Interactions between phenolics, alcohol and acidity in determining the mouthfeel and bitterness of white wine

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The bitterness of white wine has traditionally been attributed to phenolics. However, phenolics in white wines comprise a diverse group of compounds. Two studies have shown which phenolics contribute to bitterness and how the alcohol content and pH of the wine affects bitterness perception. The effects of different juice handling and extraction methods (whole bunch pressing, hyperoxidation, pressings, skin contact, partial skin and solids fermentation) on phenolic content and white wine bitterness are also explored.

Palate textures such as viscosity and even perhaps light astringency are becoming an accepted part of full-bodied white wine styles, while other characters such as bitterness, metallic taste and hotness are clearly unacceptable. What these positive and negative mouthfeel attributes have in common is that they all have been attributed to wine phenolics.

Wine phenolics comprise a broad family of small and mostly monomeric compounds that possess at least one six carbon ring with one or more hydroxyl groups (-OH) attached. While some are found in a simple free form, most are more complex, present as esters of tartaric acid or ethanol, bound to amino acids, or bound to sugars such as glucose, rhamnose and glucuronic acid. These basic modifications together with other structural arrangements can influence how they taste and feel in the mouth.

The chemistry of white wine phenolics has been extensively reviewed (see Monagas *et al.* 2005). In summary:

- Hydroxycinnamic acids (e.g. caffeic and coumaric acids) are phenolic acids that are located in the vacuoles of the pulp and skin cells of grapes. In wine they can exist in their free form, but they are mostly found as their respective tartaric acid esters (e.g. caftaric and coutaric acids).
- Grape reaction product (GRP) is an enzymatically formed complex of caftaric acid and the grape amino acid glutathione, and is particularly abundant in wines made using oxidative juice handling.
- Hydroxybenzoic acids are phenolic acids which are also found as ethyl or methyl esters.
- Flavonols are a major phenolic class in wine that originate from the grape skin particularly during skin maceration prior to fermentation. They mostly exist in glycosylated forms (e.g. as glucosides, glucuronides and rhamnosides).
- Flavanols are also located in the skins, but also in the seeds and stems. They exist either in a free form (e.g. epicatechin) or as gallic acid esters (e.g. epicatechin gallate).
- Flavanonols are also found in grape stems and skins, with astilbin (the rhamnoside of dihydroquercetin) and its aglycone both found in white wine (Trousdale and Singleton 1983). The sensory effects of this class of compounds are currently unknown.

New analytical techniques have expanded current knowledge regarding the number and complexity of phenolic compounds that exist in white wines. However, understanding of how white wine phenolics influence taste and mouthfeel in the context of differences in alcohol and acidity remains largely unexplored. In an attempt to address these knowledge gaps, work has been done to:

1. Correlate the intensity of taste and mouthfeel characteristics of white wines of similar acidity and alcohol made using different must handling and extraction techniques with their phenolic composition (study 1)
2. Assess the interactions between phenolic composition and pH and alcohol with respect to mouthfeel and taste (study 2).

METHODS

Study 1

Different techniques were used to produce wines with different phenolic profiles to assess their effects on white wine mouthfeel and bitterness. Riesling (Eden Valley), Chardonnay (Lyndoch) and Viognier (Western Barossa) wines from the 2011 vintage were made using the following seven different juice extraction and handling methods:

- free run juice, obtained by draining and pressing at less than 0.5 bar
- heavy press juice, obtained by draining and pressing 1-2 bar
- hyperoxidised free run juice produced by sparging the free run juice with oxygen
- hyperoxidised heavy press juice, produced by sparging the heavy press juice with oxygen
- maceration on skins conducted for 60 hours at 5°C prior to pressing
- partial (10% by weight) skin fermentation
- full solids fermentations.

Replicate ferments were conducted (*S. cerevisiae* EC1118 strain + 1g/L bentonite). As perceived viscosity and astringency in white wine have been shown to be strongly influenced by pH

(Gawel *et al.* 2014) the wines were adjusted to approximately the same pH (3.2). Phenolic composition was determined by HPLC using tandem C6-Phenyl columns coupled with mass spectroscopy. Fourteen assessors experienced in the texture profiling of white wine were trained to rate the intensity of eight mouthfeel/taste attributes using a 15cm unstructured line scale. The wines were assessed in triplicate over four tasting sessions using accepted tasting conditions and experimental design protocols.

Study 2

Whole phenolics were extracted from free run, hard pressings and skin macerated wines before being divided into two fractions using a combination of multilayer counter-current chromatography and preparative scale C18 reverse phase chromatography. The two fractions were differentiated by the amount of skin-derived flavonols and ethyl esters of hydroxycinnamic acids (Figure 1). The fractions were dissolved in model wines at the same total phenolic concentration (measured using absorbance at 280nm) at pH 3.3 and 3.5 and alcohol levels of 11.5% and 13.5% v/v. The bitterness, palate hotness and perceived acidity were assessed by the trained tasters, using the same tasters and protocols as study 1.

RESULTS AND DISCUSSION

Study 1

Twenty phenolic compounds were positively identified based on matched HPLC retention time, UV-spectra and mass

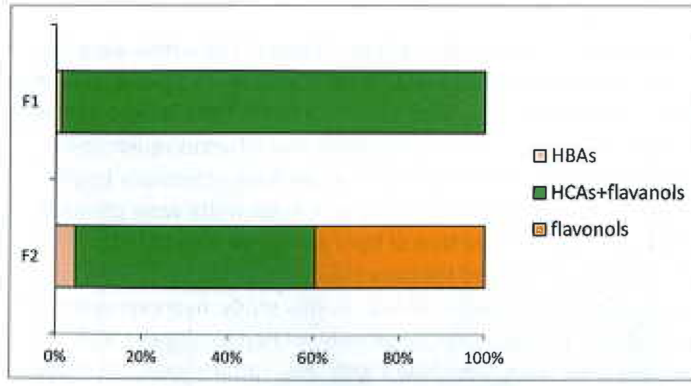

Figure 1. Phenolic composition of the two fractions: HBA=hydroxybenzoic acids: HCA= hydroxycinnamic acids. HPLC analysis showed the fractions were composed mainly of these classes of compounds or their derivatives.

spectra to that of their standards (listed in Table 1, see page 32). Statistically significant variations in wine mouthfeel attributes as a result of juice extraction and handling were observed (Smith and Waters 2012). The correlations between the concentration of the identified phenolic compounds (grouped by class) and the mouthfeel intensity ratings are shown in Table 1.

The hydroxycinnamic acids and their derivatives were consistently positively correlated with perceived acidity. While these phenolic acids individually are found in low concentrations (<30mg/L) and have pKa values around 4.4, which implies that they are only weakly acidic (Beltran *et al.* 2003), the results of both studies suggest that their presence can accentuate the perception of acidity in white wine.

Palate hotness and burning aftertaste in the wines were correlated with their flavanol concentrations. The perception of burning aftertaste was also associated with the concentrations of hydroxybenzoic acids, flavanonols and dihydroxyquercetin. While none of these compound classes have previously been associated with increases in hotness, total white wine phenolics at a level equivalent to that of hard pressings was able to increase the perceived hotness of lower alcohol (11.5% v/v) model wine (Gawel *et al.* 2013a). In this study, hydroxycinnamic acid concentrations were negatively related to hotness and burning aftertaste. Consistent with this, caftaric acid (the major hydroxycinnamic acid in white wine) was found to suppress the burn sensation produced by another white wine phenolics and also ethanol (Gawel *et al.* 2013b).

Viscosity and oiliness are two sensory characters normally associated with full-bodied white wines. These attributes were correlated with syringic and gentisic acids, quercetin glucuronide and dihydroquercetin (Table 1). Higher perceived viscosity in white wines has been shown to occur in the presence of higher total phenolics (Cejudo-Bastante *et al.* 2011), and greater oiliness was observed in model wines containing higher concentrations of the phenolic compound, grape reaction product (Gawel *et al.* 2013b). The wines with the highest polysaccharide levels were also deemed to be the most oily.

The wines made from juices high in solids were perceived to be more metallic than the other treatments which did not differ (data not shown). However, none of the phenolic classes (which represent the broad spectrum of white wine phenolics types) were positively associated with metallic character, suggesting that non-phenolic compounds may be responsible for the metallic taste in these wines.

A flavonol rutinoside has been reported to be a potent astringent compound in red wines (Hufnagel and Hoffman 2008). However, in contrast, the two major flavonol glycosides including a rutinoside were found to be negatively associated with perceived astringency. The reason for this is unclear. Astringency was positively associated with the concentration of flavanols, which are known to elicit astringency at least in high concentrations (Fischer and Noble 1984).

The relationships between flavanol concentrations and the intensity of the mouthfeel attributes were diametrically opposed to that of their flavonol concentrations. Specifically, flavanols were positively associated with, and flavonols negatively associated with, the intensity of bitterness, hotness and burning aftertaste. Whilst correlation does not necessarily imply causation, these results suggest that minimising seed rather than skin extraction could improve the mouthfeel of white wine.

Study 2

Two phenolic fractions (F1 and F2) were produced (Figure 1). F2 was found to contain phenolics that would be expected to mostly derive from the skins (flavonols), which were absent from F1. Both fractions contained flavanols which are extracted from both seeds and skins during winemaking and hydroxycinnamic

Table 1. 'Heatmap' showing the correlations between mouthfeel attributes and compounds identified in white wines made from three varieties using various juice extraction and handling methods. Green indicates positive correlation, purple negative. Deeper colours imply stronger correlations. EE=ethyl ester, * Flavanonol, ** Flavanone.

		Astring	Viscosity	Oily	Bitter	Metallic	Hotness	Burn	Acidity
Hydroxybenzoic acids	Gallic acid	0.22	0.34	0.09	0.35	0.09	0.30	0.21	0.01
	Syringic acid	0.44	0.37	0.24	0.11	0.06	0.10	0.40	0.20
	Gentisic acid	0.52	0.38	0.32	0.12	0.05	0.10	0.39	0.44
	Hydroxybenzoic acid	0.37	0.07	0.09	0.15	0.25	0.14	0.09	0.28
	Protocatechuic acid	0.30	0.00	0.15	0.21	0.01	0.10	0.24	0.02
	Gallic acid EE	0.23	0.36	0.13	0.37	0.07	0.32	0.22	0.07
Hydroxycinnamic acids	Coumaric acid	0.11	0.36	0.27	0.03	0.17	0.10	0.20	0.46
	Ferulic acid	0.43	0.08	0.12	0.19	0.25	0.38	0.34	0.25
	Caffeic acid	0.32	0.64	0.40	0.20	0.06	0.06	0.23	0.41
	Caftaric acid	0.02	0.38	0.23	0.09	0.08	0.18	0.26	0.35
	Caffeic acid EE	0.19	0.59	0.41	0.09	0.12	0.14	0.31	0.50
	Ferulic acid EE	0.09	0.42	0.39	0.32	0.15	0.27	0.45	0.62
Flavanols	Catechin	0.13	0.38	0.09	0.37	0.01	0.28	0.23	0.03
	Epicatechin	0.18	0.36	0.10	0.40	0.00	0.31	0.24	0.08
	Procyanidin B2	0.24	0.36	0.12	0.35	0.09	0.30	0.19	0.09
Flavonols	Quercetin (Q)	0.21	0.03	0.14	0.15	0.08	0.21	0.12	0.45
	Q-3-glucuronide	0.40	0.30	0.32	0.23	0.32	0.16	0.01	0.42
	Q-O-rutinoside	0.46	0.13	0.07	0.43	0.37	0.36	0.23	0.08
*	Dihydroquercetin	0.41	0.07	0.22	0.24	0.06	0.09	0.31	0.27
**	Naringenin	0.40	0.01	0.08	0.17	0.24	0.17	0.00	0.11

acids which are mostly derived from the pulp but also the skins.

Both phenolic fractions and the wine matrix (acidity and alcohol) contributed to the taste and mouthfeel characteristics rated by the sensory panel. As expected, higher alcohol model wines were perceived as more 'bitter' (Figure 2) and 'hot' (Figure 4) than the lower alcohol model wines, and the lower pH model wines were perceived as being more acidic than the higher pH wines (Figure 3).

BITTERNESS

Figure 2 shows a significant interaction between phenolic type and wine matrix with respect to bitterness. The 13.5% model wines were perceived to be more bitter than the 11.5% model wines. F1 phenolics did not increase bitterness at any pH or alcohol level and, while not significant, a trend was observed of lower bitterness in the lower pH wines. While F1 contained flavanols which are known bitterants, it was dominated by hydroxycinnamic acids which may have acted as a suppressant due to their contribution to perceived acidity (Figure 1, Figure 3). Bitterness was increased in the presence of F2 phenolics, particularly when pH was higher and alcohol lower, with the influence of pH being greater than that of alcohol. The results of study 1 indicate that the flavonols (i.e., skin phenolics) which distinguished F2 from F1 did not contribute to bitterness to the wines. The study 1 wines had an average pH of 3.2 and alcohol content of 13.0% v/v. Adding F2 phenolics to a model wine of similar composition (e.g. pH 3.3, alcohol 13.5%) had the least effect on bitterness compared with any other pH/alcohol combination, which is consistent with the results of study 1. The substantial increase in bitterness in the higher pH wine compared with the lower pH wine at the same low alcohol level (11.5%) suggests that the phenolic bitterness was elicited from F2 but was masked by acidity. At the higher alcohol level, the model wines were perceived as more bitter, and the F2 fraction had less of an effect on bitterness as a result.

PERCEIVED ACIDITY

When the acidity and alcohol content of the base wine was low, the addition of both phenolic fractions significantly increased perceived acidity. Both fractions contained hydroxycinnamic acids, which may account for this (study 1). When added to a similar model wine matrix to that of the real wines in study 1 (pH 3.3, alcohol 13.5%), neither phenolic fraction contributed to perceived acidity. Interpreting combined results from model studies involving additions and sensory studies of real wines is problematic. However, there is some evidence to suggest in both studies that hydroxycinnamic acids may contribute to perceived acidity in white wine.

HOTNESS

Previously work has shown that whole white wine phenolics added to both model or real wine increased perceived hotness, particularly in wines that would be considered low in alcohol (Gawel *et al.* 2013a). In this study, the effect of phenolics on ethanol hotness appeared to be neutral or marginally suppressive (Figure 4). The reason for this is unclear, but it is known that caftaric acid which was present in both fractions, and is one of the dominant phenolic compounds in white wine, has the ability to reduce the hot aftertaste produced by ethanol (Gawel *et al.* 2013b).

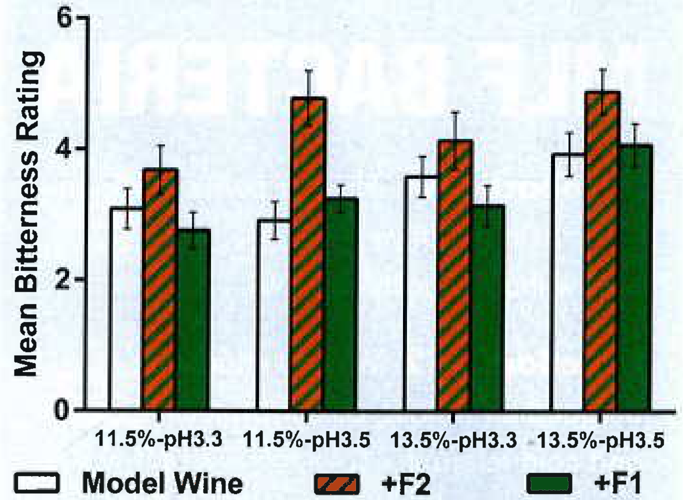

Figure 2. Effect of phenolic type, pH and alcohol on perceived bitterness intensity.

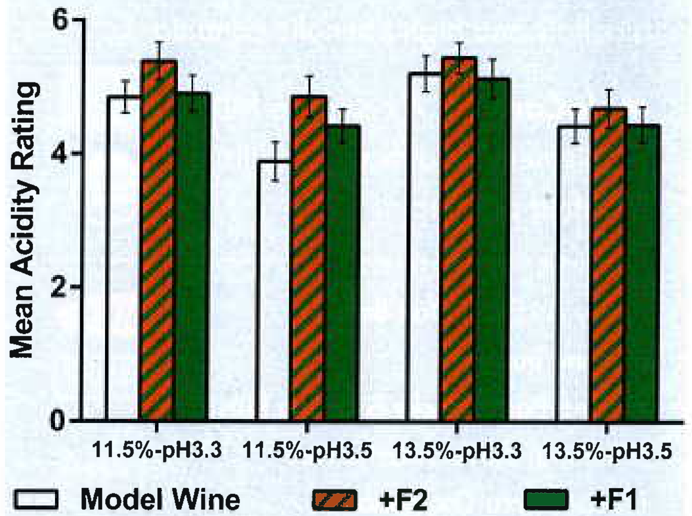

Figure 3. Effect of phenolic type, pH and alcohol on perceived acidity intensity.

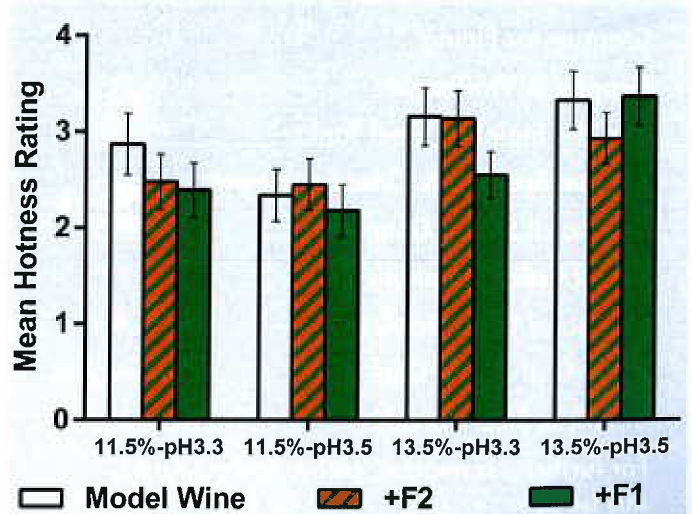

Figure 4. Effect of phenolic type, pH and alcohol on perceived in-mouth hotness intensity.

Many active molecules have complex taste profiles in that they are not purely acidic, sweet, salty or bitter. In the case of hydroxycinnamic acids which contain both phenolic and carboxyl (acidic) functional groups, this may be the case. In informal tastings of phenolic fractions rich in hydroxycinnamic acids experienced wine tasters have reported perceiving both acidic and metallic/hard water like tastes. Whilst this is only anecdotal, the role of the hydroxycinnamic acids in wine taste and texture may merit further investigation in the context of understanding the concept of 'hardness' in white wine.

CONCLUSIONS

Different phenolic classes impacted differently on mouthfeel attributes and on bitterness and acidity, suggesting that skin and seed management during juice extraction and handling can be used to manipulate the mouthfeel and taste of white wine. Increases in bitterness and acidity of phenolic fractions containing more 'skin-derived' phenolics was dependent on wine pH and alcohol content, being higher in wines of higher pH and lower alcohol. Phenolics that are mostly 'pulp' derived also enhanced perceived acidity at low alcohol and high pH. However, perceived bitterness and acidity were significantly affected by alcohol concentration and wine pH, respectively.

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