

Available online at www.sciencedirect.com



FOOD CHEMISTRY

Food Chemistry 109 (2008) 755-762

www.elsevier.com/locate/foodchem

Effect of postharvest dehydration on the composition of pinot noir grapes (*Vitis vinifera* L.) and wine

Jorge J. Moreno^a, Fiorella Cerpa-Calderón^b, Seth D. Cohen^b, Yu Fang^b, Michael Qian^b, James A. Kennedy^{b,*}

^a Department of Food Engineering, University of Bio-Bio, Casilla 447, Chillán, Chile ^b Department of Food Science and Technology, Oregon State University, Corvallis, OR 97331-7304, USA

Received 30 November 2007; received in revised form 16 January 2008; accepted 18 January 2008

Abstract

This study was conducted in order to improve our understanding of how phenolics and aroma compounds change in wine grapes during postharvest dehydration. Pinot noir grapes grown in the Willamette Valley of Oregon were harvested at 22.0 and 24.0 °Brix. Grapes harvested at 22.0 °Brix were divided into three equal lots with one lot immediately used for wine production, and the remaining two lots placed inside an air tunnel with an air speed of $1.0-1.8 \text{ m s}^{-1}$, 38% relative humidity and a temperature of 22 °C. The soluble solids content and weight loss were measured daily and wines were made from grapes when they reached 24.8 and 26.7 °Brix. The soluble solids of grapes increased about 1 °Brix per day; therefore, on the third and fourth day the berries reached the desired concentration; weight loss was 14 and 16%, respectively. Results from berry phenolic analysis indicated that per berry anthocyanin amount remained unchanged during dehydration. The composition of proanthocyanidins isolated from berries changed during dehydration. Volatile compounds in wines made from dehydrated grapes contained more terpenes and norisoprenoids (β -ionone, β -damascenone) when compared to wine made from the original fruit. Wines made from increasingly dehydrated grapes tended to resemble the composition and flavour profile of wines made from grapes left on the vine (i.e. with extended ripening). The results of this study suggest that postharvest flavour changes consistent with changes during fruit ripening can occur in grapes when harvested early and allowed to dehydrate under controlled conditions prior to fermentation.

© 2008 Elsevier Ltd. All rights reserved.

Keywords: Wine; Grapes; Anthocyanins; Proanthocyanidins; Volatiles; Aroma; Postharvest; Dehydration; Pinot noir

1. Introduction

Postharvest dehydration is an important step in the processing of some fruits, and is typically accomplished by sun exposure or tunnel drying (Barbosa-Canovas & Vega-Mercado, 2000). Research on the postharvest dehydration of grapes for wine production has shown that in addition to sugar concentration, phenolics and aroma compounds are either concentrated or produced (Bellincontro, De Santis, Botondi, Villa, & Mencarelli, 2004; Constantini, Bellincontro, De Santis, Botondi, & Mencarelli, 2006). Phenolic compounds are abundant in grapes and play an important role in the quality of wines. Anthocyanins are found in the skin tissue and are responsible for the colour of red wine. Flavan-3-ols are found in the skin and seed tissue (Cheynier & Rigaud, 1986; Kennedy, Matthews, & Waterhouse, 2002; Mazza, 1995; Mistry, Cai, Lilley, & Haslam, 1991; Souquet, Cheyner, Brossaud, & Moutonet, 1996; Kovac, Alonsa, Bourzeix, & Revilla, 1992) and are responsible for the bitter and astringent properties of red wine (Gawel, 1998). Many factors can affect phenolic accumulation in the grape, including maturity (Kennedy, Matthews, & Waterhouse, 2000, 2002), temperature (Spayd, Tarara, Mee, & Ferguson, 2002), light (Dokoozlian & Kliewer, 1996; Keller & Hrazdina, 1998) and vine water status

^{*} Corresponding author. Tel.: +1 541 737 9150; fax: +1 541 737 1877. *E-mail address:* james.kennedy@oregonstate.edu (J.A. Kennedy).

 $^{0308\}text{-}8146/\$$ - see front matter \circledast 2008 Elsevier Ltd. All rights reserved. doi:10.1016/j.foodchem.2008.01.035

(Bellincontro et al., 2004; Kennedy et al., 2002; Ojeda, Andary, Kreava, Carbonneau, & Deloire, 2002). Aroma compounds are also important in wine quality and are influenced by several factors such as grape variety and maturity, growing climate, alcoholic fermentation and wine age (Bueno et al., 2003; Gomez, Laencina, & Martinez, 1994; Nykänen, 1986; Oliveira, Barbosa, Silva Ferreira, Guerra, & Guedes de Pinho, 2006).

Because fruit maturity has a tremendous influence on the composition of grapes at harvest, winemakers are aware of the significance that harvest decisions have on the final wine composition. Some winemakers practice extended ripening on the vine in order to achieve a desired flavour profile. Extended ripening is the period of time that fruit is left on the vine beyond the time needed for an acceptable sugar concentration. The extended ripening occurs in order to achieve a more desirable flavour composition and/or concentration. The purpose of this study was to monitor how the phenolic and aroma compounds in under ripe wine grapes changed in fruit and subsequent wine following postharvest dehydration in order to better understand the role of the vine in extended ripening flavour development. From a practical standpoint, this study was carried out to better understand if this form of sugar concentration and flavour development could be utilized for the production of dry red table wines from fruit that would otherwise be considered to be underripe.

2. Materials and methods

2.1. Fruit

Grapes (*Vitis vinifera* L. cv Pinot noir) grown in the Willamette Valley of Oregon in 2005 were harvested at two maturities: Sept 27 and Oct 11 with soluble solids of 22.0 and 24.0 °Brix, respectively. Fruit harvested at 22.0 °Brix were divided into three equal lots with one lot immediately used for wine production, and the remaining two lots placed inside an air tunnel for dehydration.

For humidity and temperature control during dehydration, the air tunnel was equipped with fans and a cooler (MovinCool Classic Plus 26; Denso Sales California, Long Beach, CA). Clusters were placed in perforated plastic boxes with an average of 4.0 kg (± 0.3 kg) fruit per box. The soluble solids content was measured daily. A total of 300 kg was placed in the air tunnel. During dehydration the temperature, air speed and relative humidity were controlled. Air speed was monitored at various points within the tunnel using an Anemometer (HHF81; Omega, Stamford, CT), and varied from 1.0–1.8 m s⁻¹. The temperature remained at 22 °C (± 2), and the relative humidity at 38% (± 2).

Grapes were removed from the dehydration tunnel when they reached 24.8 and 26.7 °Brix so that wines could be produced. Samples (16 clusters for each treatment) were frozen and stored at -20 °C for later analysis. Frozen berries were removed from the rachis, and samples of 150 berries were randomly collected (5 replicates) for phenolic analysis. The remaining berries were randomly separated (3 replicates) for titratable acidity, pH and sugar analysis.

2.2. Chemicals

All chromatographic solvents were HPLC grade. Acetonitrile, methanol, ethanol, acetic acid, ascorbic acid, and potassium hydroxide were purchased from J.T. Baker (Phillipsburg, NJ, USA). Phloroglucinol, (+)-catechin, and (-)-epicatechin were procured from Sigma (St. Louis, MO, USA). Ammonium phosphate monobasic and orthophosphoric acid were obtained from Fisher Scientific (Santa Clara, CA, USA). Hydrochloric acid and anhydrous sodium acetate were obtained from E.M. Science (Gibbstown, NJ, USA) and Mallinckrodt (Phillipsburg, NJ, USA), respectively. All aroma standards were purchased from Sigma-Aldrich (St. Louis, MO, USA). Tartaric acid was obtained from Mallinckrodt Inc. (Paris, KY, USA).

2.3. Instrumentation

An Agilent model 1100 HPLC (Palo Alto, CA), consisting of a vacuum degasser, autosampler, quaternary pump, diode array detector, and column heater and operated by a computer workstation and Chemstation software, was used for HPLC chromatographic analysis.

An Agilent 5973 GC–MS equipped with a TDU autosampler (Gerstel, Inc., Baltimore, MD) was used for volatile analysis. The electron impact (EI) energy was 70 eV, and the ion source temperature was set at 230 °C. Enhanced ChemStation Software (GCA v. D.00.01.08, Agilent Technologies Inc.) was used for data acquisition and analysis.

2.4. Phenolic extraction

Berry samples reserved for phenolic analysis were removed from the freezer and processed as previously described (Cortell, Halbleib, Gallagher, Righetti, & Kennedy, 2005).

2.5. Winemaking

A total of four wines were produced (replicated three times). These wines consisted of the following: vine produced with fruit harvested at 22.0 °Brix (T1) and 24.0 °Brix (T2); and fruit harvested at 22.0 °Brix but dehydrated to 24.8 °Brix (T3) and 26.7 °Brix (T4). Wines were produced as previously described (Pastor del Río & Kennedy, 2006). For wine analysis, all wines were analyzed within 2 months after malolactic fermentation and final SO₂ addition.

2.6. General wine analysis

Alcohol was determined with an ebulliometer (Dujardin-Salleron, Paris, France). A Thermo Orion pH meter, Model 370 (Thermo, Beverly, MA), was used to measure pH. Titratable acidity (TA) was measured by titration of 10 mL grape juice or wine, with constant and gentle stirring, with a solution of 0.1 N NaOH until a pH 8.2 using a pH meter as an indicator. The results were expressed g/L tartaric acid. Soluble solids were measured with an Atago Digital Wine Refractometer (model WM-7, Atago, Japan). Reducing sugar was measured by HPLC as previously described (Ellefson, 2003).

2.7. Flavan-3-ol analysis

Flavan-3-ol monomer content was measured by reversed-phase HPLC as previously described (Lamuela-Raventos & Waterhouse, 1994). Proanthocyanidin isolates were characterized by acid-catalysis in the presence of excess phloroglucinol followed by reversed-phase HPLC (phloroglucinolysis) (Kennedy & Jones, 2001), using a modified HPLC method (Kennedy & Taylor, 2003). To prepare samples for analysis, 3 mL seed or skin extract was freeze-dried and then dissolved in 5 or 2 mL methanol, respectively.

For wines, proanthocyanidin (PA) analysis was carried out after the final SO_2 addition. To prepare samples, 10 mL wine was evaporated in a centrivap concentrator (Labconco, Kansas City, MO), redissolved in 6 mL of water, and prepared as previously described (Pastor del Río & Kennedy, 2006).

The proportion of seed and skin proanthocyanidin extracted into wine was calculated using a previously described method (Peyrot des Gachons & Kennedy, 2003). Wine extract was determined as previously described (Pastor del Río & Kennedy, 2006).

2.8. Volatile analysis

The volatile analysis was performed according to a previously described procedure (Fang & Qian, 2006). A synthetic wine solution was made by dissolving L-tartaric acid (3.5 gm) in 1 L of 12% v/v ethanol solution, and adjusting the pH to 3.5 with 1 N NaOH. Standard stock solutions (1000 mg/L) were prepared in ethanol first and then diluted to the proper concentrations of working standards in synthetic wine. An internal standard solution was made as described previously (Fang & Qian, 2006).

Each standard solution (10 mL) was diluted with 10 mL water in a 40 mL vial, in which 6 g of sodium chloride had been added, and 20 μ L of internal standard solution was added to the vial. A stir bar coated with Poly(dimethylsiloxane) (PDMS) phase (1 cm length, 0.5 mm thickness, Gerstel Inc.) was used to extract the volatiles as described previously (Fang & Qian, 2006).

Analytes were thermally desorbed at the Thermal Desorption Unit (TDU, Gerstel Inc.) and refocused in a programmed temperature vaporizing (PTV) injector (CIS 4, Gerstel, Inc.) with liquid nitrogen (-60 °C). After desorption, the PTV was heated to 250 °C and held for 3 min. The solvent vent injection mode was employed. A RTX-1 capillary GC column (60 m, 0.25 mm I.D., 0.5 µm film thickness, Resteck Inc., Bellefonte, PA) was employed to separate the analytes. Helium at a constant flow of 1.8 mL/min was used as the carrier gas. The oven temperature was initially set at 50 °C for 2 min, raised to 210 °C at a rate of 2 °C/min, then to 250 °C at a rate of 10 °C/min, and held at 250 °C for 15 min.

Selective ion-monitoring (SIM) mass spectrometry was used to quantify the aroma compounds. The calibration curve for individual target compounds was built by plotting the selected ion abundance ratio of target compounds with their respective internal standard against the concentration ratio.

Wine samples were pooled from three replicates. The pooled wine samples were analyzed using the same procedure as described for the standard curve. Triplicate analyses were performed on each sample.

2.9. Statistical analysis

Statistical analysis of data was performed through an analysis of variance (ANOVA) using Statgraphics Plus 5.0 Software. Differences among mean values were established by the least significant difference (LSD) test at a significance level of $\alpha \leq 0.05$.

3. Results and discussion

3.1. Dehydration

The composition of fresh and dehydrated fruit is shown in Table 1. Grapes harvested at 22 °Brix (T1) and 24 °Brix (T2) showed a slight difference in pH values, with an increase in pH observed for T2. Dehydrated grapes that reached 24.8 °Brix (T3) and 26.7 °Brix (T4) showed an increase in TA, consistent with expectations based upon water loss. Mean berry weight at harvest was 1.05 gm for both T1 and T2, but was reduced upon dehydration (T3 and T4). An inverse effect was observed in the dry skin weight. No differences in dry seed weight were observed, consistent with previous studies on temporal development (Cortell et al., 2005; Pastor del Río & Kennedy, 2006).

Changes in berry weight and soluble solids during dehydration can be explained by evaporative weight loss and concentration. Weight loss during the first two days averaged 5% per day, decreasing to 4% and 2% on days 3 and 4, respectively. By the third and fourth day berries achieved a total weight loss of 14 and 16% respectively indicating that dehydration induced a rapid weight loss in cv. Pinot noir, consistent with previous results for others varieties (Bellincontro et al., 2004; Constantini et al., Table 1

Treatment	TA (g/L)	pH	Soluble solids (°Brix)	Berry wt (gm)	Seed # (per berry)	Dry seed wt (mg)	Dry skin wt (mg)
T1	6.7 ± 0.2	3.51 ± 0.06	22.0 ± 0.1	1.11 ± 0.06	1.4 ± 0.1	33.78 ± 2.48	20.40 ± 3.98
T2	6.7 ± 0.1	3.65 ± 0.01	24.0 ± 0.2	1.00 ± 0.04	1.5 ± 0.1	35.41 ± 2.11	20.40 ± 1.26
T3	7.5 ± 0.1	3.54 ± 0.01	24.8 ± 0.1	0.92 ± 0.02	1.4 ± 0.1	35.13 ± 1.11	24.08 ± 2.38
T4	9.4 ± 0.4	3.43 ± 0.08	26.7 ± 0.3	0.87 ± 0.03	1.5 ± 0.1	35.87 ± 2.05	25.72 ± 1.63

Average berry titratable acidity (TA), pH, soluble solids, seeds per berry and berry, skin and seed weights, for fruit harvested in the vineyard (T1 and T2) or harvested in the vineyard at 22 °Brix, followed by postharvest dehydration (T3 and T4)

Ave \pm SEM, N = 5.

2006). Soluble solids measurements indicated when to end dehydration (T3 and T4). The soluble solids increased about 1°Brix per day; therefore, on the third and fourth day the berries reached the desired concentration. The increase in soluble solids strongly correlated with the loss of weight as opposed to carbohydrate metabolism (Constantini et al., 2006).

3.2. Skin analysis

The effect of postharvest dehydration on anthocyanins is shown in Table 2. An increase in anthocyanins and pigmented polymer concentration in treated berries was observed when expressed on a weight basis. When anthocyanins and pigmented polymers were expressed on a per berry basis however, no significant difference was observed. This is consistent with a concentration effect due to water loss during dehydration and not biosynthesis. T2 did not show a significant difference from T1 with regard to anthocyanin content per berry suggesting that anthocyanins were not biosynthesized in the fruit during the two harvest dates. Previous reports have found that in addition to anthocyanins increasing on a weight basis during dehydration, per berry anthocyanin amounts increased as well (Constantini et al., 2006). The increase was not significant in this study.

By phloroglucinolysis, proanthocyanidin (PA) amount per berry decreased in skin for all treatments (Table 2). (+)-Catechin (C) was the only flavan-3-ol monomer observed in the skin. (-)-Epicatechin (EC), (-)-epigallocatechin (EGC), (-)-epicatechin-3-*O*-gallate (ECG) were present as extension subunits. Extension subunit composition was primarily EC and EGC. From the total extension subunit pool, $\sim 60\%$ (by mol) corresponded to EC and $\sim 34\%$ to EGC. Skin extension subunit composition changed little between harvest and dehydration treatments. The skin PA average degree of polymerization (mDP) decreased during dehydration (37.6 to 25.7) and the same occurred with increasing time in the vineyard (37.6-27.8). Overall, dehydration appeared to cause a reduction in proanthocyanidin amount on a per berry basis as well as a reduction in mDP, and these results are consistent with those observed with extended ripening. It was somewhat surprising that despite the reduction in berry weight, there was not a consistent increase in skin proanthocyanidin amount on a fruit weight basis. A possible explanation for this may be that the fruit lost physiological integrity during dehydration and the proanthocyanidins reacted with other cell components.

3.3. Analysis of seed

The effect of postharvest dehydration on seed PA is shown in Table 3. Seeds showed a significant increase in PA concentration during dehydration when expressed on a fruit weight basis. This change is consistent with a concentration effect. By mole, C made up nearly 60% of total terminal subunits, EC had the second highest, representing \sim 31% of the total terminal subunits. Seed PA extension subunit composition changed little between vineyard and dehydration treatments. The seed PA mDP in dehydration treatments experienced a decrease (3.31 to 3.02) and the same occurred with the vineyard samples (3.31–3.16). Overall, the changes due to dehydration were consistent

Table 2

Skin colour content (malvidin-3-glucoside equivalents) and proanthocyanidin (PA) concentration, mean degree of polymerization (mDP), and composition for fruit harvested in the vineyard (T1 and T2) or harvested in the vineyard at 22 °Brix, followed by postharvest dehydration (T3 and T4) (Ave \pm SEM, N = 5)

Treatment	Skin colour			Skin proanthocyanidin							
	Anthocyanin		Pigmented polymer		Concentration		mDP	Subunit composition (mol%)			
	(mg/kg fruit)	(mg/berry)	(mg/kg fruit)	(mg/berry)	(mg/kg fruit)	(mg/berry)		CA	EC	EGC	ECG
T1	$458\pm30~a^{B}$	$0.51\pm0.04~a$	56.7 ± 4.5 a	0.063 ± 0.006 b	$735\pm34~ab$	$0.81\pm0.02~b$	$37.6\pm2.4~\text{b}$	2.9 a	59.7 a	35.0 bc	2.3 a
T2	561 ± 13 bc	$0.56\pm0.02~a$	$62.6\pm2.5~ab$	0.063 ± 0.003 ab	$772\pm 61~ab$	0.77 ± 0.06 a	$27.8\pm3.2~a$	2.6 a	60.9 b	33.9 b	2.5 a
Т3	$533\pm25ab$	$0.49\pm0.02~a$	58.2 ± 2.2 b	0.054 ± 0.002 a	642 ± 42 a	$0.59\pm0.04~\mathrm{a}$	$26.8\pm2.5~a$	2.8 a	58.6 a	36.3 c	2.3 a
T4	$636\pm53~c$	$0.55\pm0.05\ a$	$68.4\pm3.2\ b$	$0.060\pm0.002~ab$	$799\pm62~b$	$0.69\pm0.05\ ab$	$25.7\pm2.5~a$	4.0 b	61.9 b	31.5 a	2.5 a

^A Subunit abbreviations: C (+)-catechin, EC (-)-epicatechin, EGC (-)-epigallocatechin, ECG (-)-epicatechin-3-O-gallate.

^B Values with different letters are significantly different ($P \le 0.05$).

Treatment	Proanthocyanidin concentration		mDP	Extension s	Extension subunit composition (mol%)			Terminal subunit composition (mol%)		
	mg/kg fruit	mg/berry		C^A	EC	ECG	С	EC	ECG	
T1	$2370\pm069~a^{B}$	$2.63\pm0.08~a$	$3.31\pm0.06~\text{b}$	11.1 a ^A	77.3 b	11.6 b	58.8 a	31.4 a	9.8 b	
T2	$2600\pm226~ab$	$2.60\pm0.23~\mathrm{a}$	$3.16\pm0.04~ab$	13.0 bc	76.6 b	10.5 a	60.0 ab	31.4 a	8.6 a	
T3 T4	3040 ± 327 bc 3319 ± 103 c	2.81 ± 0.31 a 2.89 ± 0.07 a	$\begin{array}{c} 3.16 \pm 0.09 \ ab \\ 3.02 \pm 0.05 \ a \end{array}$	12.0 ab 13.4 c	76.8 b 75.0 a	11.2 b 11.7 b	61.3 b 60.5 ab	30.1 a 31.1 a	8.6 a 8.4 a	

Seed proanthocyanidin concentration mean degree of polymerization (mDP), and composition (Ave \pm SEM, N = 5)

^A Subunit abbreviations: C (+)-catechin, EC (-)-epicatechin, ECG (-)-epicatechin-3-O-gallate.

^B Values with different letters are significantly different (P < 0.05).

with those from extended ripening (Pastor del Río & Kennedy, 2006).

3.4. Wine analysis

Table 3

A partial composition of wines is shown in Table 4. Differences between wine ethanol concentrations were associated with the differences in soluble solids. The pH and TA values are consistent with expected results. An increase in the concentration of T4 reducing sugar concentration was consistent with expectation based upon the high soluble solids for T4 musts. Overall, these compositional components are consistent with expectations based upon a combination of dehydration and extended ripening.

Information on wine phenolic composition is shown in Tables 4 and 5. An increase in wine anthocyanins was observed with an increase in fruit maturity (T1 versus T2) and with a variable response from dehydration (Table 4). There was little difference in per berry amounts of anthocyanins (Table 2) suggesting that differences in wine

anthocyanin concentration are driven by differences in berry weight. The exception to this is for T4 where despite a reduction in berry weight and little difference in per berry amount of anthocyanin, no difference in wine anthocyanin concentration was observed (compared to T1). Given that anthocyanins are reactive compounds and the concentration of solutes is likely to be higher in T4 due to berry weight reduction, one possible explanation for the lack of difference in anthocyanin concentration is that the anthocvanins have become modified after extraction into the wine. Consistent with this, an incremental increase in pigmented polymers was observed with dehydration, with the T4 pigmented polymer concentration almost twice that of T1. The colour of young red wine is mostly due to the presence of grape-based anthocyanins which during maturation and ageing become modified (Sáenz-López, Fernandez-Zurbano, & Tena, 2004).

An increase in PA concentration in wines was observed with dehydration and extended ripening (Table 5). The large increase in PA concentration beyond expected

Table 4 Composition of wines (Ave \pm SD, N = 3)

Treatment	TA (g/L)	pH	Reducing sugar ^A (g/L)	Ethanol (% v/v)	Wine colour ^B		
					Anthocyanin (mg/L)	Pigmented polymer (mg/L)	
T1	6.7 ± 0.2	3.48 ± 0.05	1.32 ± 0.09	11.8 ± 0.1	$339\pm7a$	$108 \pm 6a$	
T2	6.2 ± 0.6	3.81 ± 0.07	1.19 ± 0.05	12.9 ± 0.1	$469 \pm 16c$	$150 \pm 9b$	
T3	6.5 ± 0.1	3.68 ± 0.03	1.56 ± 0.21	14.1 ± 0.2	$395\pm7b$	$162 \pm 4b$	
T4	6.3 ± 0.4	3.83 ± 0.08	3.42 ± 0.55	15.7 ± 0.1	$337\pm7a$	$201 \pm 7c$	

Values with different letters are significantly different (P < 0.05).

^A Glucose + fructose.

^B Malvidin-3-O-glucoside equivalents.

Table 5 Wine proanthocyanidin concentration, mean degree of polymerization (mDP), and composition, (Ave \pm SEM, N = 3)

Treatment	Proanthocyanidin concentration			mDP	Extension subunit composition (mol%)			on (mol%)	Terminal subunit composition (mol%)	
	Skin (mg/L)	Seed (mg/L)	Total (mg/L)		$\mathbf{C}^{\mathbf{A}}$	EC	ECG	EGC	С	EC
T1	125 a ^B	127 a	253 a	2.47 a	18.3 a	61.3 a	2.7 a	17.7 ab	74.3 ab	25.7 bc
T2	178 ab	129 a	307 ab	2.81 b	13.4 a	62.3 a	4.5 b	19.8 b	73.1 a	26.9 c
T3	172 ab	179 b	352 b	2.84 b	15.0 a	62.9 a	2.9 a	19.2 ab	74.9 bc	25.1 ab
T4	211 b	245 c	456 c	2.79 b	13.8 a	68.1 b	2.1 a	16.0 a	76.1 c	23.9 a

^A Subunit abbreviations: C (+)-catechin, EC (-)-epicatechin, EGC (-)-epigallocatechin, ECG (-)-epicatechin-3-O-gallate.

^B Values with different letters are significantly different ($P \le 0.05$).

differences based upon the PA concentration in the fruit suggests that the diffusional barrier between the PA localization in the plant cell vacuole and the fermentation vessel have become modified. Because plant cell walls become modified during ripening (Nunan, Sims, Bacic, Robinson, & Fincher, 1998), it would be expected that the barrier to diffusion would become modified as well. Dehydration seemed to have a greater influence on PA concentration in the wine than did extended ripening although our data is limited.

The PA mDP for all wines was significantly lower than skin (Table 2), and slightly less than seed PA (Table 3). The differences in PA mDP observed between grape skin and wine are likely to be due to selectivity during extraction as observed in other studies (Kennedy et al., 2002; Pastor del Río & Kennedy, 2006). Overall, dehydration and extended ripening behaved similarly.

The proportion of EGC in wine PA increased with extended maturity (T1 versus T2), and because there was little difference in skin PA EGC, this indicates that the proportion of skin PA increased (Table 5). This increase in skin PA proportion with fruit maturity is inconsistent with previous research (Pastor del Río & Kennedy, 2006). With dehydration, the proportion of skin PA declined, consistent

Table 6 Concentration (μ g/L) of wine aroma compounds (Ave \pm SD, N = 3)

in this case with expected observations based upon grape maturity (Pastor del Río & Kennedy, 2006; De Freitas, Glories, & Monique, 2000; Monagas, Gómez-Cordovés, Bartolomé, Laureano, & Da Silva, 2003). The general conclusions from PA analysis indicate that the greatest factor affected by dehydration is the concentration of PA in the wine. PA composition, mDP and skin PA proportion, if affected by dehydration (and extended ripening), were influenced in a minor way.

3.5. Wine aroma analysis

Results for wine aroma analysis are shown in Table 6. The dehydration of grapes resulted in an increase in several aroma compounds including guaiacol, citronellol, geraniol, citronellol, eugenol. The increase in some of these compounds is beyond that expected by simple concentration and suggests that the production of important flavour compounds occurs after harvest. It is expected that these compounds would contribute to an increase in floral and fruity characters. Of particular interest, the concentrations of specific norisoprenoids (β -ionone, β -damascenone), which were similar to those reported elsewhere (Ferreira, López, & Cacho, 2000; Francis & Newton, 2005), also

Compounds	T1	T2	T3	T4
Trans-carveol (IS)				
Guaiacol	38.4 ± 5.3	25.5 ± 3.2	38.2 ± 4.3	56.0 ± 7.6
Linalool	11.2 ± 1.2	8.5 ± 0.1	9.9 ± 0.2	11.3 ± 0.4
Geraniol	10.1 ± 0.8	14.4 ± 1.0	13.3 ± 0.3	16.6 ± 1.3
Eugenol	3.0 ± 0.2	2.3 ± 0.1	3.4 ± 0.1	5.2 ± 0.5
Benzylethanol (mg/L)	64.2 ± 3.7	39.5 ± 0.8	35.4 ± 0.7	32.9 ± 2.1
Citronellol	18.5 ± 3.0	20.9 ± 0.3	22.5 ± 0.7	31.9 ± 1.2
4-Ethylguaiacol	4.1 ± 0.3	3.3 ± 0.1	4.9 ± 0.5	7.1 ± 0.6
Hexyl formate (IS)				
Ethyl isobutyrate	186 ± 8	167 ± 9	261 ± 22	143 ± 17
Ethyl butyrate	377 ± 80	385 ± 26	549 ± 53	521 ± 51
Isoamyl acetate	364 ± 18	279 ± 15	306 ± 14	287 ± 31
2-Methylbutyl acetate	102 ± 15	85 ± 5	87 ± 4	69 ± 8
Ethyl isovalerate	23.4 ± 5.8	12.7 ± 1.0	21.4 ± 1.9	13.0 ± 1.0
Octyl propionate (IS)				
Ethyl hexanoate	282 ± 22	246 ± 17	258 ± 25	210 ± 20
Ethyl octanoate	181 ± 10	175 ± 9	193 ± 12	185 ± 17
Ethyl decanoate	62 ± 3	70 ± 7	83 ± 2	101 ± 10
2-Nonenal (IS)				
β-Damascenone	6.8 ± 0.5	7.3 ± 0.3	7.1 ± 0.1	7.7 ± 0.7
β-Ionone	0.36 ± 0.03	0.35 ± 0.02	0.40 ± 0.01	0.63 ± 0.06
γ-Nonalactone	14.8 ± 0.8	16.3 ± 1.0	11.8 ± 1.3	6.9 ± 1.9
Linalyl isobutyrate (IS)				
Ethyl phenylacetate	2.5 ± 0.3	1.6 ± 0.1	1.2 ± 0.2	1.0 ± 0.1
Ethyl dihydrocinnamate	0.4 ± 0.1	0.3 ± 0.1	0.3 ± 0.1	0.3 ± 0.1
Ethyl cinnamate	6.4 ± 0.8	8.7 ± 0.7	7.0 ± 0.7	6.3 ± 0.8
Methyl vanillate	28.9 ± 5.7	30.6 ± 0.5	32.0 ± 4.5	29.9 ± 2.9
Ethyl vanillate	6.3 ± 0.7	8.5 ± 0.7	6.4 ± 0.5	8.0 ± 1.0
Phenethyl acetate	21.6 ± 1.7	17.2 ± 1.6	12.9 ± 1.5	11.3 ± 1.3
Ethyl 3-phenylpropionate	0.5 ± 0.1	0.6 ± 0.1	0.4 ± 0.1	0.4 ± 0.1

increased during dehydration. β -damascenone has a very low sensory threshold of 0.05 µg/L in 10% alcohol solution (Guth, 1997) and is associated with a fruity, floral, honey, berry-like aroma. β -Ionone has a raspberry, dry fruit violet aroma. The changes in aroma compounds suggest that an increase in floral aroma attributes is possible (Bueno et al., 2003; Sabon, Revel, Kotseridis, & Bertrand, 2002). In general, the aroma compound changes with dehydration were consistent with those occurring with extended ripening.

3.6. Accounting for weight loss from dehydration

To understand if dehydration influences wine solute concentration beyond simple concentration, specific wine component concentrations were adjusted downward by adjusting their values relative to berry weight information (Table 1). Differences in ethanol concentration after correction were minimal suggesting that correcting solute concentrations for water loss in fruit reasonably accounts for concentration changes due to dehydration (data not shown). The adjusted concentration of anthocyanins declined with dehydration suggesting that anthocyanins degraded in the grape upon dehydration. On the contrary, adjusted pigmented polymer and proanthocyanidin concentrations increased beyond expectation indicating that dehydration affected the amount of this material in wine beyond the expected changes due to dehydration. An explanation for these observations could be that the physiological integrity of the grape berry becomes compromised. If this occurs, it would be expected that the rate of reaction of compounds would increase in addition to their rate of diffusion into the fermentation vessel. Extract amount, while increasing significantly during dehydration, changed very little after correction for water loss (data not shown). Overall, changes due to extended ripening (T2) were similar to changes in composition following dehydration.

In summary, the results of this study indicate that postharvest dehydration for the purposes of concentrating under-ripe grapes to appropriate sugar levels, results in postharvest changes consistent with those expected during extended ripening on the vine. The observed chemical changes in grapes and wine suggest that positive postharvest flavour development can occur.

References

- Barbosa-Canovas, G., & Vega-Mercado, H. (2000). "Deshidratación de Alimentos". Ed. Acribia, Zaragoza, Spain.
- Bellincontro, A., De Santis, D., Botondi, R., Villa, I., & Mencarelli, F. (2004). Different postharvest dehydration rates affect quality characteristics and volatile compounds of Malvasia, Trebbiano and Sangiovese grapes for wine production. *Journal of the Science of Food and Agriculture*, 84, 1791–1800.
- Bueno, J. E., Peinado, R., Moreno, J., Medina, M., Moyano, L., & Zea, L. (2003). Selection of volatile aroma compounds by statistical and enological criteria for analytical differentiation of musts and wines of two grape varieties. *Journal of Food Science*, 68, 158–163.

- Cheynier, V., & Rigaud, J. (1986). HPLC separation and characterization of flavonols in the skin of *Vitis vinifera* var. Cinsault. *American Journal of Enology and Viticulture*, 37, 248–252.
- Constantini, V., Bellincontro, A., De Santis, D., Botondi, R., & Mencarelli, F. (2006). Metabolic changes of Malvasia grapes for wine production during postharvest drying. *Journal of Agricultural and Food Chemistry*, 54, 3334–3340.
- Cortell, J. M., Halbleib, M., Gallagher, A. V., Righetti, T. L., & Kennedy, J. A. (2005). Influence of vine vigor on grape (*Vitis vinifera* L. Cv. Pinot noir) and wine proanthocyanidins. *Journal of Agricultural and Food Chemistry*, 53, 5798–5808.
- De Freitas, V. A. P., Glories, Y., & Monique, A. (2000). Developmental changes of procyanidins in grapes of red *Vitis vinifera* varieties and their composition in respective wines. *American Journal of Enology* and Viticulture, 51, 397–403.
- Dokoozlian, N. K., & Kliewer, W. M. (1996). Influence of light on grape berry growth and composition varies during fruit development. *Journal of the American Society for Horticulture Science*, 121, 869–874.
- Ellefson, W. (2003). In R. E. Wrolstad (Ed.). Current protocols in food analytical chemistry: mono- and oligosaccharides E1 (Vol. 2, pp. E1.2.6–E1.2.7). New York: John Wiley & Sons.
- Fang, Y., & Qian, M. C. (2006). Quantification of selected aroma-active compounds in Pinot noir wines from different grape maturities. *Journal* of Agricultural and Food Chemistry, 54, 8567–8573.
- Ferreira, V., López, R., & Cacho, J. F. (2000). Quantitative determination of the odorants of young red wines from different grape varieties. *Journal of the Science of Food and Agriculture*, 80, 1659–1666.
- Francis, I. L., & Newton, J. L. (2005). Determining wine aroma from compositional data. Australian Journal of Grape and Wine Research, 11, 114–126.
- Gawel, R. (1998). Red wine astringency: A review. Australian Journal of Grape and Wine Research, 4, 74–95.
- Gomez, E., Laencina, J., & Martinez, A. (1994). Vinification effect on changes in volatile compounds of wine. *Journal of Food Science*, 59, 406–409.
- Guth, H. (1997). Quantification and sensory studies of character impact odorants of different white wine varieties. *Journal of Agricultural and Food Chemistry*, 45, 3027–3032.
- Keller, M., & Hrazdina, G. (1998). Interaction of nitrogen availability during bloom and light intensity during veraison. II. Effects on anthocyanin and phenolic development during grape ripening. *American Journal of Enology and Viticulture*, 49, 341–349.
- Kennedy, J. A., Matthews, M. A., & Waterhouse, A. L. (2000). Changes in grape seed polyphenols during fruit ripening. *Phytochemistry*, 55, 77–85.
- Kennedy, J. A., & Jones, G. P. (2001). Analysis of proanthocyanidin cleavage products following acid-catalysis in the presence of excess phloroglucinol. *Journal of Agricultural and Food Chemistry*, 49, 1740–1746.
- Kennedy, J. A., Matthews, M. A., & Waterhouse, A. L. (2002). Effect of maturity and vine water status on grape skin and wine flavonoids. *American Journal of Enology and Viticulture*, 53, 268–274.
- Kennedy, J. A., & Taylor, A. W. (2003). Analysis of proanthocyanidins by high-performance gel permeation chromatography. *Journal of Chro*matography A, 995, 99–107.
- Kovac, V. E., Alonso, E., Bourzeix, M., & Revilla, E. (1992). Effect of several enological practices on the content of catechins and proanthocyanidins of red wines. *Journal of Agricultural and Food Chemistry*, 40, 1953–1957.
- Lamuela-Raventos, R. M., & Waterhouse, A. L. (1994). A direct HPLC separation of wine phenolics. *American Journal of Enology and Viticulture*, 45, 1–5.
- Mazza, G. (1995). Anthocyanins in grapes and grape products. Critical Reviews in Food science and Nutrition, 35, 341–371.
- Mistry, T. V., Cai, Y., Lilley, T. H., & Haslam, E. (1991). Polyphenol interactions. Part 5. Anthocyanin co-pigmentation. *Journal of the Chemical Society, Perkin Transactions, 2*, 1287–1296.

- Monagas, M., Gómez-Cordovés, C., Bartolomé, B., Laureano, O., & Da Silva, R. J. (2003). Monomeric, oligomeric, and polymeric flavan-3-ol composition of wines and grapes from *Vitis vinifera* L. Cv. Graciano, Tempranillo, and Cabernet Suavignon. *Journal of Agricultural and Food Chemistry*, 51, 6475–6481.
- Nunan, K. J., Sims, I. M., Bacic, A., Robinson, S. P., & Fincher, G. B. (1998). Changes in cell wall composition during ripening of grape berries. *Plant Physiology*, 118, 738–792.
- Nykänen, L. (1986). Formation and occurrence of flavor compounds in wine and distilled alcohol beverages. *American Journal of Enology* and Viticulture, 37, 84–96.
- Ojeda, H., Andary, C., Kreava, E., Carbonneau, A., & Deloire, A. (2002). Influence of pre-and postveraison water deficit on synthesis and concentration of skin phenolic compound during berry growth of *Vitis vinfera cv.* Shiraz. *American Journal of Enology and Viticulture*, 53, 261–267.
- Oliveira, C., Barbosa, A., Silva Ferreira, A. C., Guerra, J., & Guedes de Pinho, P. (2006). Carotenoid profile in grapes related to aromatic compounds in wines from Douro region. *Journal of Food Science*, 71, S1–S7.

- Pastor del Río, J., & Kennedy, J. A. (2006). Development of proanthocyanidin in *Vitis vinifera* L. cv. Pinot noir grapes and extraction into wine. *American Journal of Enology and Viticulture*, 57, 125–132.
- Peyrot des Gachons, C., & Kennedy, J. A. (2003). Direct method for determining seed and skin proanthocyanidin extraction in red wine. *Journal of Agricultural and Food Chemistry*, 51, 5877–5881.
- Sabon, I., Revel, G., Kotseridis, Y., & Bertrand, A. (2002). Determination of volatile compounds in Grenache wines in relation with different terroirs in the Rhone Valley. *Journal of Agricultural and Food Chemistry*, 50, 6341–6345.
- Sáenz-López, R., Fernandez-Zurbano, P., & Tena, M. T. (2004). Analysis of aged red wine pigments by capillary zone electrophoresis. *Journal of Chromatography A*, 1052, 191–197.
- Souquet, J. M., Cheyner, V., Brossaud, F., & Moutonet, M. (1996). Polymeric proanthocyanidin from grape skin. *Phytochemistry*, 43, 509–512.
- Spayd, S. E., Tarara, J. M., Mee, D. L., & Ferguson, J. C. (2002). Separation of sunlight and temperature effects on the composition of *Vitis vinifera* cv. Merlot berries. *American Journal of Enology and Viticulture*, 53, 171–182.