

A Comparison of the Color Components and Color Stability of Red Wine from Noble and Cabernet Sauvignon at Various pH Levels

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A study was designed to compare the color components and color stability of red wine from Noble (Vitis rotundifolia) and Cabernet Sauvignon (Vitis vinifera) at four pH levels (2.8, 3.0, 3.3, 3.8). Noble browned to a much greater extent and lost more color after 10 and 16 months than did Cabernet, and Noble did not increase in chemical age (level of polymeric anthocyanin) to nearly the extent that Cabernet did. This lack of anthocyanin-tannin polymerization in Noble seems to be responsible for the color instability. A higher pH resulted in greater browning and color loss in both species, but in Noble to a greater extent than in Cabernet. Greater anthocyanin-tannin polymerization was probably responsible for the greater color stability at lower pH.

Muscadine grapes (*Vitis rotundifolia*) are the most widely planted grapes in the south and southeast United States because of their suitability in these areas. Most of the commercial muscadine grape crop is used to produce wine. Wine made from suitable cultivars (2,6,7,16) of muscadine grapes possesses a very fruity, unique character that appeals to many people in the South. However, muscadine grape products are very susceptible to browning and overall loss of color quality during processing and storage (1,8,9,10,11,18,21). This color instability is severely limiting the marketability of red muscadine wines.

Several factors have been shown to influence the color quality and stability of red muscadine wines. The anthocyanin content and composition and conditions of processing and storage have been shown to have major effects on the color and stability of red muscadine products (1,2,3,8,10,11,16,18). Muscadine grapes contain only the 3,5-diglucoside anthocyanins (1), which have been reported to be more susceptible to browning than are the monoglucoside anthocyanins (17). This might indicate why red muscadine wines tend to brown.

The effects of pH on the color of red *Vitis vinifera* wines has been well documented (5,23,24,26,27,28). In general, as the pH rises from 3.0 to 4.0, the colorless pseudobase form of the anthocyanin becomes increasingly dominant over the red carbonium ion form. The blueviolet anhydro base form of the anthocyanin also begins to appear as the pH approaches 4.0. These effects of pH have also been observed in red muscadine wine (18).

In the same research (18), red muscadine wine with a higher pH browned to a much greater extent than did wine with a lower pH. Lower pH wine also had a greater loss of pH-responsive anthocyanins than higher pH wine, which indicated greater polymerization of anthocyanins at lower pH. The formation of various anthocyanin-tannin complexes or polymers during aging of red wines has been well documented (4,5,12,15,22,23), and these polymers have been shown to stabilize the color of *Vitis vinifera* red wines (19,29).

Research is needed to determine whether lack of anthocyanin-tannin polymerization is related to browning of red muscadine wine. To do this, the color and anthocyanin polymerization of red muscadine wine were compared to those of Cabernet Sauvignon (*V. vinifera*) which has stable red color and only the monoglucoside anthocyanins (21). Additionally, there is a need to compare the effects of pH on the color and color stability of red muscadine wine and red *vinifera* wine since these two wines contain different types of anthocyanins (diglucoside vs. monoglucoside) and should react differently to pH (23).

Therefore, the purpose of this study was to compare the color, color stability and anthocyanin-tannin polymerization of wine made from the red cultivar Noble with wine made from Cabernet Sauvignon at various pH levels.

Materials and Methods

Noble and Cabernet grapes were obtained from commercial vineyards in Arkansas in 1982. The grapes were hand harvested at commercial harvest and transported to the University of Arkansas Food Science Department in Fayetteville. The grapes of both species were crushed within 12 hours after harvest, 100 ppm SO₂ was added as potassium metabisulfite, and the percent soluble solids was adjusted to 22% with dry sugar. The musts were placed in polyethylene containers and fermented at about 25°C with *Saccharomyces cerevisiae*, Montrachet. The musts were pressed at about 6° Brix and allowed to finish fermenting at 25°C in glass carboys. The wines were fermented to dryness, racked, and cold stabilized at 3 to 4°C for two months. The wines were stored in glass carboys at 4°C until treatments could be established (ca one month).

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Four pH levels (2.8, 3.0, 3.3, 3.8) were established in the two wines using CaCO₃ and 10% hydrochloric acid. The levels of CaCO₃ and HCl that were needed to achieve the desired pH were determined through preliminary trials. The Noble had an initial pH of 3.0, and this was used as one pH level. The 2.8 pH treatment for the Noble was established by adding 5 mL of 10% HCl/L wine. The 3.3 and 3.8 pH treatments were established by adding

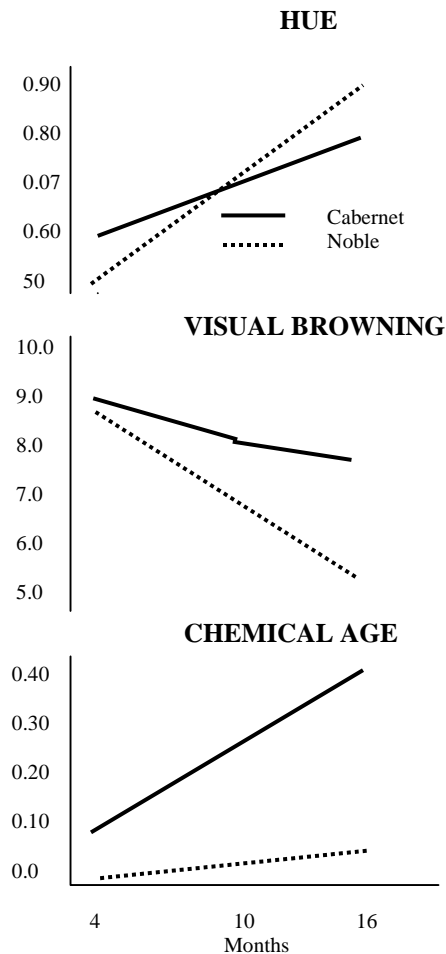


Fig. 1. Interactive effects of species x storage on the hue, visual browning and chemical age.

The color characteristics and chemical age (level of polymeric anthocyanins) were determined by the method of Somers and Evans (24) using a Varian (Series 6345) double-beam spectrophotometer. The spectra of the wines were not recorded as the procedures specified. A slit width of 1.0 nm was used for all determinations and a 1 or 10 mm pathlength was used, depending on the particular determination. All absorbancies were corrected to the 10 mm path length. The wine hue was calculated as the ratio of the absorbance at 520 nm to the absorbance at 420 nm (23). The chemical age, or level of polymeric anthocyanin, was calculated as the A_{SO_2}/A_{HCl} , where $A_{SO_2} = A$ at 520 nm after reacting the wine with excessive SO₂, and $A_{HCl} = A$ at 520 nm after acidifying the wine to less than pH 1.0 with HCl (23). The ionization of anthocyanin (%) was calculated as $(A \text{ at } 520 \text{ nm} - A_{SO_2}) / [(A_{HCl} - 5/3) (A_{SO_2})] \times 100$ (23) and represents the anthocyanins in the red carbonium ion or colored form.

For statistical analysis, all data were subjected to factorial analysis of variance. Duncan's multiple range test was used to separate means of the main effects. Least significant difference (LSD) was used to separate means of the significant interactions.

Results and Discussion

The use of CaCO₃ and 10% HCl were effective in altering the pH of Noble and Cabernet wines to equivalent levels (Table 1). The adjustment of pH resulted in expected changes in the titratable acidity levels. The pH and titratable acidity levels that were established initially (4 mo) did not change much after 10 or 16 months.

1 g CaCO₃/L wine and 2 g CaCO₃/L wine, respectively. CaCO₃ has been shown to lower acidity and increase pH of wines through precipitation of tartaric and malic acid (13,14,25). The CaCO₃ was added to cold wine (5°C) and allowed to settle for four days at 5°C. The Cabernet had an initial pH of 3.65. The 2.8, 3.0 and 3.3 pH treatments for Cabernet were established by adding 27.5 mL, 20.0 mL and 13.0 mL of 10% HCl/L wine, respectively. The 3.8 pH treatment for Cabernet was established by adding 0.3 g CaCO₃/L wine as described previously. The pH and titratable acidity were checked for each treatment after the pH adjustments were made, and no further adjustments were needed to establish the pH levels.

The wines were bottled in 400 mL round wine bottles and sealed with screw-on closures. All the wines contained 20 to 25 ppm free SO₂ at the time of bottling. The wines were analyzed initially (chemical age: four months old) and after six and 12 months of storage in the dark at 20°C (10 and 16 months old). The experiment was designed as a factorial with three replications.

The pH was determined with a glass electrode and a Corning Model 130 pH meter that had been standardized to pH 4.00 and 7.00 with standard buffer solution. Titratable acidity was determined by diluting 5 mL of wine to 125 mL with deionized water and titrating to pH 8.2 with 0.1 N NaOH. Titratable acidity is reported as milliequivalents (meq) of acid. The color of the wine was also rated visually for browning (1 = severe browning, 5 = borderline acceptance, 10 = no browning) by five trained panelists.

Table 1. Effects of acidity adjustments on the pH and titratable acidity of Noble and Cabernet wines.

Treatment	pH			Titratable acidity (meq)		
	4 mo	10 mo	16 mo	4 mo	10 mo	16 mo
<i>Noble</i>						
5 mL 10% HCl/L	2.78d ^z	2.79d	2.79d	0.45a	0.46a	0.45a
None	2.99c	3.01c	2.99c	0.42b	0.42b	0.43b
1 g CaCO ₃ /L	3.32b	3.31 b	3.28b	0.34c	0.36c	0.35c
2 g CaCO ₃ /L	3.79a	3.77a	3.79a	0.27d	0.29d	0.27d
<i>Cabernet</i>						
27.5 mL 10% HCl/L	2.80d	2.84d	2.80d	0.58a	0.54a	0.54a
20.0 mL 10% HCl/L	3.06c	3.05c	3.06c	0.55b	0.51 b	0.51 b
13.0 mL 10% HCl/L	3.31b	3.30b	3.32b	0.51c	0.47c	0.48c
0.3 g CaCO ₃ /L	3.80a	3.78a	3.79a	0.42d	0.39d	0.39d

^zMeans within storage time and species separated by Duncan's multiple range test at the 5% level.

The interactive effects of species X storage showed that Noble had better color initially (4 mo), but had browned to a much greater extent and lost more redness after 10 and 16 months of storage than had Cabernet, as indicated by higher hue values and lower visual browning ratings (Fig. 1). This greater decrease in color quality of

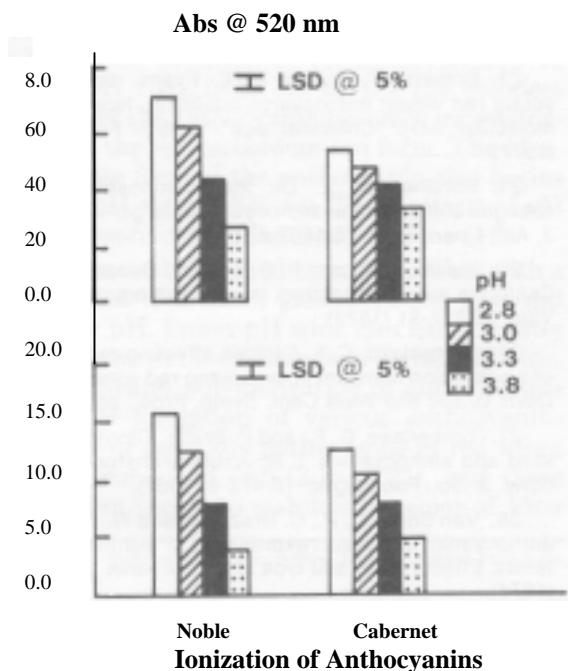


Fig. 2. Interactive effects of species x pH on the A at 520 nm and ionization of anthocyanins (average of 3 storage times).

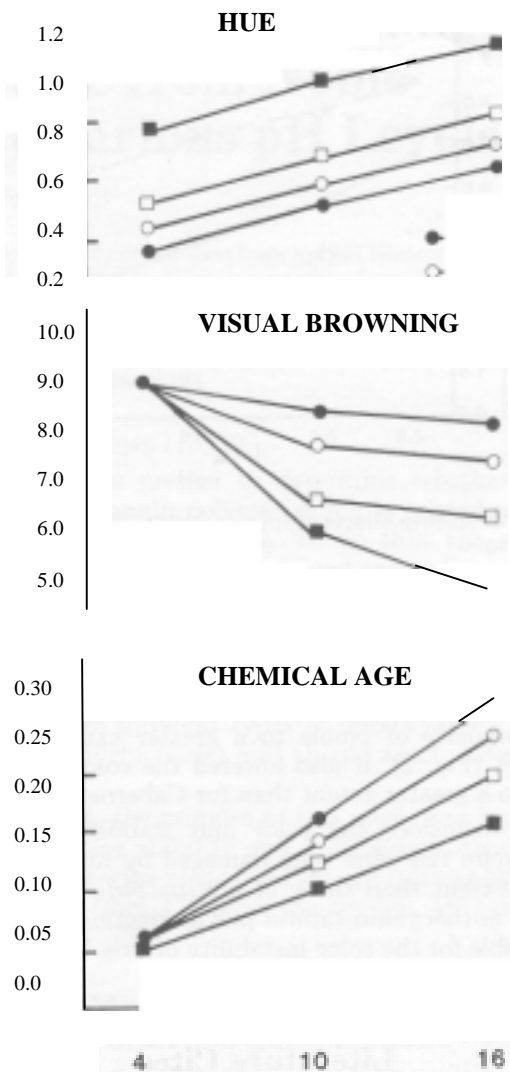


Fig. 3. Interactive effects of pH x storage on the hue, visual browning and chemical age.

The interactive effects of pH x storage indicate that wine from both species browned to a greater extent and lost more color (lower visual browning rating and higher hue) after storage for 10 and 16 months at a higher pH (Fig. 3). A higher pH wine also had lower chemical age after storage (Fig. 3). This lower anthocyanin-tannin polymerization at higher pH seems to be a primary reason for increased browning and loss of color. The red carbonium ion form of the anthocyanins (ionized anthocyanins) may be more readily incorporated into a tannin polymer than the pseudobase form of the anthocyanin. Previous research by Sims and Morris (18) has also shown that a red muscadine wine browned to a greater extent and had lower chemical age at a higher pH.

The interaction of species x pH indicated that Noble browned (lower visual browning ratings) to a greater extent at higher pH than Cabernet after 16 months of storage (Fig. 4). The lack of anthocyanin-tannin polymerization in Noble rendered the color much more unstable at a higher pH. Noble had unacceptable levels of visual browning after 16 months if the pH was 3.3 or higher, while Cabernet had acceptable levels of browning at all pH levels. Thus, a higher pH not only lowered the color intensity of Noble to a greater extent than for Cabernet (Fig. 2), it also lowered the color stability of Noble to a greater extent than for Cabernet.

In conclusion, the color and stability of a *Vitis rotundifolia* red wine were damaged by higher pH to a greater extent than those of a *Vitis vinifera* red wine. Lack of anthocyanin-tannin polymerization seems to be responsible for the color instability of this *Vitis rotundifolia* red wine.

Noble was related to the chemical age (level of polymeric anthocyanins). Noble had much lower chemical age after all storages than did Cabernet and did not increase in chemical age during storage (Fig. 1). Thus, red muscadine wine does not incorporate anthocyanins into tannin polymers to any large extent, and consequently, has unstable color. Other research (19,29) has shown that increased polymerization of anthocyanins stabilizes red wine color. Red muscadine wines may lack the necessary tannin species (leucoanthocyanins and/or catechins) for binding with anthocyanins, or the diglucoside anthocyanins are not as readily incorporated into a tannin polymer as are the monoglucoside anthocyanins.

A higher pH lowered the color intensity (A at 520 nm) of both wines, but the interactive effects of pH x species (average of three storage times) showed that a higher pH decreased the color intensity of Noble to a greater extent than for Cabernet as shown by the A at 520 nm (Fig. 2). The averages of three storage times are presented because the interaction showed the same results at all storages.

This greater decrease in color intensity of Noble at higher pH was due to greater decreases in the ionization of anthocyanins in Noble at higher pH (Fig. 2). The ionization of anthocyanins indicates the percentage of anthocyanins in the colored or red carbonium ion form (23). The diglucoside anthocyanins in Noble have lower pH values than do the monoglucoside anthocyanins in Cabernet (23). Thus, as the pH increases, more of the ionized or colored anthocyanins in Noble would be converted to the colorless form, as compared to Cabernet. Other research has shown that a higher pH lowered the ionization of anthocyanins in *Vitis vinifera* wines (23), and the general effects of pH on the color of these wines agree with other research (5,23,24,26,27,28). However, because of the presence of diglucoside anthocyanins, the color of the *Vitis rotundifolia* red wine was affected by high pH to a greater extent than was the color of the *Vitis vinifera* red wine.

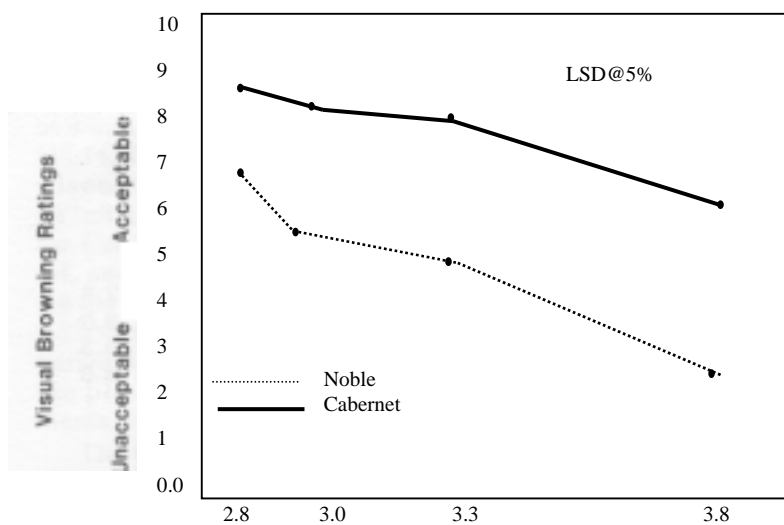


Fig. 4. Interactive effects of species \times pH on the visual browning after 16 mo.

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