

WINEMAKING

Phenolic extraction in red wine production

BY James A. Kennedy & Catherine Peyrot des Gachons,
 Department of Food Science & Technology,
 Oregon State University, Corvallis, OR

Wine quality is commonly believed to be related to fruit quality. For red wine, another critical parameter is the period of time when phenolic extraction occurs: maceration.³

Not only is the style of wine clearly affected by maceration (where any given lot of red wine grapes is capable

of becoming a rosé or a full-bodied dry red wine), but also even when a specific style of wine is targeted, the subtleties of extraction can mean the difference between a balanced and an unbalanced wine.

The variables associated with maceration involve phenolics to a great degree. Phenolics are important for the overall color of red wine and its astringency, or more broadly speaking, texture. Therefore, the focus of maceration is to optimize the color and texture of wine.

Combining the variability associated with a vintage with the variability in

approaches that winemakers can take toward production makes for a bewildering array of possibilities regarding ultimate wine composition. Advances in maceration techniques are important in the evolution of red wine production. New techniques are developed with the intent to provide ideal conditions for phenolic extraction and development.

Yet given the tremendous variability in fruit composition, the response of fruit to any given maceration technique is highly variable. To customize maceration techniques to fruit composition, it is helpful to consider the fun-

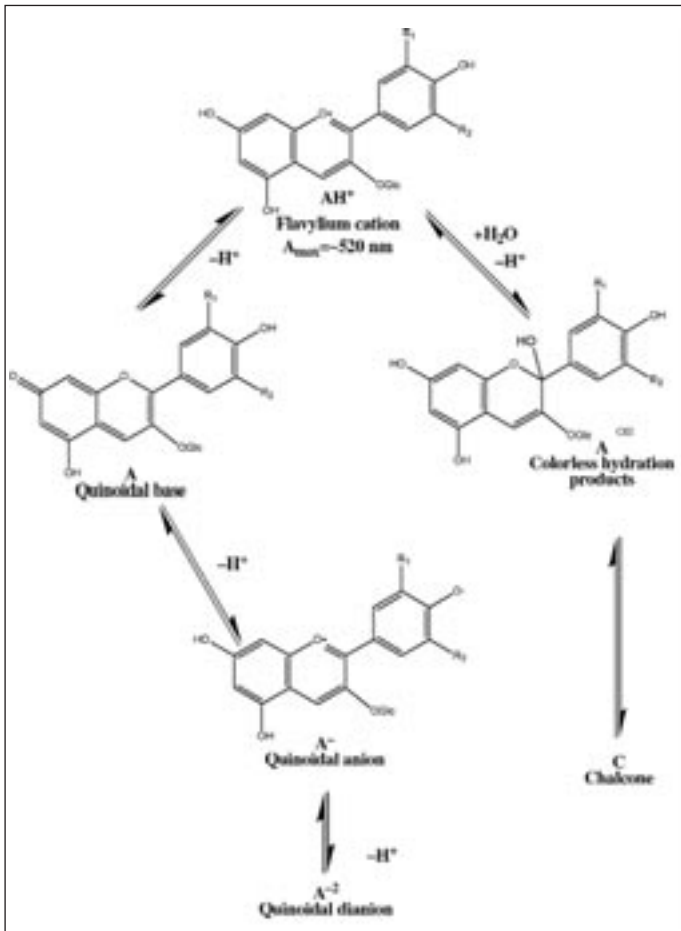


Figure 1. General anthocyanin structure and equilibrium forms.

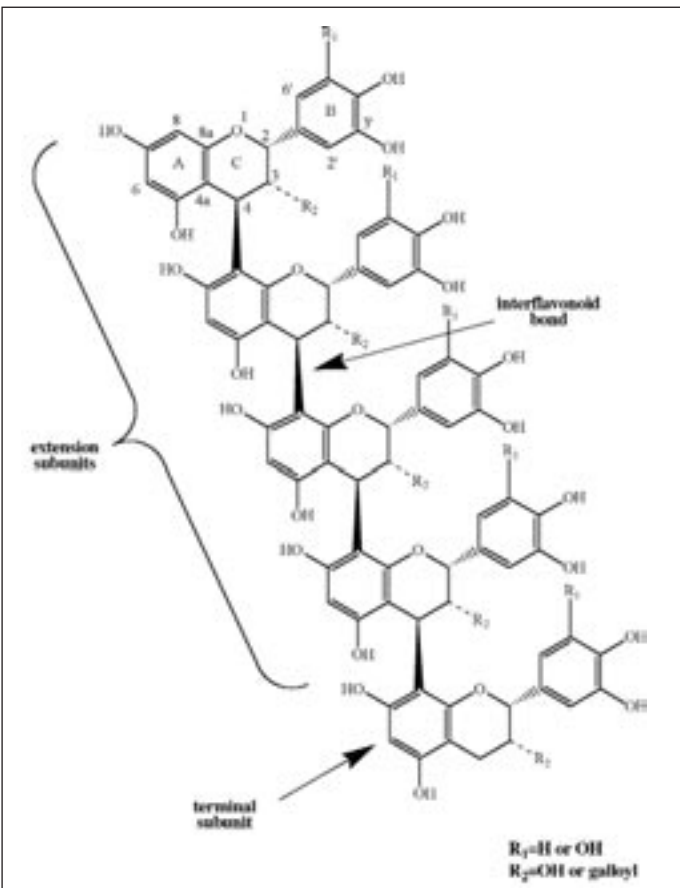


Figure 2. General grape tannin structure indicating subunit and major interflavonoid bond location. Tannins can vary from a single subunit to over 80 subunits in length.

WINEMAKING

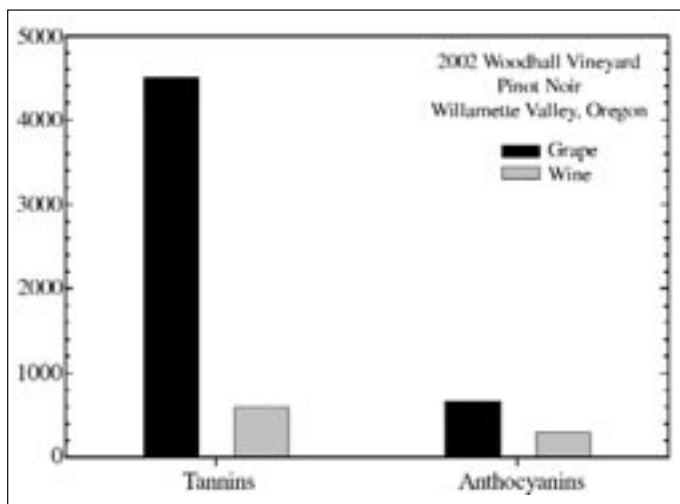


Figure 3. Amount of anthocyanins and tannins in Pinot Noir grapes grown during the 2002 growing season and the equivalent amounts in the corresponding wine (expressed in mg/kg original fruit weight).

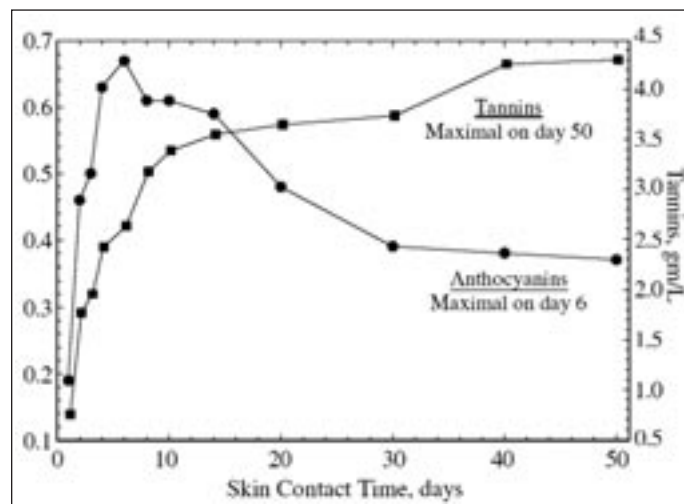


Figure 4. Generalized anthocyanin and tannin extraction during fermentation (after Ribéreau-Gayon, 1970).

damental variables that affect the extraction of phenolic compounds.

Compounds of interest

First, let's review the compounds of interest: anthocyanins (Figure I) and tannins (Figure II), which are respectively responsible for color and astringency in red wine.^{4,9} These compounds are localized in the solid parts of the grape berry, with the anthocyanins, in almost all instances, restricted to the skin tissue, and the tannins localized in the skin and seed tissue.

The ultimate goal of maceration is to be able to extract a sufficient amount of phenolic material so that a satisfactory balance is achieved. For dry red table wine production, the winemaker generally would like to maximize color extraction while maintaining a balanced wine in terms of tannin extraction (more on this below).

Anthocyanins (Figure I), can exist in several forms, only one of which gives wine its red color (the flavylium form). This form makes up a small proportion of the overall pool of anthocyanins extracted into wine, with the colorless hydration product making up the majority of the anthocyanins. The molecular weight of anthocyanins covers a small range, roughly 450 to 500 g/mol. At commercial maturity, the concentration of anthocyanins in grapes will vary

from 500 to 1,200 mg/kg. The variation is due to variety, location, vintage, and cultural practices.

Tannins are the second class of compounds of major importance (Figure II), and unlike anthocyanins, their molecular weight can vary tremendously, from a low of roughly 300 g/mol to an upper limit in excess of 20,000 g/mol having been reported. Seed tannins have a lower overall molecular weight distribution than skin tannins, and essentially all of the tannins that have bitterness attributes (lowest molecular weight tannins) are seed-derived.

At harvest, the overall concentration of tannins in grapes is roughly 1,000 to 6,000 mg/kg, with the concentration of tannins in the seed generally one to three times that in the skin. Again, variations due to grape variety, location, vintage, and cultural practices are well established.

Anthocyanin and tannin concentration in wine

If you compare the concentration of anthocyanins and tannins found in grapes with their concentration in wine, it is clear that not all of the grape material ends up in the wine.

Assuming that an average commercial fermentation yields 150 gallons (570 L) of wine per ton of fruit (0.62 L/kg), if all of the anthocyanins and tannins were extracted into wine, a very dark

and astringent wine would result. The much lower amount of color and tannin in wine is generally attributable to a combination of fining, incomplete extraction, and the reaction of these compounds during fermentation.

How much color and tannin are actually extracted? Using data collected during the 2002 vintage (Figure III), and for color and tannin extraction, a small fraction of the total amount present in the fruit was actually extracted.⁵

In this study, the maximum amount of color that could be extracted was roughly 50% of what was available, and a balanced wine was achieved when only 15% of the tannins were extracted. These numbers, while informative, tell only part of the extraction story. To fully understand the issues of extraction you need to follow the extraction of these components during maceration.

Extraction of anthocyanins and tannins

...the broad fact remains that in all cases the maximum of color was reached, and its diminution began, long before the fermentation was completed....But during the whole time, there was a steady increase in the tannin contents.

E.W. Hilgard, Dec. 30, 1887

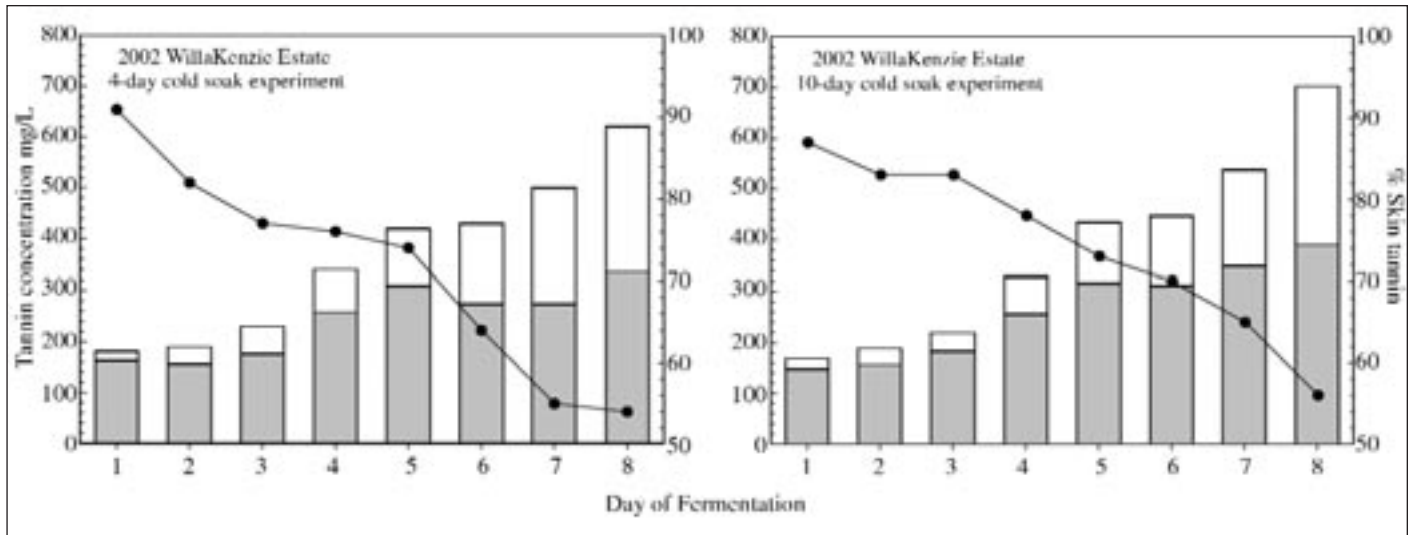


Figure 5. Pinot Noir fermentations with 4-day (upper) and 10-day (lower) cold soaks prior to fermentation showing skin and seed tannin extraction (gray and white bars respectively), and with the % skin tannin (line graph) shown.

As evidenced above, the general extraction pattern of anthocyanins and tannins has been known for some time. Anthocyanin extraction generally peaks prior to the end of fermentation (two to six days) and tannin extraction increases continuously (Figure IV).

When preparing this report, we conducted a cursory review of the issues that researchers and winemakers have dealt with over the past century, and how their approaches have since changed. What is particularly revealing is that maceration techniques in use a century ago are eerily similar to techniques used today (such as submerged cap fermentations, use of pressure from CO₂ evolution during fermentation to pump fermenting must onto the cap, elevated SO₂ amounts to enhance anthocyanin extraction). What we concluded from this exercise, and what readers should realize is the following:

- Phenolic extraction issues and concerns are perennial, they rarely change;
- Wine production techniques with regard to phenolic extraction haven't changed very much over the years.

Yes, our level of control has improved dramatically over the past century, and yes, there are some new tricks in the bag, but in large part, the issues and approaches are the same.

So, as you read through the latest and greatest innovations in phenolic extraction practices, the daunting equipment options and groovy techniques, it should be comforting to know that there really is nothing new under the rainbow.

What you want to know is: How do you make a specific style of wine from a particular variety? Phenolic extraction boils down to controlling the diffusion, adsorption, and reactivity of anthocyanins and tannins.

Diffusion

Diffusion is simply the process by which a compound moves from a region of high concentration toward a region of lower concentration (such as from the plant cell into the wine). Considering the generally observed extraction curves for anthocyanins and tannins and the effects that wine processing variables have on the rate of these compounds' extraction, the overall process is consistent with diffusion (with a twist in the case of anthocyanins). The rate of diffusion is dependent upon the following:

1. Temperature
2. Molecular weight/size and type of molecule
3. Concentration gradient
4. Cell permeability
5. Surface area over the concentration gradient
6. Composition of extraction medium (such as ethanol concentration).¹⁵

In all instances except molecular size, these variables contribute positively to the rate of diffusion. That is, an increase in that variable will increase the rate of diffusion.

Past research tells us that, in any given fermentation, time and temperature are the two critical variables in determining the ultimate amount of anthocyanin and tannin present in wine.^{1,2,6,7,10,13,14,18} These are easily the most studied variables.

For anthocyanins, higher temperatures reduce the time to maximum concentration, and increase the maximal amount.

For tannins, higher temperatures increase the rate of extraction.

Besides the most obvious variables of time and temperature, the other variables undoubtedly also play a role in phenolic extraction. Determining their relative importance however is difficult because of the compound nature of their effects.

Regarding molecular size and the type of molecule, this can most easily be seen when you consider the extraction of anthocyanins and tannins. Anthocyanin concentrations increase more rapidly into wine than do tannins (Figure IV). A possible explanation for this is that the anthocyanins are much smaller in size than the tannins, and therefore, will diffuse more rapidly. Additionally, anthocyanins are structurally different than tannins, which may lead to diffusion differences as well.⁸

WINEMAKING

Explanations other than molecular size and chemistry can be presented to explain the observed differences between concentration changes in anthocyanins and tannins. The difficult-to-separate effects of concentration gradient, cell permeability, and surface area clearly affect the concentration increases observed in fermenting musts.

Anthocyanins and tannins are initially contained within the vacuole of the plant cell. As the plant cell dies, the membranes become leaky and their contents diffuse into the surrounding medium. From a production standpoint, some processes where these factors play a role are:

- Extent to which grapes are crushed;
- Punch-down, pump-over frequency and duration;
- Aspect ratio of the fermentor;
- Addition of SO₂;
- Addition of exogenous enzymes.

These process effects can be explained in one or more of the following ways:

- Disruption of cell membranes,
- Increase in exposed surface area,
- Increase in dispersive currents around concentration extremes.

These factors become particularly important with regard to tannin extraction. Since tannins are localized in two different tissues, and given that the sensory properties of these two tannin pools appears to be quite different, there is a considerable amount of interest in controlling not only the amount of tannin extracted into the wine, but also, controlling the compartment from which the tannins are derived.

Missing information

Unfortunately, tannin extraction from the skins and seeds is not understood very well at this time. Studies have been done, and they provide important information in a simplified extraction system.^{12,16} Fermenting musts, however, are incredibly complex systems.

We have reviewed some of the diffusional aspects of the system, yet there are other variables that affect the final amount of anthocyanins and tannins in wine. Figure IV demonstrates this very nicely. Although the anthocyanins are extracted with relative ease, they begin to decrease well before the end of fermentation. This has variously been ascribed to

adsorption (onto yeast and grape cell wall material), and/or reaction once extracted.

While diffusion is an important part of anthocyanin and tannin extraction, it by no means provides a complete picture of the extraction. In order to fully understand not only the effect of various extraction approaches on anthocyanin and tannin extraction, but also their sensory impact, it is necessary to develop methods that can be used to monitor actual fermentations.

New information

The American Vineyard Foundation is currently funding a research project to improve our understanding of maceration practice on phenolic extraction. The overall goals of the project are to monitor the quantity of tannin extracted from the individual seed and skin compartments, to understand the extent to which tannin proportions can be manipulated through cap management practices, and to understand the overall effect of skin-to-seed tannin proportion on red wine mouth-feel properties.

In our first year of experimentation, we developed an analytical method for determining skin and seed tannin extraction.¹¹ This analytical method was used to monitor the extraction in commercial-scale fermentations to provide a preliminary assessment of seed and skin tannin extraction. These experiments took place at WillaKenzie Estate, in the Willamette Valley in Oregon.

In this study, Pinot Noir fruit was harvested and underwent pre-fermentation maceration (~50°F/10°C). The purpose of this investigation was to understand how the duration of cold soaking (4 or 10 days) affected the proportion of skin tannin extracted into red wine. The experiments took place in two 3-ton open-top fermentors.

Following the cold-soak period, the musts were warmed, inoculated, and fermented. During fermentation, samples were taken daily (after punch-down) for analysis. The cap was managed by punch-down, the total for both treatments being similar at the time the wine was pressed (146 and 156 punch-downs for four and 10 days, respectively).

This experiment provides insight into some maceration dynamics (Figure V). Figure V contains the results for both treatments. Both fermentations progressed in a similar fashion, with minor differences in initial fruit composition and temperature during fermentation.

The rationale behind cold soaking prior to fermentation is that the maceration favors extraction of more hydrophilic material and, as such, it is believed that skin extraction is favored. From this experiment it was concluded that cold soak duration did not have a large affect on must/wine composition with regard to:

- Proportion of skin tannin,
- Amount of total tannin,
- Relative rates of tannin extraction.

As the fermentation progressed, the overall amount and proportion of seed tannin increased. Interestingly, the rate of tannin extraction varies in the pattern of increase. Toward the end of fermentation, the data for the treatments deviated, with extraction in the 10-day treatment increasing overall (although the proportion of skin tannin was similar to the four-day treatment). This may indicate that the extended period of time prior to fermentation (10-day treatment), resulted in more advanced grape tissue breakdown, and hence more extraction later in the fermentation.

Information that is being developed from this project will provide not only an improved understanding of the dynamics that affect phenolic extraction during maceration, but will also improve our ability to develop new techniques to control this tremendously important aspect of red wine production. ■

Acknowledgements

The authors gratefully acknowledge Bernard Lacroute and WillaKenzie Estate for cooperation and the use of their facilities. The Oregon Wine Advisory Board and the American Vineyard Foundation funded portions of the projects discussed.

References

1. Aubert, S., C. Poux (1969) "Extraction des composés Phénoliques du raisin II. Taux de passage dans les vins." *Ann. Technol. Agric.* 18:111-127.

2. Berg, H.W., M. Akiyoshi (1956) "The effect of contact time of juice with pomace on the color and tannin content of red wines." *Am. J. Enol. & Vitic.* 7:84-90.

3. Boulton, R. (1995) *Red Wines*. In: *Fermented Beverage Production* A.G.H. Lea and J.R. Piggott editors; Blackie Academic and Professional, New York.

4. Gawel, R. "Red wine astringency: A review." (1998) *Austral. J. Grape Wine Res.*, 4, 74-96.

5. Kennedy, J.A., Pastor, J.L., Watson, B.T. (2003) "Development of anthocyanins and tannins in Pinot noir grapes and their relative importance in wine." *Proceedings of the 2003 Oregon State University Winegrape Research Days* Corvallis, OR, pp.29-33.

6. Kovac, V.; Alonso, E.; Bourzeix, M.; Revilla, E. (1992) "Effect of several enological practices on the content of catechins and proanthocyanidins of red wines." *J. Agric. Food Chem.* 40:1953-1957.

7. Mayen, M., J. Merida, M. Medina (1994) "Free anthocyanins and polymeric pigments during the fermentation and post-fermentation standing of musts from Cabernet Sauvignon and Tempranillo grapes." *Am. J. Enol. & Vitic.* 45:161-166.

8. Nagel, C.W., L.W. Wulf (1979) "Changes in the anthocyanins, flavonoids and hydroxycinnamic acid esters during fermentation and aging of Merlot and Cabernet Sauvignon." *Am. J. Enol. & Vitic.* 30:111-116.

9. Noble, A.C. (1990) *Bitterness and astringency in wine*. In: *Developments in Food Science* 25. Bitterness in Foods and Beverages. Rouseff, R.L. (Ed), Elsevier: New York, 145-158.

10. Ough, C.S., M.A. Amerine (1961) "Studies on controlled fermentation V. Effects on color, composition and quality of red wine." *Am. J. Enol. & Vitic.* 12:9-19.

11. Peyrot des Gachons, C., J.A. Kennedy (2003) "Direct method for determining seed and skin proanthocyanidin extraction into red wine." *J. Agric. Food Chem.* Submitted.

12. Ribéreau-Gayon, P., J.C. Milhé (1970) "Reserches technologiques sur les composés phenoliques des vin rouges I. Influence des différentes parties de la grappe." *Conn. Vigne Vin* 4:63-74.

13. Ribéreau-Gayon, P., P. Sudraud, J.C. Milhé, A. Canbas (1970) "Reserches technologiques sur les composés phenoliques des

vin rouges II. Les facteurs de dissolution des composés phenoliques." *Conn. Vigne Vin* 4:133-144.

14. Scudamore-Smith, P.D.; Hooper, R.L.; McLaran, E.D. (1990) "Color and phenolic changes of Cabernet Sauvignon wine made by simultaneous yeast/bacterial fermentation and extended pomace contact." *Am. J. Enol. & Vitic.* 41:57-67.

15. Singleton, V.L., D.E. Draper (1964) "The transfer of polyphenolic compounds from grape seeds into wines." *Am. J. Enol. & Vitic.* 15:34-40.

16. Sun, B.S.; Pinto, T.; Leandro, M.C.; Ricardo da Silva, J.M.; Spranger, M.I. (1999) "Transfer of catechins and proanthocyanidins from solid parts of the grape cluster into wine." *Am. J. Enol. & Vitic.* 50:179-184.

17. Timberlake, C.F., P. Bridle (1976) "The effect of processing and other factors on the colour characteristics of some red wines." *Vitis* 15:37-49.

18. Zimman, A., W.S. Joslin, M.L. Lyon, J. Meier, A.L. Waterhouse (2002) "Maceration variables affecting phenolic composition in commercial-scale Cabernet Sauvignon wine-making trials." *Am. J. Enol. & Vitic.* 53:93-98.

Reprinted from:



58 Paul Drive, Ste. D, San Rafael, CA 94903 • 415-479-5819

Visit our website:

www.practicalwinery.com
to learn more about **PWV**.