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Antioxidant capacity and stilbene contents of wines produced in the Snake River Valley of Idaho

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Abstract

Forty-two wines produced from grapes grown in Idaho were examined in this study. The samples examined were from four monovarietal wines (12 Cabernet Sauvignon, 9 Merlot, 7 Riesling, 14 Chardonnay). Wine samples represented twelve wineries that obtain their fruit from vineyards located within Idaho's Snake River Valley. Titratable acidity, pH, specific gravity, colour measurements (lightness, chroma, and hue), % haze, total anthocyanins, total phenolics, total tannins, antioxidant capacity, and individual stilbene measurements were performed. The antioxidant capacities (ORAC values) of Idaho wines ranged from 3.1 (Merlot wine) to 87.0 (Cabernet Sauvignon wine) μmol of Trolox/ml (mean = 38.5 μmol of Trolox/ml). Mean ORAC values of Merlot wines (mean = 27.6 μmol of Trolox/ml) were lower than the other three styles (mean for Cabernet Sauvignon wines = 41.0 μmol of Trolox/ml, mean for Chardonnay wines = 42.8 μmol of Trolox/ml, and mean for Riesling wines = 39.4 μmol of Trolox/ml). Free stilbene levels (four different stilbenes) were examined by direct-HPLC/DAD/ESI-MS/MS method. Piceid and resveratrol (both *trans*- and *cis*-) were found in the samples. Stilbene levels ranged from 0.97 (Riesling wine) to 12.88 (Cabernet Sauvignon wine) mg (expressed as *trans*-resveratrol)/l. This is the first paper to report the current chemical composition of Idaho wines.
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Keywords: *Vitis vinefera*; Wine; ORAC; Stilbene; Resveratrol; Piceid; Idaho; Quality

1. Introduction

Moderate consumption of red wine has been frequently found to be beneficial (Renaud et al., 2004; Wollin & Jones, 2001). Antioxidant activity and stilbene content of fruit and fruit products have received a great deal of attention and may aid in the prevention of some chronic diseases (Baht, Kosmeder, & Pezzuto, 2001; López-Vélez, Martinez-Martinez, & Del Valle-Ribes, 2003). Stilbenes (a phenolic phytoalexin) can be found in a wide variety of foods including grapes, peanuts, blueberries, cranberries, strawberries, red currants, cowberries, and hops. They can also be found in products made from those starting materials (Burns, Yokota, Ashirara, Lean, & Crozier, 2002; Callemien, Jerkovic, Rozenberg, & Collin, 2005; Ibern-Gomex, Roig-Perez, Lamuela-Raventos, & de la Torre-Boronat, 2000; Lyons et al., 2003; Sanders, McMichael, & Hendrix, 2000; Sobolev & Cole, 1999; Wang, Catana, Yang, Roderick, & van Breemen, 2002). Resveratrol (3,4′,5-trihydroxystilbene) and piceid (3,4′,5-trihydroxystilbene-3-β-D-glucoside) are two of many secondary metabolites produced by plants, and two of the many polyphenolics that may contribute to the potential health benefits of wine. Varying levels of stilbenes found in wine have been attributed to cultivar, rootstock, growing season conditions, cultural practices, environmental factors, vinification, and age of wine (Bavaresco, 2003; Burns et al., 2001; Goldberg & Ng, 1996; Moreno-Labanda et al., 2004; Siemann & Creasy, 1992; Stervbo, Vang, & Bonnesen, 2007). Cardioprotective, neuroprotective, and antileukemic effect of stilbenes have been demonstrated in

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rats and in humans (Gao et al., 2002; Hung, Chen, Huang, Lee, & Su, 2000; Urpi-Sarda et al., 2005; Virgili & Contestabile, 2000).

Although Idaho's wine industry is fairly new and growing, there are records of wine grapes planted in the region as far back as the late 1800's (Idaho Grape Growers and Wine Producers commission, personal communication). To date, there has been no published research on the chemical quality of wine grapes and wines commercially grown and produced in Idaho. This paper will help with establishing a baseline to better understand the quality of current and future Idaho grapes and wines. The climate of Idaho Snake River Valley has high temperatures during the growing season combined with low precipitation (annual rainfall of less than 25 cm) and low relative humidity. During the hottest month of the year (July) temperatures range from 18 to 36 °C and during the coldest month of the year (January) temperatures range from −7 to 4 °C, which is similar to the established wine grape growing region of Eastern Washington (US Army Corps of Engineers; National Climatic Data Center).

The objective of this study was to determine the basic chemical properties of four major monovarietal wines produced from grapes cultivated in the Snake River Valley of Idaho. Additionally, their antioxidant capacities (by oxygen radical absorbance capacity method) and free stilbene content (by direct injection and HPLC/DAD/ESI-MS/MS) were determined. This is the first paper to address the chemical composition of Idaho wines available in the marketplace.

2. Materials and methods

2.1. Wine samples

Forty-two commercially available (12 Cabernet Sauvignon, 9 Merlot, 7 Riesling, and 14 Chardonnay) Idaho grown and produced monovarietal wine samples (in 750 ml bottles) were obtained from three local markets in Boise, ID (in April 2005). Prices ranged from $5.99 to $25.00 a bottle. The average price of a bottle of Cabernet Sauvignon ($15.84) wine was the highest, while Riesling ($7.32) wine was the lowest. Wine samples represented 12 commercial wineries (coded A to L) and vintages were from 2000 to 2004 (Table 1). Wines were brought to the laboratory, aliquoted into vials, immediately flushed with nitrogen gas, and stored at −80 °C until analysis.

2.2. Reagents and standards

All chemicals and reagents used in this study were analytical and high performance liquid chromatography (HPLC) grade and were obtained from Sigma Chemical Co. (St. Louis, MO). Standards for *cis*-resveratrol were prepared by exposing *trans*-resveratrol (100 ppm dissolved in methanol) to a UV-C (254 nm) lamp for 2 h.

2.3. Titratable acidity (TA), pH, specific gravity, and color measurements

TAs were determined by titrating wine samples (10 ml) with a Brinkmann 716 DMX Titrino coupled with a model 730 Sample Changer Autotitrator (Brinkmann Instruments, Inc., Westbury, NY). Samples were titrated with standardized 0.1 N NaOH to an end point of pH 8.1. TA was expressed as tartaric acid equivalents (g tartaric acid/l of wine). The pH of the wines was determined with a Mettler-Toledo SevenMulti pH meter (Mettler-Toledo Inc., Columbus, OH) equipped with a Mettler-Toledo InLab 410 electrode. Specific gravity of the samples were determined using a Mettler-Toledo Densito 30P. Color measurements were made with a HunterLab CT1100 ColorQuest colorimeter (Hunter Associate Laboratories, Inc., Reston, VA). The colorimeter mode was as follows: total transmittance mode, Illuminant D65, and 10° observer angle. An optical 0.1 cm pathlength colorimeter cell for red wines and 1 cm pathlength colorimeter cell for white wines (Hellma, Borough Hall Station, NY) were used. Three color parameters were recorded: Hunter CIE lightness (L^*), chroma (saturation, C^*), hue angle (color itself, $h°$). Haze (%) was also measured with the colorimeter. All measurements were conducted in triplicates.

2.4. Total anthocyanins (ACY), total phenolics (TP), and total tannins (TT) determination

A Beckman DU520 UV–vis spectrophotometer (Beckman Coulter, Inc., Fullerton, CA) was used for all three measurements. Total anthocyanins (ACY) were determined using a modified pH differential method (Lee, Durst, & Wrolstad, 2005). The pH 1.0 buffer absorbance values were used to calculate total ACY. Absorbance was measured at 520 nm. The unit for ACY was mg of anthocyanins/100 ml of wine, and ACY was expressed as cyanidin 3-glucoside (molar extinction coefficient of 26,900 l cm^{-1} mol^{-1} and molecular weight of 449.2 g $mol^{-1}$was used). Only red wines ACY were measured. TP were measured by the Folin–Ciocalteu (FC) method (Waterhouse, 2002). Absorbances were measured at 765 nm. TP values were expressed as mg of catechin/100 ml of wine. The method described by Harbertson, Picciotto, and Adams (2003) was used to determine TT in samples and was expressed as mg of catechin/100 ml of wine. All measurements were conducted in two replications. Absorbance was measured at 510 nm. Details of these methods are in the references listed (Harbertson et al., 2003; Lee et al., 2005; Waterhouse, 2002).

2.5. Oxygen radical absorbance capacity (ORAC) assay

A SpectraMax M2 microplate reader (Molecular Devices Corp., Sunnyvale, CA) and black 96-well flat bottom plate were used for ORAC assay. Details of this method are described by Huang, Ou, Hampsch-Woodill, Flanagan,

Table 1
Chemical composition of 42 commercially available Idaho wines

Sample coding[a]	Style	Winery	Vintage	TA[b]	pH	Specific gravity[c]	Colour measurements[d]			Haze (%)	ACY[e]	TP[f]	TT[g]
							L^*	C^*	$h°$				
C1	Cabernet Sauvignon	A	2000	6.53	3.4	0.995	79.7	22.7	21.0	0.9	8.4	226	23.8
C2	Cabernet Sauvignon	A	2001	5.70	3.6	0.995	80.4	21.5	23.1	0.9	7.5	180	31.3
C3	Cabernet Sauvignon	B	2001	5.83	3.7	0.997	85.0	15.8	27.7	0.8	11.4	92.1	13.0
C4	Cabernet Sauvignon	B	2001	5.77	3.7	0.997	81.1	21.5	21.3	0.7	12.2	183	15.8
C5	Cabernet Sauvignon	D	2002	5.83	3.6	0.998	65.1	35.6	11.7	0.7	17.2	171	66.1
C6	Cabernet Sauvignon	E	2003	5.97	3.6	0.993	79.2	23.8	9.5	0.5	13.4	233	58.1
C7	Cabernet Sauvignon	F	2002	5.80	3.6	0.997	81.7	20.3	29.8	1.0	10.9	174	28.0
C8	Cabernet Sauvignon	I	2002	6.03	3.7	0.992	71.3	32.4	26.1	0.5	23.2	355	90.7
C9	Cabernet Sauvignon	J	2001	6.83	3.5	0.994	67.3	35.5	20.3	6.5	15.0	325	75.8
C10	Cabernet Sauvignon	K	2002	6.70	3.3	0.998	70.2	34.8	19.2	0.5	14.4	347	86.5
C11	Cabernet Sauvignon	K	2002	6.67	3.3	1.015	69.8	35.4	17.0	0.5	16.6	353	86.6
C12	Cabernet Sauvignon	I	2000	5.77	3.8	0.996	78.4	27.4	35.9	0.6	11.4	338	77.7
H1	Chardonnay	A	2001	4.40	3.7	0.993	100.0	8.7	99.3	1.2	–	87.9	0.04
H2	Chardonnay	A	2002	4.55	3.8	0.992	100.0	9.4	99.7	0.7	–	249	–
H3	Chardonnay	B	2000	4.10	3.8	0.993	100.0	10.0	99.3	1.3	–	92.7	–
H4	Chardonnay	D	2002	5.50	3.5	1.010	100.0	10.4	100.4	1.0	–	127	0.12
H5	Chardonnay	D	2002	5.30	3.5	0.995	100.0	10.5	101.2	1.0	-	90.8	0.16
H6	Chardonnay	F	2002	4.43	3.8	1.016	100.0	9.7	100.0	1.5	–	91.3	–
H7	Chardonnay	G	2002	5.67	3.3	0.993	100.0	6.1	103.6	2.3	–	89.5	–
H8	Chardonnay	G	2001	5.60	3.3	0.992	100.0	8.2	101.5	2.7	–	90.0	–
H9	Chardonnay	H	2002	4.90	3.7	0.999	100.0	7.8	102.3	0.9	–	91.3	–
H10	Chardonnay	I	2002	6.07	3.6	0.994	100.0	7.6	101.1	1.3	–	92.7	–
H11	Chardonnay	J	2002	5.60	3.4	1.000	100.0	9.9	100.0	4.0	–	85.5	–
H12	Chardonnay	K	2003	5.20	3.5	0.999	100.0	5.5	102.6	1.1	–	95.1	0.12
H13	Chardonnay	K	2002	6.03	3.5	0.999	100.0	7.1	100.1	1.0	–	94.8	0.12
H14	Chardonnay	L	2001	6.17	3.5	0.998	100.0	10.8	98.7	0.9	–	91.9	0.04
M1	Merlot	B	2001	4.97	3.8	0.998	87.5	15.8	27.7	0.5	16.5	242	32.7
M2	Merlot	D	2002	5.30	3.6	0.994	70.9	31.1	13.9	1.0	14.7	148	44.0
M3	Merlot	F	2002	5.73	3.5	0.994	78.3	24.9	19.4	1.3	9.8	167	17.6
M4	Merlot	G	2002	6.37	3.3	0.996	70.6	34.6	12.0	0.6	16.7	340	83.4
M5	Merlot	I	2002	5.40	3.7	1.000	75.4	28.9	28.1	1.0	19.4	345	82.1
M6	Merlot	J	2002	6.90	3.6	0.999	63.2	37.6	17.7	4.4	15.6	276	76.3
M7	Merlot	K	2003	6.87	3.3	0.995	79.1	26.4	15.4	0.5	13.7	298	80.9
M8	Merlot	K	2002	6.37	3.3	1.004	71.7	33.9	22.8	0.5	14.2	345	78.8
M9	Merlot	I	2000	6.67	3.5	0.996	78.8	26.7	31.0	0.6	8.9	301	74.9
R1	Riesling	B	2001	4.70	3.4	1.010	100.0	7.3	100.2	1.6	–	148	0.08
R2	Riesling	C	2002	5.60	3.1	1.010	100.0	5.3	102.2	0.7	–	89.5	0.08
R3	Riesling	E	2003	6.03	3.1	0.994	100.0	10.8	96.9	2.4	–	86.0	–
R4	Riesling	J	2004	6.57	3.1	0.994	100.0	5.2	103.0	1.6	–	86.3	–
R5	Riesling	K	2003	6.43	3.0	0.997	100.0	6.1	97.4	1.1	–	93.2	0.04
R6	Riesling	K	2003	6.40	3.0	0.995	100.0	6.5	99.1	0.9	–	89.5	0.08
R7	Riesling	K	2004	6.43	3.0	0.998	100.0	4.2	94.4	1.1	–	87.1	–
Mean	Cabernet Sauvignon	n.a.	n.a.	6.12	3.6	0.997	75.8	27.2	21.9	1.2	13.5	248	54.5
	Chardonnay	n.a.	n.a.	5.25	3.6	0.998	100.0	8.7	100.7	1.5	n.a.	105	0.10
	Merlot	n.a.	n.a.	6.06	3.5	0.998	75.0	28.9	20.9	1.2	14.4	274	63.4
	Riesling	n.a.	n.a.	6.02	3.1	1.000	100.0	6.5	99.0	1.3	n.a.	97.1	0.07

Two red (Cabernet Sauvignon and Merlot) wines and two white (Chardonnay and Riesling) wines were examined. –, ACY was not determined or TT content was present in less than 0.04 mg/100 ml of wine.

[a] C, Cabernet Sauvignon; H, Chardonnay; M, Merlot; and R, Riesling.

[b] TA was expressed as g of tartaric acid/l.

[c] There is no units for the specific gravity values.

[d] Colour measurements were conducted with illuminant D65, 10° observer angle, 0.1 cm pathlength cell for red wines, 1 cm pathlength cell for white wines.

[e] ACY were expressed as mg of cyanidin 3-glucoside/100 ml of wine (molar extinction coefficient of 26 900 l cm^{-1} mol^{-1} and molecular weight of 449.2 g mol^{-1} was used).

[f] TP were expressed as mg of catechin/100 ml of wine.

[g] The units for TT were expressed as mg of catechin/100 ml of wine.; n.a., not applicable.

and Prior (2002) and Dávalos, Gomez-Cordoves, and Bartolome (2004). Fluorescein (3′,6′-dihydroxy-spriro[isobenzofuran-1[3*H*], 9′[9*H*]-xanthen]-3-one) was used as the fluorescent probe. Fluorescein acted as target for the peroxyl radicals generated by AAPH (2,2′-azobis(2-amidinopropane)dihydrochloride, a peroxyl generator that destroys

the fluorescence). Fluorescence was measured every minute for 35 min, at 485 nm (excitation wavelength) and 530 nm (emission wavelength). ORAC was conducted in two replicates. ORAC values were expressed as μmol of Trolox (6-hydroxy-2,5,7,8-tetramethyl-2-carboxylic acid)/ml of wine.

2.6. HPLC/DAD/ESI-MS/MS analysis of stilbenes

A HP1100 system equipped with a diode array detector and XCT ion trap mass spectrometer (HPLC/DAD/ESI-MS/MS, Agilent Technologies Inc., Palo Alto, CA) was used to quantify and confirm the identification of the resveratrol and piceid (both *trans*- and *cis*-). A Synergi Hydro-RP 80 Å (150 × 2 mm, 4 μm) column, fitted with a 4.0 × 3.0 mm i.d. guard column (Phenomenex, Torrance, CA) was used. Absorbance spectra were collected for all peaks. The solvent flow rate was 0.2 ml/min and injection volume was 20 μl. Solvent A consisted of 2% acetic acid in water (v/v). Solvent B was 0.5% acetic acid in water and acetonitrile (50%:50% = v/v). The initial solvent composition was 90% solvent A (10% solvent B); then a linear gradient of 90–60% solvent A (10–40% solvent B) in 60 min; 60–1% solvent A (40–99% solvent B) in 10 min; then held for 6 min with detection at 310 nm. Column temperature was 25 °C. The ESI parameters were as follows: negative mode; nebulizer pressure, 30 psi; N_2 drying gas, 12 ml/min; drying gas temperature, 350 °C; trap drive, 52.5; skimmer, −40 V; octopole RF amplitude, 187.1 Vpp; capillary exit, −128.5 V. Scan range was m/z 50–1000. Trap ICC was 100 000 units and accumulation time was 200 ms. Fragmentation amplitude was 1.50 V and Threshold ABS was 10 000 units for the MS/MS condition. Stilbenes were quantified with the external standard *trans*-resveratrol. Quantifications were conducted with the results obtained from the LC/DAD. Peak assignments were made according to the UV–visible spectra, retention time, co-chromatography with authentic standards (when available), and mass spectra information (mass-to-charge ratio, m/z, of the molecular ion and fragmented ion). Samples were filtered through a 0.45 μm Millipore filter (Millipore Corp., Bedford, MA), placed in brown sample vials, flushed with nitrogen, and injected into the system immediately. Only free resveratrol and piceid isomers were identified and quantified. Samples were prepared carefully to avoid light induced isomerization of *trans*-resveratrol and *trans*-piceid to their *cis*-forms.

2.7. Statistical analysis

Statistica for Windows version 7.0 was used (StatSoft, Inc., Tulsa, OK). Cluster analysis was conducted on the values (excluding *cis*-resveratrol content) obtained using squared Euclidean distance and the Ward's method. From the dendogram (data not shown), the decision was made to use three clusters (= groups). Differences among group means were tested using Tukey Honest Significant Difference (HSD) at $\alpha = 0.05$ level.

3. Results and discussion

3.1. General composition (TA, pH, specific gravity, color measurements, % haze, ACY, TP, and TT) of Idaho wines

The chemical composition of all samples is summarized in Table 1. Sample TAs ranged from 4.10 to 6.90 g of tartaric acid/l. Average TAs for the white wines (average Chardonnay wine TA = 5.25 g of tartaric acid/l and average Riesling wines TA = 6.02 g of tartaric acid/l) were lower than the red wines (average TA of Cabernet Sauvignon wine = 6.12 g of tartaric acid/l and average TA of Merlot wine = 6.06 g of tartaric acid/l). The pH of the wines ranged from 3.0 to 3.8. Riesling wine (average pH 3.1), as a group, had lower pH than the other three wine styles. Specific gravity values ranged from 0.992 to 1.015.

Cabernet Sauvignon wine (C5) from winery D was the darkest (L^* value of 65.1), while winery B's wine (C3) was the lightest (L^* value of 85.0) in colour (Table 1). Merlot wine L^* values ranged from 63.2 to 87.5, varying greatly in L^* values. Chardonnay and Riesling wines L^* values were not distinguishable (all white wines L^* values were 100.0, the maximum value obtainable for lightness). A colorimeter cell with a pathlength greater than 1 cm should have been used for measurements of white wine lightness to detect a difference.

Chroma (saturation, C^*) of Cabernet Sauvignon and Merlot wines ranged from 15.8 to 35.6 and 15.8 to 37.6, respectively (Table 1). Merlot wine samples had a larger range of chroma (21.8) than Cabernet Sauvignon wines (19.8). Hue angle (color, h°) ranged from 9.5° to 35.9° and from 12.0° to 31.0° for Cabernet Sauvignon and Merlot wines, respectively. Cabernet Sauvignon wines (26.4°) had a wider range of colour (hue angle values) than Merlot (19.0°). Overall, Cabernet Sauvignon wines (mean hue angle value = 21.9°) were slightly more orange than Merlot wines (mean hue angle value = 20.9°). Merlot wine average chroma values (28.9) were slightly higher than those for Cabernet Sauvignon wine average chroma (27.2). Both red wines (C9 and M6) produced by winery J had high haze values (6.5% and 4.4% for Cabernet Sauvignon and Merlot wines, respectively), which were noted visually. White wine chroma ranged from 4.2 to 10.8, and hue angle ranged from 94.4° to 103.6°. Overall, Chardonnay (mean hue angle = 100.7°) and Riesling (mean hue angle = 99.0°) wines had similar colour, with the Chardonnay wines being more saturated (mean Riesling wines chroma values = 6.5 and mean Chardonnay wines chroma values = 8.7). Winery J's Chardonnay wine (H11) also had the highest amount of haze (4.0 %). Only winery J had wines (C9, H11, and M6) with a haze value greater than 3.0%.

Of the Cabernet Sauvignon wines, winery A's samples (C1 and C2) had the least ACY (7.5 and 8.4 mg/100 ml, Table 1). Winery B had the lowest Cabernet Sauvignon (C3) TP value (92.1 mg/100 ml), and winery B wines (C3 and C4) also had the two lowest Cabernet Sauvignon TT values (13.0 and 15.8 mg/100 ml, respectively). Merlot

wines had higher mean values of ACY (14.4 mg/100 ml), TP (274 mg/100 ml), and TT (63.4 mg/100 ml) than Cabernet Sauvignon wines (ACY = 13.5 mg/100 ml, TP = 248 mg/100 ml, and TT = 54.5 mg/100 ml). Of the Chardonnay wines, one had a uniquely high TP value (H2, TP = 249 mg/100 ml). As expected, all white wines had low TT content.

3.2. ORAC values of Idaho wines

ORAC values (Table 2) of all wine samples ranged from 3.1 to 87.0 μmol of Trolox/ml, which is similar to other reports that used the same method and using the same fluorescent probe (Dávalos et al., 2004). ORAC values for all wines varied considerably (6.0–87.0 μmol of Trolox/ml for Cabernet Sauvignon, 7.4–86.0 μmol of Trolox/ml for Chardonnay, 3.1–82.8 μmol of Trolox/ml for Merlot, and 10.0–77.0 μmol of Trolox/ml for Riesling). Merlot wine's average ORAC values were the lowest (27.6 μmol of Trolox/ml). Six of the nine Merlot wine samples had less than 20 μmol of Trolox/ml. The Chardonnay wine's average ORAC value was the greatest (42.8 μmol of Trolox/ml). Winery K had the highest ORAC values in three of the four varieties examined: Cabernet Sauvignon (C11, 87.0 μmol of Trolox/ml), Chardonnay (H12, 86.0 μmol of Trolox/ml), and Riesling (R7, 77.0 μmol of Trolox/ml). The highest ORAC value for a Merlot wine was M10 from winery I (82.8 μmol of Trolox/ml).

ORAC values measured by Dávalos et al. (2004) using the same analysis method and fluorescent probe in wines produced in Spain ranged from 3.2 to 63.8 μmol of Trolox/ml. Care should be taken when comparing reported ORAC values from the literature, since the fluorescein has proven a better choice for a fluorescent probe and it gives higher values than β-phycoerythrin, as it is more photostable and does not interact with the analyte (Dávalos et al., 2004; Huang et al., 2002; Ou, Hampsch-Woodill, & Prior, 2001).

3.3. Stilbene levels of Idaho wines

Fig. 1a has a typical chromatogram (sample C1 from winery A) obtained from the HPLC analysis monitored at 310 nm. Piceid isomers (peaks 1 and 2) were identified based on retention times, mass spectra of mother ions (*m*/*z* 389), and their fragments (*m*/*z* 227). Identification of *trans*- (peak 3) and *cis*-resveratrol (peak 4) in wine samples were determined by comparing retention times, mass spectra of mother ions (*m*/*z* 227), and their fragmented ions (*m*/*z* 185 and 159) of standards (purchased and synthesized). Fig. 1b–e shows the mass spectra of the mother and daughter ions of *trans*-piceid and *trans*-resveratrol. The isomers of *trans*-piceid and *trans*-resveratrol had the same mass spectra pattern, but a later retention time for their corresponding *cis*-isomer (Fig. 1a). *cis*-Resveratrol was found, but at levels not quantifiable by absorbance at 310 nm, and was masked by other compounds eluting at the same retention time (from UV–visible and mass spectra data). Presence of *cis*-resveratrol was determined by *m*/*z* 227 extracted ion chromatogram by MS.

Only free stilbene monomer content was examined in this study (Table 2). *trans*-Piceid levels present in Cabernet Sauvignon wines ranged from 1.03 to 6.48 mg/l. Both piceid isomers were not detected in three Cabernet Sauvignon wines (C3, C9, and C11) and two Merlot wines (M1 and M2). Merlot wines piceid (*trans*- and *cis*-) content ranged from 1.75 to 4.58 mg/l. In the red wines, only one Cabernet Sauvignon wine sample (C10) and one Merlot sample (M6) had no detectable level of *trans*-resveratrol. All other Cabernet Sauvignon wines ($n = 8$), with the exception of C12, had more *cis*-piceid than its isomer. The opposite of this trend was observed with Merlot wine samples. Besides M3 and M7 all other Merlot wines ($n = 5$) had more *trans*-piceid than *cis*-piceid. There were no *trans*-piceid, *cis*-piceid, and *trans*-resveratrol detected in any Chardonnay wine samples, with the exception of wines from wineries A (H1and H2) and D (H5). Three Riesling wines (R2, R4, and R6) had *trans*-piceid present, and *trans*-resveratrol was found in three other Riesling wines (R1–R3). *cis*-Resveratrol was not detected in any Chardonnay and Riesling wine samples. Thirteen out of the 42 samples had trace levels of *cis*-resveratrol.

Stilbene levels found in Idaho wines (0.97 to 12.9 mg/l; R6 and C12, respectively) were within the range of concentrations reported by other researchers (total stilbenes ranging from 0.05 to 30.9 mg/l), using direct injection and by HPLC analysis (Abril, Negueruela, Perez, Juan, & Estopanan, 2005; Careri, Corradini, Elviri, Nicoletti, & Zagnoni, 2003; Clare, Skurray, & Shalliker, 2004; Gerogiannaki-Christopoulou, Athanasopoulos, Kyriakidis, Gerogiannaki, & Spanos, 2006; Lamuela-Ramentós, Romero-Perez, Waterhouse, & de la Torre-Boronat, 1995; Moreno-Labanda et al., 2004; Romero-Pérez, Lamuela-Raventos, Waterhouse, & de la Torre-Boronat, 1996). Overall, there were greater levels of piceid than resveratrol (from samples that stilbene levels could be quantified = 26 wines out of 42 total), except C3, C9, C11, M1, M2, and R2 (which had more resveratrol than piceid). Red wines had more stilbenes (average stilbene content of Merlot wines = 6.22 mg/l and Cabernet Sauvignon wines = 5.54 mg/l) than in white wines (average stilbene content of Riesling wines = 0.65 mg/l, and Chardonnay wines = 0.39 mg/l). These trends have been reported by numerous researchers (Abril et al., 2005; Dourtoglou, Makris, Bois-Dounas, & Zonas, 1999; Ribeiro de Lima et al., 1999; Romero-Pérez et al., 1996). Since there is much more grape skin contact time in red wine making than with white wine making, and resveratrol levels are concentrated in grape skin (Jeandet, Bessis, & Gautheron, 2004). However, due to the low concentration of stilbene levels found in wine, its contribution towards ORAC values seems minimal.

Table 2
Antioxidant capacity (ORAC values) and the levels of *trans*-piceid, *cis*-piceid, *trans*-resveratrol, and *cis*-resveratrol (in the order of elution)

Sample coding[a]	ORAC values[b]	*trans*-piceid[c]	*cis*-piceid[c]	*trans*-resveratrol[c]	*cis*-resveratrol[c]	Total stilbene content[d]	Groups[e]
C1	39.7	2.64	2.97	1.37	t	6.98	1
C2	44.6	1.32	2.52	1.09	n.d.	4.93	1
C3	6.0	n.d.	n.d.	2.65	t	2.65	3
C4	59.3	1.09	1.92	1.92	t	4.93	1
C5	6.3	1.13	3.48	1.11	n.d.	5.72	1
C6	45.9	1.03	1.56	1.19	t	3.78	1
C7	28.9	1.43	2.84	1.28	t	5.55	1
C8	13.7	2.56	4.45	1.36	n.d.	8.37	2
C9	83.2	n.d.	n.d.	1.29	n.d.	1.29	2
C10	19.7	2.08	5.15	n.d.	n.d.	8.34	2
C11	87.0	n.d.	n.d.	1.07	n.d.	1.07	2
C12	58.2	6.48	3.33	3.07	n.d.	12.9	2
H1	42.9	n.d.	1.68	n.d.	n.d.	1.68	3
H2	8.7	1.91	1.89	n.d.	n.d.	3.80	1
H3	50.4	n.d.	n.d.	n.d.	n.d.	n.a.	3
H4	44.6	n.d.	n.d.	n.d.	n.d.	n.a.	3
H5	7.4	n.d.	n.d.	t	n.d.	n.a.	3
H6	48.7	n.d.	n.d.	n.d.	n.d.	n.a.	3
H7	40.7	n.d.	n.d.	n.d.	n.d.	n.a.	3
H8	73.0	n.d.	n.d.	n.d.	n.d.	n.a.	3
H9	16.8	n.d.	n.d.	n.d.	n.d.	n.a.	3
H10	73.8	n.d.	n.d.	n.d.	n.d.	n.a.	3
H11	80.1	n.d.	n.d.	n.d.	n.d.	n.a.	3
H12	86.0	n.d.	n.d.	n.d.	n.d.	n.a.	3
H13	13.9	n.d.	n.d.	n.d.	n.d.	n.a.	3
H14	12.1	n.d.	n.d.	n.d.	n.d.	n.a.	3
M1	10.5	n.d.	n.d.	2.13	t	2.13	1
M2	14.9	n.d.	n.d.	1.22	t	1.22	1
M3	17.8	1.84	2.55	1.32	t	5.71	1
M4	11.9	4.58	2.76	1.73	t	9.07	2
M5	22.4	4.12	3.18	1.61	t	8.92	2
M6	6.2	2.66	2.62	n.d.	t	7.13	1
M7	3.1	1.75	2.11	1.41	t	5.27	1
M8	78.5	4.21	3.36	1.42	t	8.99	2
M9	82.8	2.92	2.78	1.79	n.d.	7.50	2
R1	16.9	n.d.	n.d.	t	n.d.	n.a.	3
R2	36.6	0.98	n.d.	1.16	n.d.	2.13	3
R3	53.1	n.d.	n.d.	t	n.d.	n.a.	3
R4	62.7	1.45	n.d.	n.d.	n.d.	1.45	3
R5	19.3	n.d.	n.d.	n.d.	n.d.	n.a.	3
R6	10.0	0.97	n.d.	n.d.	n.d.	0.97	3
R7	77.0	n.d.	n.d.	n.d.	n.d.	n.a.	3
mean C	41.0	1.65	2.35	1.45	n.a.	5.54	n.a.
mean H	42.8	0.14	0.26	0.00	n.a.	0.39	n.a.
mean M	27.6	3.15	2.76	1.58	n.a.	6.22	n.a.
mean R	39.4	0.49	0.00	0.17	n.a.	0.65	n.a.

Assignment of the three groups (1–3) from the cluster analysis is also listed.
[a] C, Cabernet Sauvignon; H, Chardonnay ; M, Merlot; and R, Riesling. More detailed descriptions of the wines are in Table 1.
[b] ORAC values were expressed as μmol Trolox/ml of wine.
[c] Values were expressed as mg of *trans*-resveratrol/l of wine.
[d] Total detected stilbene content was calculated by summing the four stilbenes identified.
[e] Clusters 1–3 were assigned from the dendogram obtained from Cluster analysis using Ward's method and squared Euclidean distance.; n.d., not detected; *t*, present at trace levels; n.a., not applicable.

3.4. Cluster analysis

Wine samples were divided into three clusters (or groups) based on cluster analysis (Tables 2 and 3). Averages of the three groups are listed in Table 3. Group 1 ($n = 12$) contained eleven red wines (6 Cabernet Sauvignon and 5 Merlot wines) and one white wine (H2). H2 could be grouped into group 1 due to its unusually high TP content (249 mg of catechin/100 ml), when compared to other Chardonnay wine samples. Group 2 ($n = 9$) consisted of only red wines (5 Cabernet Sauvignon and 4 Merlot wine samples). Group 2 had the highest ACY, TP, TT, *trans*-piceid, *cis*-piceid, *trans*-resveratrol, and total stilbenes ($p \leqslant 0.05$). Group 2 also had the highest ORAC values. Group 3 ($n = 21$, majority of the

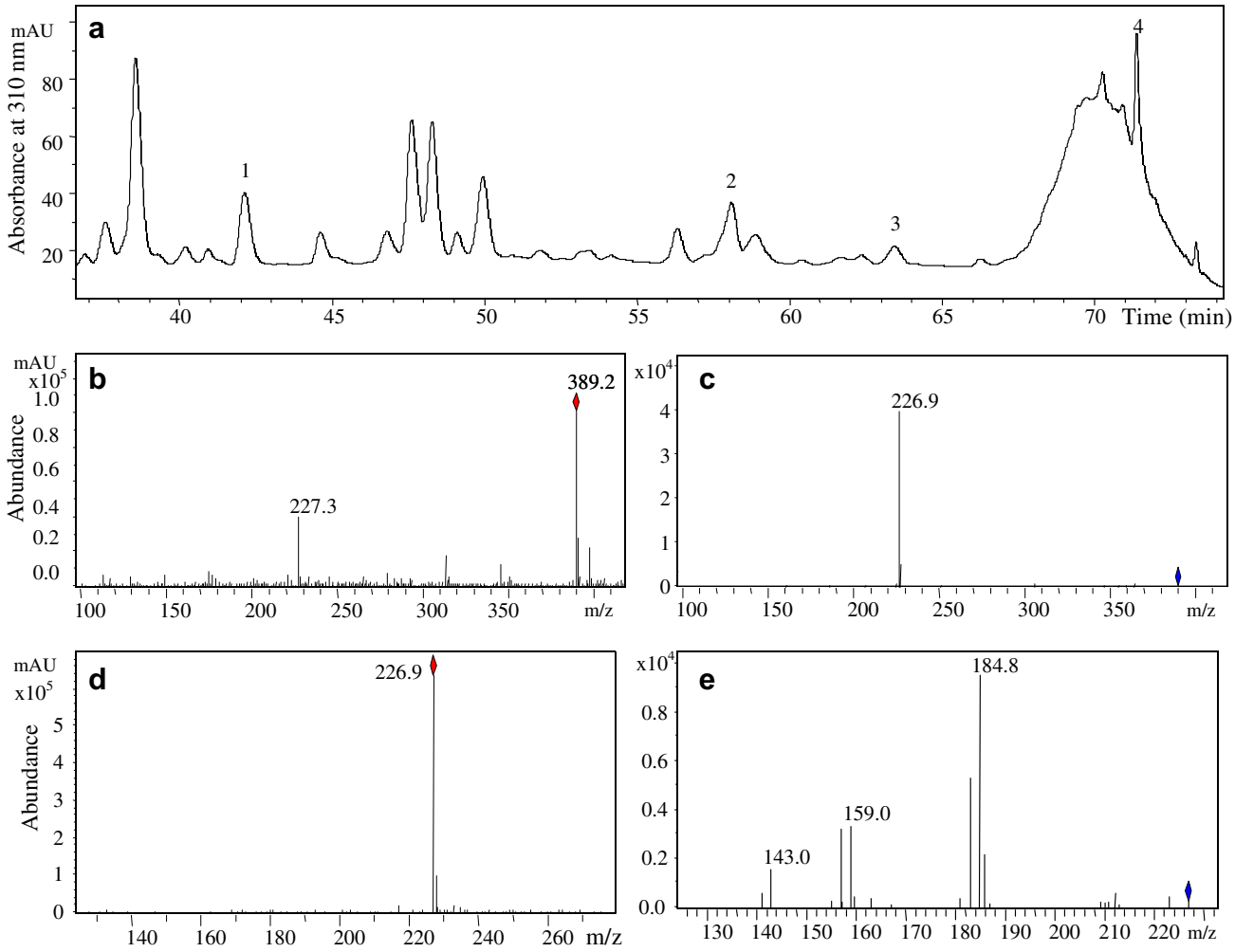

Fig. 1. HPLC chromatogram of a Cabernet Sauvignon wine sample (C1) monitored at 310 nm (a). Corresponding peak assignments: 1: *trans*-piceid, 2: *cis*-piceid, 3: *trans*-resveratrol and 4: *cis*-resveratrol. *trans*-Piceid's mother ion ($[M–H]^-$) is *m/z* 389, (b). C is the mass spectra of the fragments of *m/z* 389. *trans*-Resveratrol's mother ion ($[M–H]^-$) is *m/z* 227 (d). E is the mass spectra of the fragments of *m/z* 227. *cis*-Resveratrol (peak 4) was only present at trace levels (identified with synthesized standard and detected by extracted ion of *m/z* 227) and appeared to coelute with other compounds.

Table 3
The results of the Tukey HSD for the three groups (or clusters) obtained from the cluster analysis

Groups	Number of samples	TA	pH	Specific gravity	Color measurements			Haze	ACY	TP	TT	ORAC values	*trans*-piceid	*cis*-piceid	*trans*-resveratrol	Total stilbenes
					L^*	C^*	$h°$									
1	12	5.83ab	3.6a	0.996a	78.9a	24.2b	25.9a	1.1a	12.7b	212b	43.2b	23.8ab	1.40b	2.04b	1.17b	4.76b
		(0.20)	(0)	(0.001)	(2.8)	(2.3)	(6.9)	(0.3)	(0.9)	(13.9)	(6.78)	(5.5)	(0.25)	(0.31)	(0.18)	(0.51)
2	9	6.31b	3.5a	0.999a	72.6a	32.2c	23.6a	1.3a	15.5c	339 c	81.8c	50.8abc	2.99c	2.78b	1.48b	7.38c
		(0.16)	(0.1)	(0.002)	(1.3)	(1.2)	(2.5)	(0.7)	(1.4)	(5.5)	(1.81)	(11.1)	(0.71)	(0.58)	(0.27)	(1.27)
3	21	5.57a	3.4a	0.999a	99.3b	8.3a	96.7b	1.4a	0.5a	94.9a	1.27a	41.5bc	0.16a	0.08a	0.18a	0.42a
		(0.16)	(0.1)	(0.001)	(0.7)	(0.6)	(3.5)	(0.2)	(0.5)	(3.2)	(0.85)	(5.8)	(0.09)	(0.08)	(0.14)	(0.18)

Details of the group assignments are listed in Table 1.
Units for all values in this table are the same as Tables 1 and 2. Average with different lower case letters (within a column) were significantly different (Tukey HSD, $p \leqslant 0.05$). Values in parenthesis are standard errors.

Chardonnay, all of the Riesling wine samples, and one Cabernet Sauvignon wine sample) had the lowest ACY, TP, TT, *trans*-piceid, *cis*-piceid, *trans*-resveratrol, *cis*-resveratrol, and total stilbenes ($p \leqslant 0.05$). The one Cabernet Sauvignon wine sample (C3 from winery B) that was assigned to group 3 had the lowest TP (92.1 mg/100 ml), TT (13.0 mg/100 ml), and ORAC (6.0 μmol of Trolox/ml) values, when compared to other samples of the same style. There were no significant differences ($p \leqslant 0.05$) in the average pH, specific gravity, and haze among all three groups.

4. Conclusion

This is the first time stilbenes and ORAC contents have been reported for Idaho produced wines. The ORAC values and stilbene levels of wines examined in this study varied considerably, but are comparable to wines produced from other regions, such as Spain, Greece, Italy, Australia, and Portugal (reports that used similar sample preparation and analytical methods). Comparison of these values should be conducted with caution since there are no officially validated analytical methods to date. Total stilbenes provided by a standard glass of Idaho wine (5 oz glass) could be as high as 1.91 mg, but depending on the wine samples the levels vary considerably.

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