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Antioxidant activity and phenolic content of 16 raisin grape (*Vitis vinifera* L.) cultivars and selections

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ABSTRACT

Six raisin grape cultivars and 10 new raisin grape selections were analyzed for antioxidant activity (ABTS assay) and for total and individual phenolic compounds. Samples were freeze–dried and values are reported on a dry weight basis. Antioxidant activity across the 16 samples ranged from 7.7 to 60.9 μmol Trolox/g DW, with A95-27 exhibiting the greatest activity. Total phenolic content, determined in gallic acid equivalents using the Folin–Ciocalteau assay, ranged from 316.3 to 1141.3 mg gallic acid/100 g DW and was strongly correlated ($r = 0.990$) with antioxidant results. Concentrations of individual phenolics were determined by HPLC. *trans*-Caftaric acid was the predominant compound in all samples. A95-15 contained the lowest concentration (153.5 μg/g DW) of caftaric acid, while Fiesta contained the highest concentration (598.7 μg/g DW). Selections A56-66, A95-15, and A95-27 had much higher levels of catechin (86.5–209.1 μg/g DW) and epicatechin (126.5–365.7 μg/g DW) than the other samples.

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1. Introduction

Raisins are an important agricultural product with 317,515 tons produced in the US in 2007/08 (USDA, 2008). About 95% of California raisins are produced from Thompson Seedless grapes, followed by Fiesta (3%) and Black Corinth grapes (1.5%) (Christensen, 2000). Recently introduced cultivars are being planted with 2225 and 713 acres of Selma Pete and DOVine, respectively (USDA, 2009). With the development of new cultivars, comes the chance to improve health benefits and at the same time other characteristics can be improved. Karadeniz and co-workers (2000) showed that Golden Thompson Seedless raisins (treated with sulphur dioxide) had significantly higher amounts of *trans*-caftaric and *trans*-coutaric acids than dipped in hot water or sun-dried Thompson Seedless raisins. Sulphur dioxide treatment resulted in less enzymatic and nonenzymatic browning reactions and therefore, Golden Thompson Seedless raisins had higher concentrations of phenolics. Flavonol glycosides were not as sensitive as hydroxycinnamates to enzymatic oxidation whereas procyanidins and flavan-3-ols were completely degraded during raisin formation (Karadeniz et al., 2000). Similarly, Yeung and co-workers (2003) have shown that Golden Thompson Seedless raisins have significantly higher antioxidant activity as well as higher total phenolics content than dipped and sun-dried Thompson Seedless raisins, which suggests that enzymatic activity reduced phenolic content and antioxidant activity. While sulphur dioxide may have desirable effects on preserving phenolic content and antioxidant activity it might be preferable to find alternatives since some individuals are sensitive to its effects (Simon, 1992; WHO, International Programme on Chemical Safety, 1999). The development of new raisin grape cultivars having high concentrations of phenolics and low polyphenoloxidase activity would be valuable to growers and consumers, since they could maintain their desirable nutritional properties without any chemical treatments.

Grapes and wine have been shown to be good sources of phenolic antioxidants (Teissedre, Frankel, Waterhouse, Peleg, & German, 1996). The phenolic composition of grapes has been studied by many researchers (Fernández de Simón, Hernández, & Estrella, 1993; Hollecker et al., 2009; Kammerer, Claus, Carle, & Schieber, 2004; Mozetič, Tomažič, Škvarč, & Trebše, 2006; Nicoletti, Bello, De Rossi, & Corradini, 2008; Pastrana-Bonilla, Akoh, Sellappan, & Krewer, 2003; Vrhovšek, 1998).

The objectives of this study were to determine the antioxidant activity and total and individual phenolic composition of different raisin grape cultivars and selections. Polyphenoloxidase activity will be reported in a separate paper.

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2. Materials and methods

2.1. Materials

Solvents, HPLC grade acetonitrile and methanol, formic acid (88%, ACS reagent grade) and HCl (conc) were purchased from Fisher Scientific Ltd. (Fair Lawn, NJ). Folin–Ciocalteu's phenol reagent (2 N), gallic acid, 2,6-di-*tert*-butyl-4-methylphenol (BHT), cinnamic acid, ascorbic acid, 2,2′-azinobis(3-ethyl-benzothiazoline-6-sulphonic acid) diammonium salt (ABTS), potassium persulfate, and 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox) were obtained from Sigma–Aldrich (St. Louis, MO). Water was deionized to ⩾18.1 MΩ/cm resistance, using a Barnstead NANOpure Deionization System (Dubuque, IA) and filtered through a 0.45 μm type HA membrane filter (Millipore, Billerica, MA) before use. Ethanol (190 proof, USP grade) was purchased from Pharmco-AAPER (Shelbyville, KY). Standards used for HPLC including gallic acid, (±)-catechin hydrate, (−)-epicatechin, resveratrol, quercetin 3-β-D-glucoside, and rutin hydrate were obtained from Sigma–Aldrich (St. Louis, MO), caftaric acid was obtained from ChromaDex (Irvine, CA), and kaempferol 3-*O*-glucoside from Indofine Chemical Company (Hillsborough, NJ). The fresh fruit for this study was harvested from the raisin cultivars and selections August 18–20, 2008, except for Thompson Seedless which was harvested September 11, 2008. Sugar levels ranged from 20.7° to 30.4° Brix at harvest. The plants were grown at the USDA/ARS research site, 9611 S. Riverbend Avenue, Parlier, CA 93648 (longitude 36°35′46″ N Latitude 119°30′46″ W). The plants were head trained and cane pruned on a double "T" trellis (72″ tall, 36″ top cross arm, 24″ bottom cross arm). Irrigation was supplied by drip irrigation at 80% of the required evapotranspiration (ET) rate. Thompson Seedless grapes used for method development were purchased from local grocery stores.

2.2. Sample preparation and extraction

Upon harvest, fruits were removed from the stem and immediately frozen at −80 °C. Frozen whole grapes were transferred to an Osterizer Classic mixer (now Jarden Consumer Solutions, Boca Raton, FL) and homogenised in the presence of dry ice. The resulting powder was freeze–dried and stored protected from light under vacuum.

A sample (250 ± 5 mg) of the ground powder was transferred to a glass screw cap vial and the powder suspended in 0.01% HCl in 8:2 MeOH/EtOH (v/v; 3 ml, Kammerer et al., 2004). The suspension was vortexed for 5 min (speed setting #5) on a VWR multi-tube vortexer (West Chester, PA). After clarification of the suspension by centrifugation (3.3 min at 2800 rpm, Fisher Scientific Marathon 8 K Centrifuge (Waltham, MA)), the supernatant was collected and the pellet extracted two more times following the same protocol. The combined supernatant was transferred to a 10 ml volumetric flask and made up to volume with 0.01% HCl in 8:2 MeOH/EtOH (v/v). Extractions were conducted in triplicate.

In preparation for analysis, extracts were clarified by centrifugation (10,000 rpm, 10 min, 4 °C) using a Sorvall RC-5C Plus centrifuge (Newtown, CT) and subsequently filtered through a Millipore 13 mm (0.45 μm) Millex®-HV syringe filter (Bedford, MA). Before HPLC analysis, an aliquot (5 ml) of each extract was transferred to a conical vial and concentrated to dryness with nitrogen at 50 °C using a Pierce Reacti-Therm heating module (Rockford, IL). The dried extract was reconstituted with 8:2 MeOH/water (v/v) in a 1 ml volumetric flask just before analysis.

2.3. ABTS radical cation decolorization assay

Antioxidant capacity as assessed by the ABTS radical cation ($ABTS^{\cdot+}$) decolorization assay was accomplished in a microtiter-format based on the method of Breksa and Manners (2006). Briefly, $ABTS^{\cdot+}$ was generated by reacting 7 mM ABTS with 2.45 mM potassium persulfate for 16 h in the dark at room temperature. An $ABTS^{\cdot+}$ working solution was prepared immediately before use by diluting the stock solution with MeOH to an absorbance of 0.70 ± 0.01 at 734 nm. Because of path length differences between the glass 96-well plate and standard cuvette, the absorbance value of the working solution was verified directly in the microtiter plate (420 μl). Positive (125 μg/ml BHT, 50 μg/ml ascorbic acid) and negative (1.0 mg/ml cinnamic acid) controls and Trolox standards (12.5–125.0 μg/ml) were prepared in MeOH. Using a Zinsser glass 96-well plate (Frankfurt, Germany) samples, positive and negative controls and standards (20 μl) were combined in triplicate with the $ABTS^{\cdot+}$ working solution (400 μl, absorbance 0.70 ± 0.01). After a brief incubation (6 min, 30 °C), the absorbance at 734 nm was read on a Molecular Devices Spectromax 384-Plus plate reader. To compensate for minor differences in incubation time resulting from using a 96-well plate, a Trolox standard (50.0 μg/ml) was included in each row of samples and its absorbance value used to normalise the absorbance values of the samples. Samples with absorbance values greater than the standards were diluted and re-evaluated. Trolox equivalents were calculated using the calibration curve generated from the standard curve.

2.4. Determination of total soluble phenolics (TSP)

The Folin–Ciocalteau method (Singleton & Rossi, 1965) for the colourimetric estimation of total polyphenols was adapted following the suggestions of Sellappan, Akoh, and Krewer (2002) and Waterhouse (2009). Standards (100 μl) were mixed with water (1500 μl) in a 2 ml polypropylene plate. Trolox (250 μg/ml) and BHT (125 μg/ml) were used as positive controls and cinnamic acid (1.0 mg/ml) was used as a negative control. Samples were mixed with water using four dilutions: 20:1580, 100:1500, 150:1450, and 200:1400 (sample:H_2O). Controls were diluted with water in the same way as samples. All dilutions were mixed with Folin–Ciocalteu's phenol reagent (1 N, 100 μl). After a brief incubation at room temperature (5 min) saturated sodium carbonate (300 μl, 75 g/l) was added. Solutions were mixed and incubation continued at room temperature. After 2 h, 300 μl were transferred to a well of a 96-well plate and the absorbance measured at 765 nm with a Molecular Devices Spectromax 384-Plus plate reader (Sunnyvale, CA). Quantification was based on the standard curve generated with 50, 100, 200, 300, 400 and 500 mg/l of gallic acid. Samples with absorbance values greater than the 500 mg/l standard were diluted and reanalyzed. Values were reported as mg gallic acid equivalents (GAE) per 100 g dry weight (DW) ± SD and represent the average of three independent analyses.

2.5. HPLC analysis

A Waters HPLC System equipped with a Model 2695 Separations Module coupled to a Waters Model 996 diode array detector (190–500 nm) (Milford, MA) was used. Instrument control and data acquisition were accomplished using Masslynx (Version 4.0). Analyses were conducted at 30 °C using a 250 × 4.6 mm i.d. Synergi Hydro-RP (Phenomenex, Torrance, CA) column (4 μm particle size) equipped with a guard column of the same stationary phase. For the mobile phase a binary gradient made up of (A) water and (B) acetonitrile, both containing 5% (v/v) formic acid (88%) was used with a flow rate of 1 ml/min. The gradient programme was based upon the method of Nicoletti et al. (2008) with some modifications and was as follows: a 3 min isocratic elution step with 5.0% B, followed by 12 min linear gradient from 5.0% to 9.0% B, 7 min linear gradient to 13.5% B, 20 min linear gradient to 18.5% B, 6 min isocratic elution with 18.5% B, 3 min linear gradient to

Table 1
List of standards, retention times and detection parameters.

	Compound	Retention time (min)	Detection (λ)	LOD (mg/l)	LOQ (mg/l)	Range of standards (mg/l)	Equation of the line	R^2
1	Gallic acid	4.54	280	0.05	0.10	25–0.05	$y = 238.46x + 9.0009$	0.9999
2	Caftaric caid	11.40	320	0.20	0.50	100–0.20	$y = 91.362x + 19.932$	0.9998
3	Catechin	14.05	280	0.20	0.50	100–0.20	$y = 173.86x + 50.334$	0.9998
4	Epicatechin	21.88	280	0.20	1.00	100–0.20	$y = 59.161x + 11.231$	0.9999
5	Rutin	34.96	370	0.05	0.10	25–0.05	$y = 427.85x - 2.1903$	1.0000
6	Quercetin 3-*O*-glucoside	36.43	370	0.10	1.25	25–0.05	$y = 126.47x + 5.323$	0.9999
7	Kaempferol 3-*O*-glucoside	44.02	370	0.05	1.25	25–0.05	$y = 115.62x - 17.542$	1.0000
8	*trans*-Resveratrol	50.72	306	0.05	0.25	25–0.05	$y = 2545.9x + 153.89$	0.9998

Table 2
Total soluble phenolic (TSP) content and antioxidant (AO) capacity determined by FC and ABTS assays. TSP AO (mg gallic acid/100 g DW[a]) (μmol Trolox/g DW[a]).

	TSP (mg gallic acid/100 g DW[a])	AO (μmol Trolox/g DW[a])
Controls		
Trolox[b]	33525 ± 2409	–
BHT[b]	51682 ± 5832	1.6 ± 0.5
Ascorbic acid[b]	–	7.4 ± 2.1
Varieties		
Diamond Muscat	387.7 ± 6.5	7.7 ± 0.9
DOVine	375.8 ± 8.1	8.9 ± 0.6
Fiesta	442.4 ± 13.9	15.1 ± 0.4
Selma Pete	423.8 ± 19.0	13.1 ± 1.1
Summer Muscat	393.2 ± 6.7	10.7 ± 0.4
A50-33	435.1 ± 50.9	15.1 ± 1.3
A50-39	316.3 ± 11.4	8.3 ± 0.8
A56-66	507.6 ± 28.3	29.4 ± 3.1
A95-15	594.2 ± 25.6	34.1 ± 0.6
A95-27	1141.3 ± 141.0	60.9 ± 1.3
B53-122	370.7 ± 2.9	8.5 ± 0.6
B58-41	413.3 ± 8.7	14.3 ± 1.0
B64-108	401.7 ± 28.3	11.9 ± 1.2
C65-81	419.9 ± 9.2	9.9 ± 0.7
C90-100	364.6 ± 21.1	10.8 ± 1.3
Thompson Seedless	357.7 ± 5.5	9.3 ± 0.4

[a] Samples were analyzed as described in the experimental section and reported as average ($n = 3$) ± SD. Since controls were analyzed with each set of samples, their reported values represent the average ± SD across all experiments.
[b] Trolox (0.250 mg/ml), BHT (0.125 mg/ml) and ascorbic acid (0.05 mg/ml).

22.5% B, 4 min isocratic elution with 22.5% B, 1 min linear gradient to 30.0% B, 1 min linear gradient to 40.0% B. At the end of the linear program, the eluent composition was brought to the initial condition in 1 min and the column was equilibrated for 15 min before the next injection. The injection volume was 5 μl.

Stock solutions of each standard compound were prepared by dissolving weighed amounts of each standard in 80% (v/v) methanol–water and diluted with the same to obtain six working solutions of each compound covering the concentration ranges listed in Table 1. Concentrations of individual compounds found in each sample were determined using the calibration curves generated from standards. Values were reported as μg/g dry weight (DW) ± SD and represent the average of three independent analyses.

3. Results and discussion

Consumers once made their decisions to purchase fresh and processed agricultural products largely upon the factors of taste, cost, and availability. However, the growing number of papers that demonstrate the influence of diet upon human health and nutrition have resulted in more and more consumers basing their purchase decisions upon a food's nutritive value and health-promoting potential. Grapes and grape-derived products have received considerable attention in this arena because of their phenolic content and associated antioxidant capacity. Protected from damage, grapes will maintain their phenolics; however, processing grapes into raisins may result in loss of phenolic and antioxidant

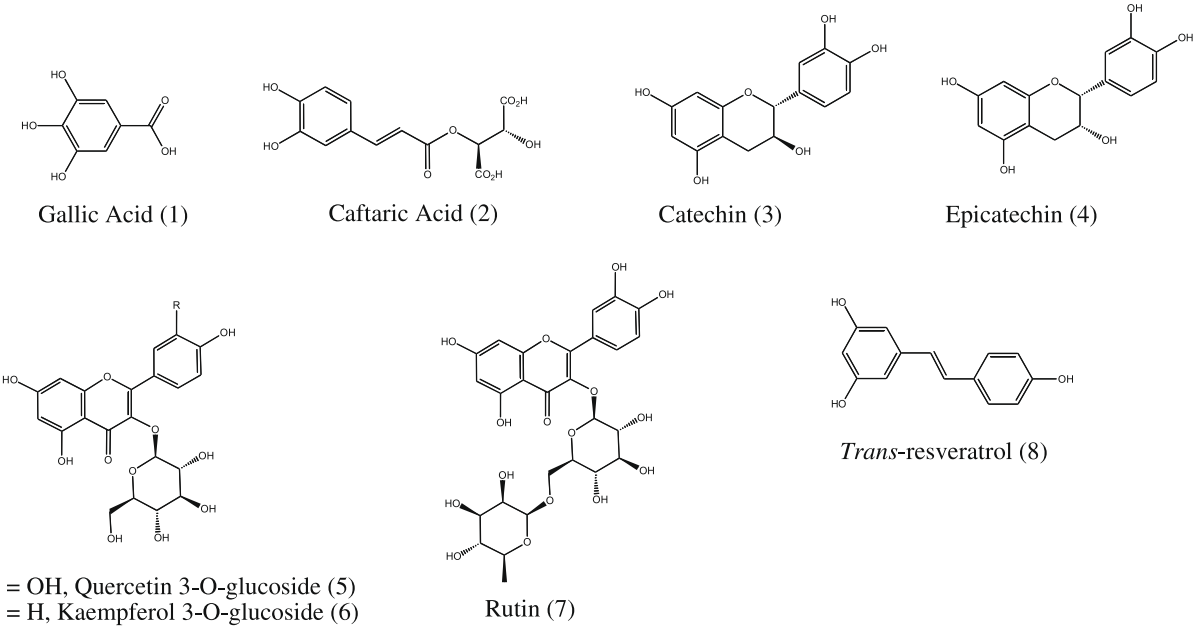

Fig. 1. Chemical structures of phenolics.

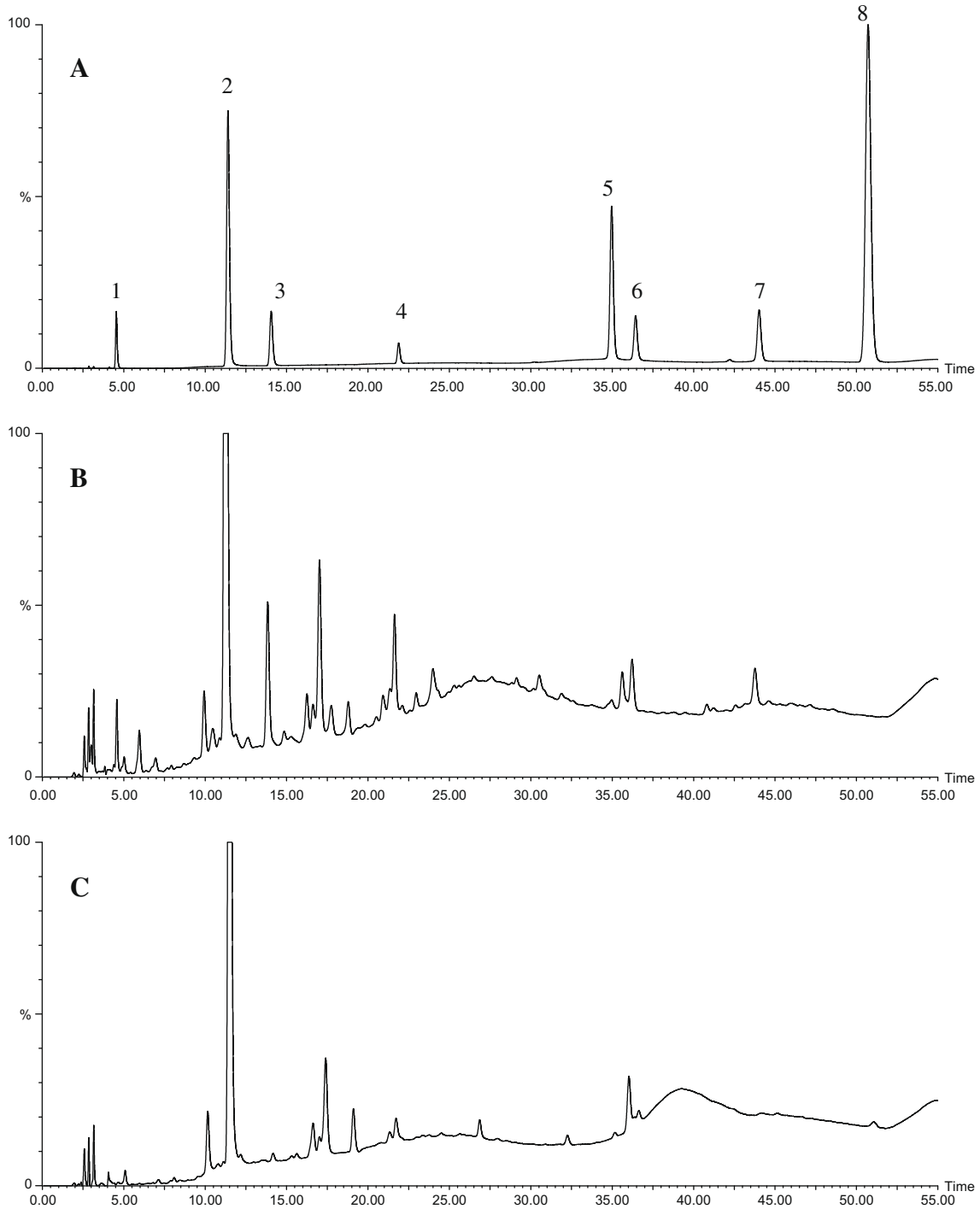

Fig. 2. HPLC–PDA (λ = 270–380 nm) chromatograms obtained for standards (A) and two different grape samples – (B) A-95-27, (C) Fiesta. Chromatograms B and C have been expanded to the same scale on the vertical axis to exemplify differences.

content resulting from enzymatic and air oxidation that occurs during drying. This problem could be partially circumvented by utilising varieties with increased phenolic concentrations to produce raisins. The purpose of this study was to evaluate six raisin grape cultivars and 10 new raisin grape selections for their antioxidant activity (ABTS assay) and total and individual phenolic compounds in order to identify varieties having increased phenolic concentrations.

Studies began with evaluating extraction conditions utilising Thompson Seedless grapes because they are the predominate variety used in raisin production. For these experiments, extraction efficiency was evaluated using the ABTS antioxidant assay. Through a series of experiments examining the influence of sample mass (25, 100, 250 and 500 mg) and the number of serial extractions needed to maximise extraction we decided upon a sample mass of 250 mg and a 3×3 ml extraction strategy that yielded 89% of the total extractable material. Inter-day variability tested, using two different batches of Thompson Seedless grapes, was found to be less than 2%.

Having established an extraction method, the antioxidant capacity of 16 cultivars and selections of white grapes, including Thompson Seedless, was investigated. Antioxidant activity ranged

Table 3
Content of phenolic compounds (μg/g DW ± SD) in berries of raisin grape cultivars and selections.

Sample	Gallic acid	Caftaric acid	Catechin	Epicatechin	Rutin	Quercetin 3-*O*-glucoside	Kaempferol 3-*O*-glucoside	*trans*-Resveratrol
Diamond Muscat	nd	202.7 ± 18.5	12.2 ± 1.7	nd	1.3 ± 0.5	13.8 ± 1.8	8.0[a] ± 2.1	nd
DOVine	nd	272.8 ± 8.8	1.8[a] ± 0.5	nd	3.7 ± 0.5	67.0 ± 7.6	10.3 ± 0.1	nd
Fiesta	nd	598.7 ± 73.8	12.2 ± 4.7	4.5[a] ± 1.2	1.6 ± 0.8	7.4[a] ± 3.9	nd	nd
Selma Pete	nd	305.8 ± 12.4	4.3 ± 0.5	nd	0.8 ± 0.1	19.7 ± 0.9	nd	nd
Summer Muscat	nd	339.1 ± 17.9	14.1 ± 1.0	1.1[a] ± 0.5	3.7 ± 0.9	14.3 ± 0.8	nd	nd
A50-33	nd	192.2 ± 8.9	19.9 ± 2.9	8.2 ± 0.9	4.5 ± 0.5	41.2 ± 2.8	10.6 ± 2.3	nd
A50-39	nd	180.1 ± 22.7	19.2 ± 1.5	14.9 ± 0.4	2.7 ± 0.5	62.2 ± 2.7	5.6[a] ± 0.8	nd
A56-66	nd	261.7 ± 9.0	86.5 ± 5.4	175.5 ± 11.0	1.6 ± 0.8	25.8 ± 5.4	7.7[a] ± 1.7	nd
A95-15	6.9 ± 1.2	153.5 ± 11.4	132.0 ± 20.3	126.5 ± 14.7	3.2 ± 0.1	30.5 ± 2.6	8.7[a] ± 0.8	nd
A95-27	24.5 ± 1.6	590.4 ± 30.1	209.1 ± 24.1	365.7 ± 28.1	0.8 ± 0.1	22.1 ± 0.5	14.1 ± 1.2	nd
B53-122	nd	417.8 ± 42.3	3.2[a] ± 0.8	nd	1.3 ± 0.5	19.1 ± 0.8	nd	0.8[a] ± 0.1
B58-41	nd	204.4 ± 2.7	8.2 ± 0.5	15.7 ± 2.3	3.2 ± 0.1	69.3 ± 5.0	10.4 ± 0.8	nd
B64-108	nd	374.2 ± 16.1	9.8 ± 0.5	1.6[a] ± 1.4	1.6 ± 0.1	8.0[a] ± 0.1	nd	nd
C65-81	nd	244.1 ± 52.9	8.2 ± 2.0	nd	0.8 ± 0.1	21.5 ± 0.9	2.1[a] ± 0.5	nd
C90-100	nd	204.5 ± 22.0	12.7 ± 0.1	66.4 ± 1.5	nd	37.5 ± 0.8	nd	nd
Thompson Seedless	nd	183.0 ± 6.3	9.0 ± 0.9	6.4[a] ± 0.1	nd	8.8 ± 0.8	nd	nd

nd, not detectable.
[a] Estimated, raw absorbance values <LOQ.

from 7.7 (Diamond Muscat) to 60.9 (A95-27) μmol Trolox/g DW (Table 2) with an average of 16.8 μmol Trolox/g DW. All grapes tested in this study possessed antioxidant capacities similar to those of wine grapes tested by Hogan, Zhang, Li, Zoecklein, and Zhou (2009); Cabernet Franc clone1, Norton and Cabernet Franc clone 313 (8.8, 7.9 and 5.4 μmol Trolox/g, respectively). Samples having the highest antioxidant activity were A95-27 followed by A95-15 (34.1 μmol Trolox/g DW) and A56-66 (29.4 μmol Trolox/g DW). The values for these samples were generally at least twice those of Fiesta (15.1 μmol Trolox/g DW) and Thompson Seedless (9.3 μmol Trolox/g DW), cultivars currently used for raisin production. A95-27 also exhibited an antioxidant activity twice the value reported for raisins (30.4 μmol Trolox /g) by Wu et al. (2004).

Using the modified Folin–Ciocalteau method described in the previous section the total soluble phenolic content of each sample was estimated in mg GAE/100 g DW (Table 2). Concentrations in commercial cultivars tested in this study ranged from 357.7 to 442.4 mg GAE/100 g, with Thompson Seedless grapes having the lowest concentration. Among the new selections, concentrations ranged from 316.3 (A50-39) to 1141.3 (A95-27) mg GAE/100 g and only one sample (A50-39) had a concentration lower than Thompson Seedless. The calculated average of all samples was 459.3 ± 192.2 mg GAE/100 g. Results from total soluble phenolic content determinations directly correlated ($r = 0.990$) with antioxidant results. Omission of the three highest values reduced the correlation ($r = 0.783$), but still yielded a value indicating a strong relationship between antioxidant capacity and phenol content and was within ranges reported by others (Orak, 2007, $r = 0.756$; Borbolán, Zorro, Guillén, & Barroso, 2003, $r = 0.886$).

Compared to the phenolic concentrations reported for other grapes, values found in the samples tested were greater than those measured in currants (151–246 mg GAE/100 g DW, Chiou et al., 2007) and were comparable to concentrations found in the skins of bronze Muscandine grapes (303.0–545.6 mg GAE/100 g FW; Pastrana-Bonilla et al., 2003). The concentration found in A95-27 represents up to a 3.2-fold increase over existing commercial cultivars used for raisin production and establishes it as a candidate for the production of raisins with increased levels of phenolics.

Although grapes targeted in our investigation were white grape cultivars, we observed a 3.6-fold difference between the lowest and highest concentrations. Our observation is similar to the 3.7-fold difference in phenolic concentrations in red grapes reported by Orak (2007). These observations together with recent micro-array results (Gatto et al., 2008) strongly support the conclusion that genetic factors (other than skin colour) and stress levels are key influencers of a cultivar's phenolic content.

For HPLC, a C18 stationary phase with hydrophilic endcapping was employed, which had been previously shown to be effective for the separation of grape phenolics (Kammerer et al., 2004). Structures of phenolic compounds quantified in this study are shown in Fig. 1. The separation of grape phenolics is displayed in Fig. 2. The top of Fig. 2 shows the separation of grape standards; the middle and bottom chromatograms shows samples A95-27 and Fiesta, respectively. Constituents were identified by their UV spectra and by comparing their retention times with reference standards. Contents of phenolics in various raisin grape cultivars and selections are listed in Table 2. *trans*-Caftaric acid was the predominant phenolic compound in all samples. A95-15 contained the lowest concentration (153.5 μg/g DW) of caftaric acid while Fiesta contained the highest concentration (598.7 μg/g DW). Singleton and co-workers (1986) examined 20 commercially important white cultivars of *Vitis vinifera* and reported that *trans*-caftaric acid concentrations in the berries ranged from 16 (Calmeria) to 295 mg/l (Palomino), with a mean of 127 mg/l. Vrhovšek (1998) studied berries of six white grape cultivars and found the following caftaric acid concentrations: 177 mg/l (Savignon Blanc), 202.9 mg/l and 341.0 mg/l (two samples of Pinot Blanc, 207.0 mg/l (Chardonnay), 257.7 mg/l (Gruner Veltliner), 270.2 mg/l (Riesling italico (Welschriesling)), and 369.5 mg/l (Riesling). Sun-dried, dipped, and golden raisins produced from Thompson Seedless grapes contained 39.6, 45.2, and 84.3 mg/kg, respectively, of *trans*-caftaric acid (Karadeniz et al., 2000). Compared with fresh Thompson Seedless grapes, a 90% loss of caftaric acid in the three types of raisins (Karadeniz et al., 2000) was found. Considerable variation in the concentration of individual phenolics in the samples was observed (Table 3). Selections A56-66, A95-15, and A95-27 had much higher levels of catechin (86.5–209.1 μg/g DW) and epicatechin (126.5–365.7 μg/g DW) than other grapes. Experimental data suggest that catechins might prevent chronic diseases in humans. Catechin and epicatechin have been shown to be powerful inhibitors of *in vitro* human LDL oxidation (Teissedre et al., 1996). Arts and co-workers (2001a) reported a strong inverse association between intake of (+)-catechin and (−)-epicatechin and death resulting from coronary heart disease. Another study concluded that catechins, whether from tea or other sources, might reduce the risk of ischaemic heart disease mortality (Arts, Hollman, Feskens, Bueno de Mesquita, & Kromhout, 2001b). Gallic acid was only detected in two selections, A95-15 and A95-27. The levels of rutin in all samples were low, ranging from not detectable to 4.5 μg/g DW. B58-41, DOVine, and A50-39 contained the highest amounts of quercetin 3-*O*-glucoside (69.3, 67.0 and 62.2 μg/g DW, respectively). Highest levels of kaempferol 3-*O*-glucoside were found in

A95-27, A50-33, B58-41 and DOVine (14.1, 10.6, 10.4 and 10.3 μg/g DW, respectively), while it was not detected in seven of the samples investigated. *trans*-Resveratrol was only detected in B53-122. Karadeniz and co-workers (2000) did not detect this compound in Thompson Seedless raisins or grapes.

4. Conclusion

Ten new raisin grape selections and six raisin grape cultivars were studied for their antioxidant activity and total and individual phenolic content. One of the new selections, A95-27 (1141.3 ± 141.0 mg gallic acid/100 g DW) had a concentration of total phenolics more than three times higher than Thompson Seedless grapes (357.7 ± 5.5 mg gallic acid/100 g DW), the most widely used grape variety in raisin production. It is noteworthy that three of the selections, A56-66, A95-15 and A95-27 (29.4 ± 3.1, 34.1 ± 0.6 and 60.9 ± 1.3 μmol Trolox/g DW, respectively), had antioxidant activities more than three times higher than Thompson Seedless grapes (9.3 ± 0.4 μmol Trolox/g DW). The same samples, A56-66, A95-15 and A95-27, had from 9 to 23 times more catechin (86.5 ± 5.4, 132.0 ± 20.3 and 209.1 ± 24.1 μg/g DW, respectively, vs. 9.0 ± 0.9 μg/g DW) and from 19 to 57 times more epicatechin (175.5 ± 11.0, 126.5 ± 14.7 and 365.7 ± 28.1 μg/g DW, respectively, vs. 6.4 ± 0.1 μg/g DW) than Thompson Seedless grapes. Due to their higher antioxidant activities and higher concentrations of catechin and epicatechin compared to Thompson Seedless grapes, selections A56-66, A95-15 and A95-27 have the potential to be new commercial raisin grapes with improved nutritional properties.

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