Phenolic Analysis in White Wines and Juices at ETS Laboratories

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Steve began working for ETS Laboratory in 1995. The recent emphasis at ETS has been to develop analytical methods for measuring phenolic compounds in the vineyard that predict eventual wine phenolic composition.

He started Price Research Services, Inc., Corvallis Oregon in 1995 which focuses on research support for wineries, development of vineyard production practices for optimum quality.

The importance of phenolic compounds in red wines is so great that the phenolic composition of white wines is often overlooked. The critical phenolic components for white wines are not as well understood, the sensory effects of these compounds have not been studied in the same depth, and the effects of viticultural and winery processes on white phenolics are not as widely known as for red grapes and wines.

At ETS Laboratories we have offered phenolic analysis of red wine for over ten years. We analyze red grape phenolics and offer rapid analytical tools for monitoring phenolics in red fermentations. Although we do not advertise the capability, we also analyze white juices and wines for phenolic composition.

Red and white, what is the difference?

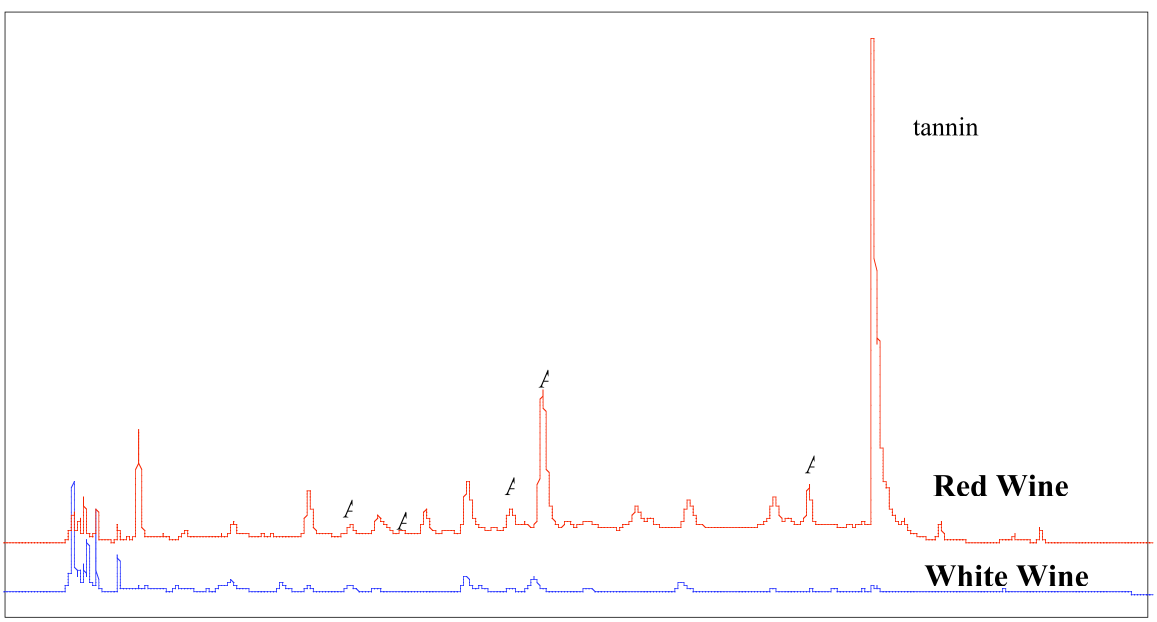
There are two major factors that cause the difference between red and white wine phenolic composition. Red grapes contain anthocyanins and red wines are fermented in the presence of grape skins and seeds.

The phenolic composition of white grapes is actually remarkably similar to red grapes. Although there is significant genetic variation between varieties, the only major difference between red grapes and white grapes is anthocyanins. Closely related varieties such as Pinot noir and Pinot blanc have identical phenolic composition of skins, seeds and juice with the lone exception of anthocyanins in the skins. A study of a white chimera in a Pinot noir red cluster (a cluster with half red grapes and half white) showed no differences in more than thirty phenolic compounds except for the five anthocyanins compounds found on the red Pinot noir side.

White grapes contain tannin in the skins, flavonols such as quercetin, tannin and flavan-3-ols in the skins and cinnamic acids in the pulp. The factors that influence phenolics in red grapes have the same effects in whites. Sun exposure causes an increase in tannin and flavonols in the skin, seed ripening reduces the extractability of the seed phenolics and ratios of juice to skins and seeds influence the potential phenolic composition of juices and wines.

The differences between red and white wine making have a greater effect on the phenolic composition of red and white wines than the effects of grape composition. With the exception of cinnamic acids in the pulp, phenolic compounds are found in the skins, seeds and stems. It is the extraction of these compounds during fermentation and maceration that create the major differences between red and white wines. Although the visual presence of anthocyanins dominates a comparison between red and white wines, it is the extraction of tannin and other phenolic compounds from the skins and seeds during winemaking that really sets red wines apart from whites. White wines typically contain 10 to 50 mg/L of tannin, red wines range from 250 to more than 2000 mg/L tannin.

A chromatogram of a red and white wine is shown below. Anthocyanins, marked with an A, are only a small part of the difference.



Phenolic compounds present in white wines

The primary grape phenolic compounds found in white wines are cinnamic acid esters, tannin, and lesser amounts of skin and seed components such as benzoic acids, flavan-3-ols, flavonols and flavanones. White wine also contains compounds modified in wine such as oxidation products of cinnamic acids, free cinnamic acids, tyrosol and flavonol aglycones.

At ETS, our standard white wine phenolic panel reports gallic acid, catechin, astilbin, caftaric acid, caffeic acid, grape reaction product, p-coumaric acid, quercetin glycosides, quercetin aglycones and tannin.

Gallic acid is a benzoic acid present in grape seeds, oak barrels and oak adjuncts. Gallic acid is typically in low concentration unless the wine has seen considerable new oak.

Catechin is a flavan-3-ol from grape seeds. Catechin seldom reaches significant levels in white wines. It is a useful marker of seed extraction related to skin contact or pressing.

Astilbin is found only in grape skins. It is a useful marker for skin extraction in pressing and skin contact studies.

Caftaric acid is present in grape pulp and grape skins along with coutaric and fertaric acid. These cinnamic acids are readily oxidized in the presence of grape oxidative enzymes. When oxidized, they form a reactive quinone that can oxidize other phenolic compounds. In the presence of glutathione, the quinone reacts to form **grape reaction product** (GRP), a caftaric acid-glutathione adduct. In the presence of additional oxygen GRP can oxidize further to form complex oxidative polymers. Caftaric acid can also loose its tartaric ester to form free **caffeic acid.** Similarly, coutaric acid can become **p-coumaric acid.** The cleavage of the ester bond is an enzymatic reaction caused by enzymes in microorganisms or by enzymes present in commercial enological enzyme preparations.

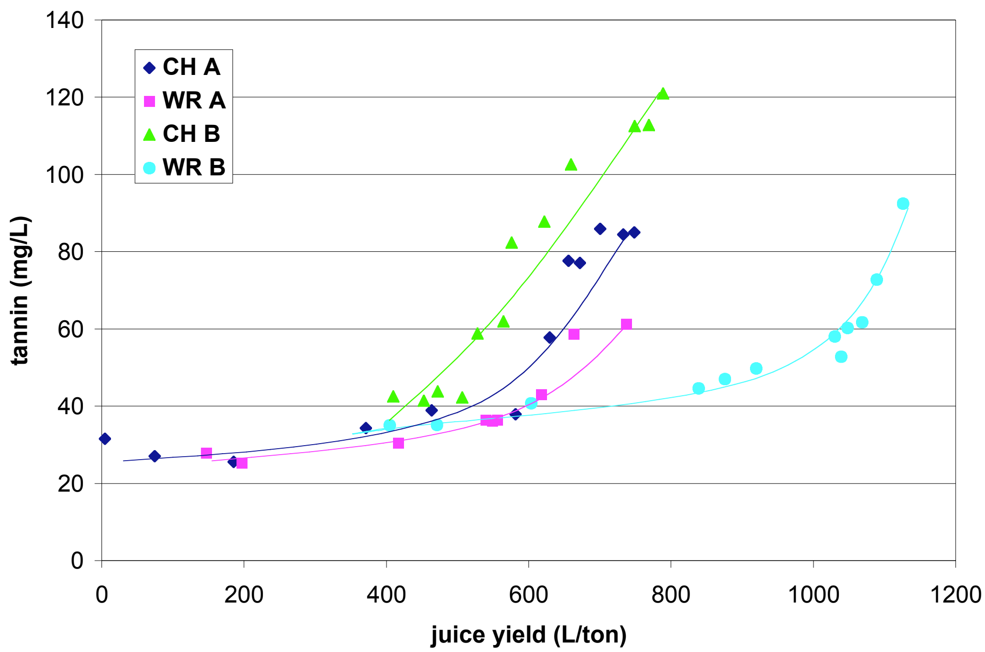
Quercetin glycosides are flavonols are present in grape skins. They are extracted into white wine during skin contact and pressing. The attached sugar may hydrolyze to form **quercetin aglycones.** The hydrolysis may be caused by glycosidase enzymes in microorganisms or by glycosidase activity in commercial enzyme preparations. Enzymes preparations high in glycosidase activity are often deliberately used in white fermentations to release glycosidically bound aroma constituents. An often unnoticed side effect is the liberation of flavonol aglycones.

These compounds are far less soluble than the glycosides and in rare instances, cause a flavonol haze.

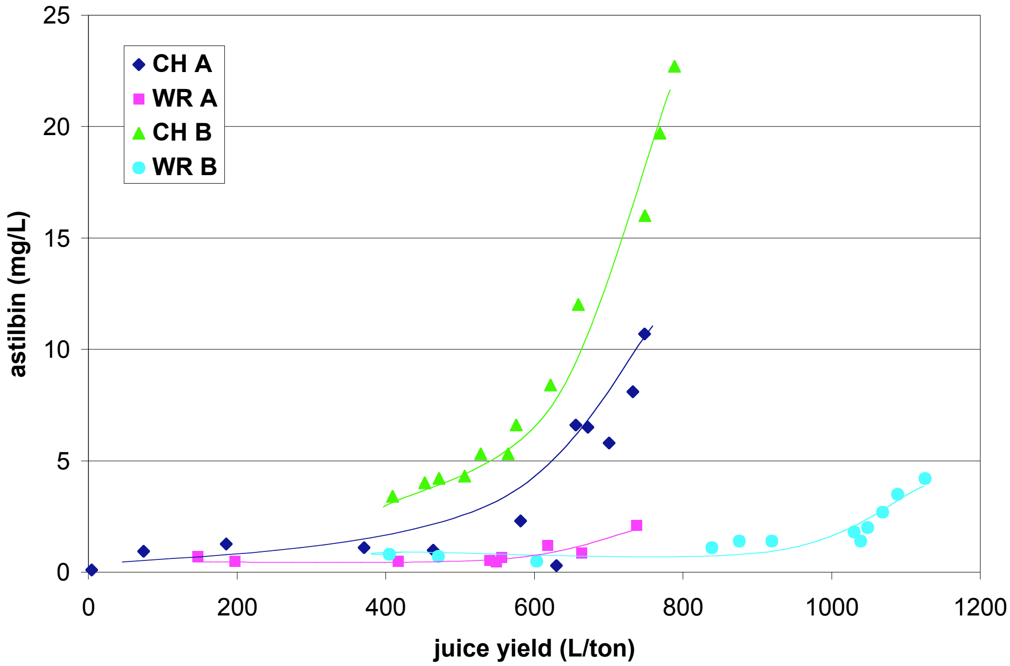
Tannin in white wine comes from grape tannin and oak. It may also include large complex oxidation products from cinnamic acid oxidation. Grape tannin is a flavonoid polymer (condensed tannin) and is extracted during skin contact and pressing. Oak tannin is a complex mix of hydrolysable tannins including ellagitannin and gallotannin. Oak toasting greatly reduces available tannin in oak and most white wines have very little tannin from oak. Tannin is defined as large complex polymers of phenolic compounds that can precipitate proteins. The oxidation products from cinnamic acid oxidation add phenolic polymers to the complex mix of tannins. Using the ETS tannin assay, these compounds can be identified at 320 nm. We have shown that they are closely related to juice browning.

Example – Press Cuts

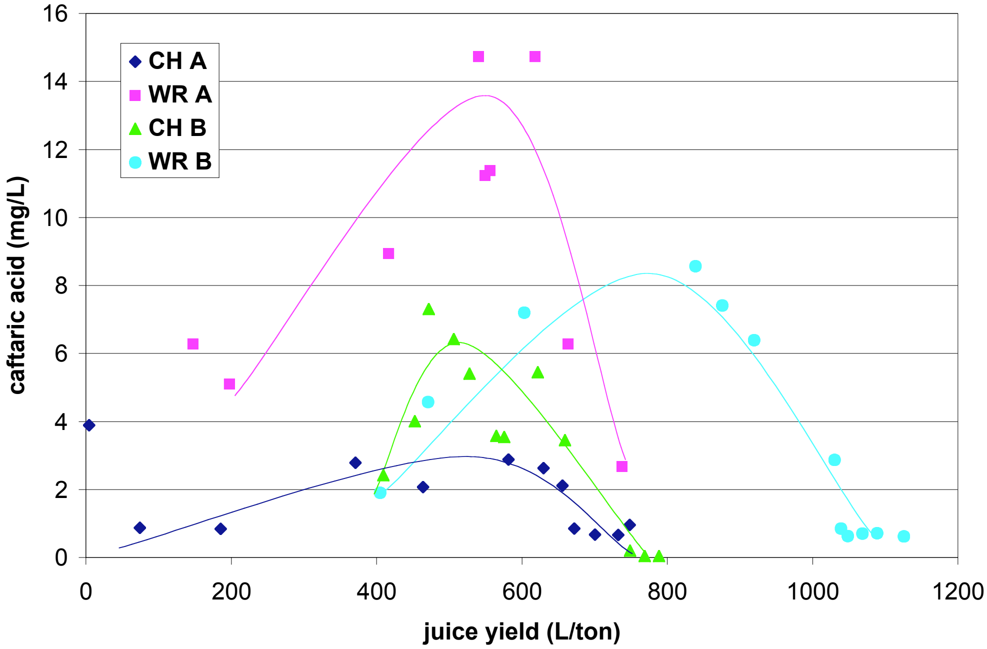
Pressing is both extractive and oxidative. In red wines, one of the signatures of a press wines is the low level of cinnamic acids. These compounds are lost due to oxidation during pressing. Extraction from skins during pressing is much less in white grapes than red wine, but it is still significant and may have important sensory relationship to harshness. The charts below show the extractive effects of pressing two Chardonnays and two Rieslings.



Tannin is readily extracted during pressing and different grapes have very different responses to pressing. The two Rieslings have distinctly different extraction curves. The tannin in Riesling A is increasing at lower juice yields than Riesling B. Pressing is resulting in tannin levels approaching red wine levels in CH B.



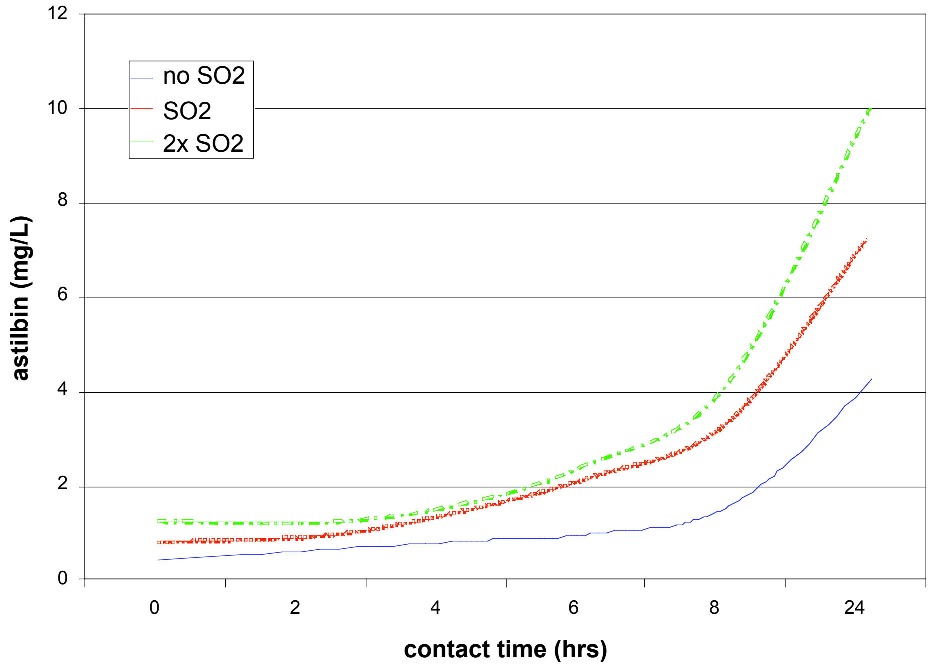
Astilbin, a marker of skin extraction shows an even stronger response than tannin, particularly in Chardonnay B, the sample with the highest tannin. The Rieslings have much lower levels or astilbin, perhaps due to lower astilbin levels in the skin. The chart clearly shows the importance of press cuts and the difficult balance between juice yield and potentially harsh phenolics.



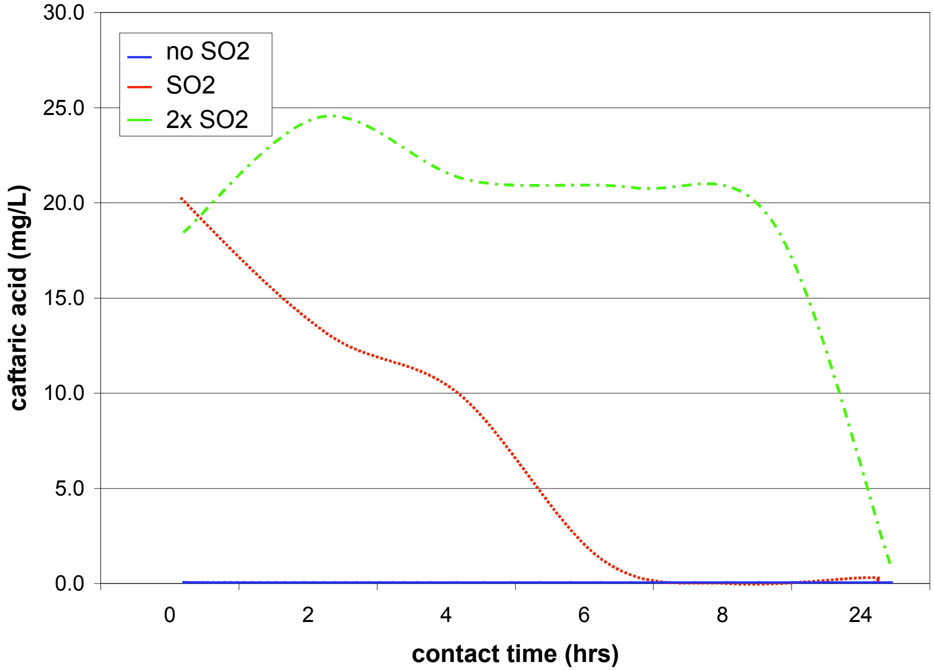
Caftaric acid is present in both grape pulp and skins. Increased pressure extracts more skin components and more caftaric acid, but the oxidation that accompanies the end of the pressing cycle results in oxidative losses that exceed any additional extraction.

Example – SO_2 and Skin Contact Time

In this example, Chardonnay grapes were lightly crushed and left at room temperature with no SO2, standard rates, or twice standard rates. The concept of the trial was to simulate the transport of mechanically harvested fruit.



Skin contact time increased extraction of astilbin. Tannin extraction increased in a similar manner (data not shown). What was surprising was the effect of SO_2 on extraction. SO_2 is added to white grape to prevent oxidation but SO_2 also increases the extraction potential of grape juice. By six hours, grapes with SO_2 had more than twice the astilbin content as grapes with no SO_2. Doubling the SO_2 increased extraction even more.



Effects of SO_2 on caftaric acid were primarily as an antioxidant. In the absence of SO_2, caftaric acid was all immediately oxidized. With standard SO2 additions, the oxidation was delayed. With twice the usual amount of SO2, there was little caftaric acid oxidation until more than 8 hours of contact time.

Conclusion

The low concentration of phenolic compounds in white wine makes them only a minor component of white wine structure and quality. As a result, phenolic compounds in white grapes, juices and wines are often ignored. There have been very few studies on the enological significance of phenolics in white wines and there is almost no information on the sensory relevance of phenolic information.

Grape growing, fruit handling and winemaking clearly do have an effect on wine phenolic composition but using that information effectively will require additional information. Perhaps the most important step for a winemaker concerned about phenolics in white wines is to carefully tie sensory impressions to phenolic information. The studies shown above were part of a larger project to identify the key control points for phenolics in white wines. In-house research as well as cooperative research with University personnel will help further knowledge and help develop tools for making white wines with appropriate phenolic levels for the style and market.

Flight No.______________ Sample No.____________ Color________________________

Fruit derived / varietal flavors: ____

Texture / Mouthfeel:____

Overall / Balance / Structure:____

Comments:____

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