al., 1996b) were smaller.

From the nutritional point of view this means that a glass of red wine (200 mL) supplies ∼1 mg of resveratrol and white wines supply only 0.2 mg.

To evaluate the amount of resveratrol contained in one serving of cv. Napoleon mature grapes, the values obtained for grape skins were converted into milligrams per kilogram of fresh weight of grapes in Table 3. Freshly harvested mature grapes provide 2.4 mg/kg of stilbenoids (resveratrol plus piceid), whereas this content can increase 2-fold after refrigerated storage at 0 °C and 3-fold after the 15 °C storage period. This means that a serving of mature grapes (200 g) provides ∼1 mg of stilbenoids, a value that is in the range of the amount supplied by a glass of red wine. The amount can be increased 2- or 3-fold in the case of grapes that have been irradiated with UVB or UVC, respectively. Thus, mature Napoleon grapes that had been irradiated with UVC light can provide up to 3 mg of resveratrol per serving.

In immature grapes, the values are divided by 2, with respect to the mature grapes (Table 3).

Table grapes also provide significant amounts of other natural antioxidants such as anthocyanins (120 mg per serving), quercetin derivatives (2 mg per serving), and caffeic acid derivatives (1 mg per serving) in the case of mature grapes (Table 3).

These results show that refrigerated storage and UV irradiation of grapes can be beneficial in terms of increasing the content of potentially health-promoting phenolics.

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