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Title: **"Maceration variables affecting phenolic composition in commercial-scale Cabernet Sauvignon wimemaking trials"**

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Many authors have studied phenolic extraction and how it can be manipulated by winemaking practices. But most of these studies used small-scale fermentations, which often failed to mimic what actually takes place at the large scale. In this article, the authors compare the effect of common winemaking procedures on phenolic composition using commercial-scale fermentations.

• First, let us review the role of the main phenolic compounds. Young red wine color is mainly due to the concentration of anthocyanins and the degree of copigmentation. In contrast, aged wine color, or stable color, depends on the formation of polymeric pigments, a product of proanthocyanidins, (also called condensed tannins or simply tannins) and anthocyanins. Flavanols, another class of phenols, contribute to a wine's bitterness and astringency. Flavanol monomers are more bitter than astringent. However, as flavanol monomers condense, they become more astringent, and less bitter.

• Before summarizing how different winemaking practices affect these compounds, it's helpful to review the methodology used to separate them. The authors use two different techniques: normal phase high pressure liquid chromatography (HPLC), and spectrophotometry. Combining both, they are able first to separate two fractions: **proanthocyanidins** and **colored proanthocyanidins** (the latter absorbing at 520 nm). Then, using HPLC, they further separate proanthocyanidins into 1) low molecular weight proanthocyanidins (LMWP) and 2) high molecular weight proanthocyanidins (HMWP). They do the same with colored proanthocyanidins to obtain 3) low molecular weight colored proanthocyanidins (LMWCP) and 4) high molecular weight colored proanthocyanidins (HMWCP). Finally, using both spectrophotometry and HPLC, they are able to separate the compounds that contribute to color into three components: 5) polymeric pigments, 6) copigmented color, and 7) free anthocyanins. Notice the latter three are all color components, as opposed to "overall color", "red color", or simply "color", which all refer to the more traditional way of measuring color: the absorbance at 520 nm.

• The authors study how these 7 fractions are affected by the following common winemaking practices: increased fermentation temperature, heat at the end of fermentation, extended maceration, the use of a rotary fermentor, the addition of oaks chips, and the use of color enzymes. They also compare the effects across 4 California viticultural areas: Lodi, Paso Robles, Sonoma and Monterey. To better mimic a production situation, wines were aged for 14 months in barrel and 4 months in bottle before analysis.

• **1) Increased fermentation temperature** . This parameter was studied only with grapes from Paso Robles. Increasing the temperature from 24^{o}C to 32^{o}C caused an important increase in HMWP, the proanthocyanidins of high molecular weight. It also increased the contribution to color due to copigmentation, and decreased the contribution of free anthocyanins. The authors note that these results disagree with previous studies. But they also point out that differences in variety, fermentation scale, time before analysis, or method of analysis would likely make results difficult to compare.

• **2) Heat at the end**. Passing the wine through a heat exchanger at the end of fermentation until it reached 32°C caused a significant increase in proanthocyanidins of high molecular weight (HMWP), in 3 of the 4 sites studied. Heat at the end also affected the contribution to color of anthocyanins, copigmentation and polymeric pigments, but these differed depending on the site. For Lodi and Paso Robles, all of these factors increased, with an overall increase in color. For Sonoma and Monterey, copigmentation also increased with a concomitant decrease in free anthocyanins. Thus, both heating at the end and increased fermentation temperature were consistent in two effects: they both increased HMWP and copigmented color.

• **3) Extended maceration**. Keeping the wine in contact with the pomace for 20 additional days after dryness caused a significant increase of both types of proanthocyanidins, HMWP and LMWP, for all of the vineyards. It also increased the high molecular weight colored proanthocyanidins (HMWCP), but only in Sonoma. In contrast, polymeric pigment measured by spectrophotometer increased for all vineyards. This illustrates a compositional difference between HMWCP and polymeric pigment, still not well understood. As for overall color, results were clearly mixed: extended maceration increased color in Lodi and Paso Robles, but it decreased color in Sonoma and Monterey.

• **4) Rotary fermentor**. This parameter was studied only with Lodi and Paso Robles fruit. Fermenting in a rotary fermentor for the first 4 days (rotating twice in each direction every 3 hours) significantly decreased both proanthocyanidins and colored proanthocyanidins. Polymeric pigments and the free anthocyanins measured with spectrophotometer also decreased. Interestingly, rotary fermentation increased copigmentation only for the Paso Robles fruit. Color was either lower or about the same as the control, for both Lodi and Paso Robles. These results are in agreement with previous studies. The authors propose that rotary tanks produce a strong mechanical maceration that tends to yield components with low degree of polymerization. They also point out that residence time in the rotary fermentor might have been insufficient to achieve full extraction (after 4 days, fermentations were finished in a regular tank).

• **5) Oak chips**. Loose French oak chips added at the beginning of fermentation at a rate of 3.6g/l had inconsistent results. HMWP increased for Lodi, but decreased for Sonoma. Similarly, LMWP, decreased only in Paso Robles. The most common effect was a decrease in free anthocyanins in 3 of the 4 sites, with the exception being Lodi. As for overall color, Lodi showed an increase, and Sonoma and Monterey a decrease. The authors note that the fact that chips turn red at the end of fermentation might account for some of the red color loss. Also, chips contain components that can alter the equilibrium of phenolic compounds in different ways depending on the original composition of the must, which would explain such a variable response.

• **6) Color enzyme.** This parameter was studied only for Sonoma and Monterey. The addition of a color enzyme (Rapidase) the first day of fermentation decreased overall color, or had about the same color as the Control, for both sites studied. Free anthocyanins also decreased for these two vineyards. Enzymes did increase the amount of higher molecular weight proanthocyanidins (HMWP), as well as the amount of colored proanthocyanidins. The authors note that even though color enzymes failed to increase the color of the wine, they did increase the amount of proanthocyanidins, which could favor future colored proanthocyanidin formation.

• **Grape composition**. The researchers found an interesting fact: a given winemaking operation did not always had the same effect, depending on the source of the grapes. For example, the grapes sourced from the vineyard in Sonoma had by far the highest concentration of proanthocyanidins and color regardless of the winemaking operation. Polymeric pigments and free anthocyanins were also the highest for this site. On the other hand, the vineyard in Monterey was the site with the highest copigmented color for all of the treatments. As the authors state, the original grape composition, dictated by the growing area and the vineyard management techniques, was able to overwhelm any differences caused by the winemaking treatment itself.

So how does grape composition compare among these sites? The authors did look at must composition for all the sites. Sonoma was the site with the highest Brix, while Monterey was the site with the lowest Brix, something that would likely have affected the parameters studied. Interestingly, both Sonoma and Monterey had the highest TA and the lowest pH, when compared to Paso Robles and Lodi.

In summary, not every practice intended to increase phenolic extraction worked for every site. Also, researchers are still trying to understand what a change in a specific phenolic fraction means in terms of its sensory impact on the wine. The phenolic fraction changes found by the authors are summarized in the table below.

		Fermentation Temperature (Paso Robles only)	**Heat @ End**	**Extended Maceration**	**Rotary Fermentor** (Paso Robles and Lodi only)	**Oak Chips**	**Color Enzymes** (Sonoma and Monterey only)
Proanthocyanidins	Large	↑	↑	↑	↓		↑
	Small	—		↑	↓		
Colored Proanthocyanidins	Large	—	↑		↓		↑
	Small	—			↓		
Contribution to color of:	Anthocyanins	↓	↑ (↓ Sonoma, Monterey)		↓	↓	↓
	Copigmentation	↑	↑		↑		
	Polymeric pigments	—	↑	↑	↓		
Red color (A520)		—	↑	↑ (↓ Sonoma, Monterey)	↓	↓ (↑ Lodi)	↓

Only main trends presented.

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