How wine pH and closure selection influence red wine colour and tannin during ageing

Introduction

Red wines change in colour, texture and complexity as they age and older wines are commonly described as 'softer' or less astringent than younger wines. The reasons for this 'softening' are not fully understood and various (sometimes contradictory) explanations have been suggested, including:

- tannins getting larger and precipitating out of the wine, leaving it less astringent (Haslam 1980)
- tannins changing structure over time and becoming less astringent (AWRI publication #1255)
- tannins getting smaller with ageing and becoming less astringent (Cheynier et al. 2006)

Previous work based on analysis of vertical series (AWRI publication #1488) has indicated that aged wine tannins are larger than younger wine tannins, but this has not been confirmed in a wine ageing trial. Further, larger tannins have been found to be more astringent than younger wine tannins and therefore the formation of larger tannins in aged wine should not soften the wine – unless other factors are also at play.

Understanding the wine matrix components that influence wine tannin structure and the changes that occur during ageing may provide winemakers with options to control mouth-feel in finished red wines. The wine matrix has been previously shown to affect reactions that occur in wine and could therefore be expected to have an impact on how wines age. The more acidic environment of lower pH wines causes polymerisation and degradation reactions to occur much more quickly and therefore the concentrations of anthocyanins can decrease more rapidly during storage than in wines of higher pH (Kontoudakis et al. 2011). The effect of pH on wine tannins has not previously been investigated. Oxygen exposure has also been shown to influence both wine texture and colour. During bottle ageing, oxygen ingress through bottle closures can induce reactions that more rapidly 'age' red wines. Oxygen can oxidise ethanol to acetaldehyde, which reacts readily with polyphenols and anthocyanins to form more stable pigments including pigmented polymers. Greater oxygen exposure has also been shown to reduce wine astringency and this effect is exacerbated in lower pH wine over several years of ageing (Gambuti et al. 2013), again, the direct effects of oxygen on tannin have not previously been investigated.

A study was therefore set up to investigate the influence of pH and oxygen ingress through two different screw cap closures on wine colour, tannin concentration and tannin composition

during bottle ageing. A single vintage Cabernet Sauvignon (CAS) wine was produced using standard winemaking techniques, including crushing, destemming and addition of cultures for primary and secondary fermentation. Just prior to bottling, the pH was adjusted to either pH 3.2, 3.5 or 3.8 and the wine was bottled under screw cap using either a SaranTin (ST) liner (to restrict all oxygen ingress) or a Saranex (Sx) liner (to allow a minimal oxygen ingress). Changes in colour and tannin were monitored over 24 months.

How tannins change with wine ageing

Changes in tannin structure have not previously been measured as part of an ageing trial, but trends have been previously investigated using vertical series of wines (AWRI publication #1488). The difficulty in drawing conclusions from vertical series is that the inevitable seasonal differences in grape composition as well as potential differences in winemaking style can alter the initial wine composition. The objective for this project was to monitor changes in a single vintage wine over time in bottle.

Over the 24 months in bottle, a substantial decrease in tannin concentration was observed (Figure 1a), presumably due to the degradation of tannins into smaller molecules. The reduction in tannin concentration would contribute to astringency softening with ageing. A decrease in tannin concentration has long been speculated as the reason for the change in wine texture with ageing, however this is the first study to confirm that this does occur.

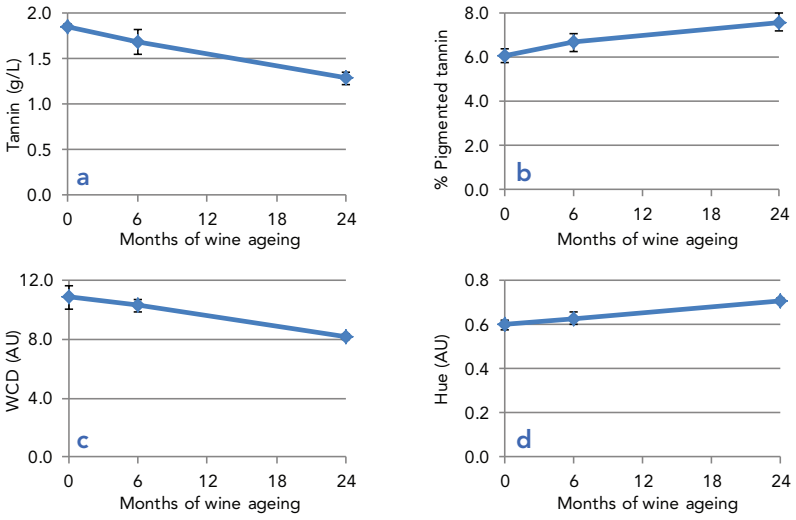

Figure 1. General trends in tannin concentration (a), proportion of pigmented tannin (as a percent of the total tannin) (b), wine colour density (WCD) (c), and Hue (d) in CAS wine with bottle ageing. Results shown are averages of all wines under both closures and all pH levels to show overall trends.

As the total amount of tannin decreased, the proportion of tannin that is pigmented gradually increased (Figure 1b). This indicated that the anthocyanins in red wine were being converted into pigmented tannins, which contribute to the longer term colour stability of wine. Wine colour density (WCD), which relates directly to the purple colour of wines, decreased gradually over time reflecting the decrease in anthocyanins (Figure 1c). Wine hue, which relates more to an orange colour in the wine, increased with ageing, further indicating that pigmented tannins are formed from the purple anthocyanins (Figure 1d).

Wine ageing also slightly decreased the size of the tannins (Figure 2). This was measured using two methods: mean degree of polymerization (mDp) and tannin molecular weight. For mDp, the tannins are broken apart into smaller fragments and the number and type of fragments are calculated to give the average number of subunits in each polymer. This method is most useful for grape tannins (due to higher % tannin fragmentation as described below), but can also be indicative of wine tannin size. A more useful method for wine tannins is to measure the average tannin molecular weight. This method also has limitations but gives a good indication of wine tannin size. In this instance, both methods indicated that tannin size decreased over the 24 months in bottle. This may also lead to the softening of wine astringency with ageing since smaller tannins are known to be less astringent than large tannins.

Impacts of wine pH and bottle closure on wine colour and tannins with ageing

Wine pH and selected closure type did not change the general trends that were observed with wine ageing but did have a dramatic impact on the speed of these reactions. Within six months, the differences in pH had started to influence wine colour and tannin structure, with these changes even more apparent after 24 months (Figure 3). The lower pH wines (pH 3.2) contained substantially fewer anthocyanins than the pH 3.8 wines (Figure 3a), and this related to the formation of more SO_2 non-bleachable pigments (% stable pigments) in the pH 3.2

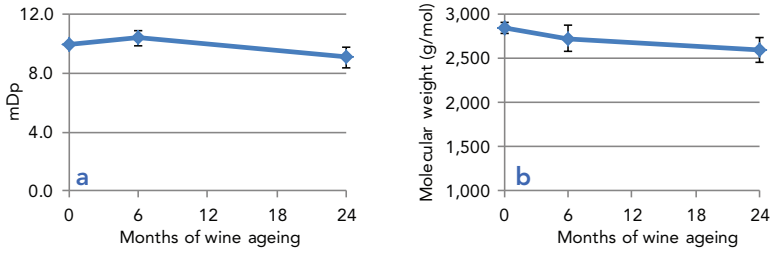

Figure 2. Impact of wine ageing on tannin size as measure by mean degree of polymerization (mDp) (a); and molecular weight (b). Results shown are averages of all wines under both closures and all pH levels to show overall trends.

wines (Figure 3b). Slight oxygen exposure through the lined screw cap (Sx) exacerbated the impact of the more acidic wine with a further decrease in overall anthocyanin concentration. Changes in the tannin structure were also affected by pH and closure type. One of the main measures for assessing tannins is how readily they break apart into smaller fragments in the presence of acid. This is referred as % yield of the reaction or % tannin fragmentation. The more readily the tannin can be fragmented (greater % tannin fragmentation), the simpler the tannin composition and, potentially, the more astringent the tannin. With wine ageing, the % tannin fragmentation decreased substantially in all wines, indicating that the tannin was becoming more complex probably due to interactions with itself as well as other components of the wine such as anthocyanins and acetaldehyde. These changes were much more apparent in the pH 3.2 wines (Figure 3c) and particularly under Sx compared with ST screw caps. Such changes to the wine tannin structure may also relate to the softening of astringency with wine ageing.

Another notable change in tannin structure was the proportion of grape seed-like tannin (% epicatechin gallate) (Figure 3d). Generally with ageing, the proportion of these tannins decreases due to oxidation. This was the case in the higher pH wines (pH 3.5 and 3.8), but at lower pH, this proportion remained fairly constant. Conversely, the proportions of the grape skin-like tannins (% epigallocatechin) did not change over time. Generally seed tannins are considered to be more astringent and more bitter than skin tannins, and therefore a decrease would soften wine astringency, as is generally observed with wine ageing. The

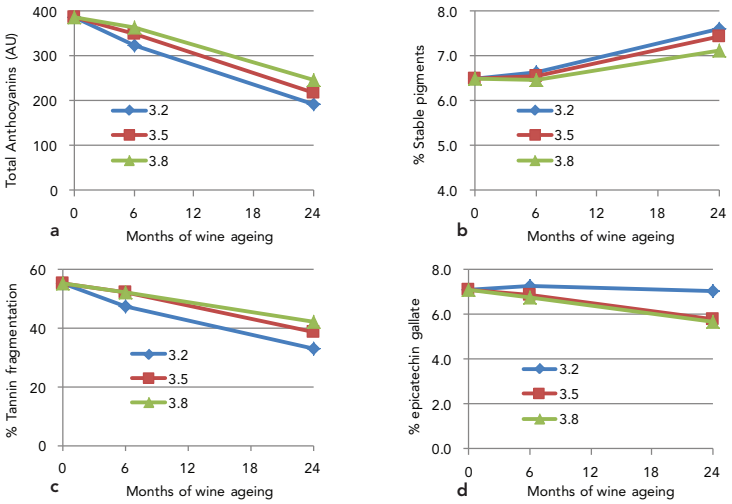

Figure 3. Impact of pH on total anthocyanins (a) and % stable pigments (b); and on tannin structure, including % tannin fragmentation (c) and % epicatechin gallate (seed-like tannins) (d).

effect of more seed-like tannin in the lower pH wines in this case is likely to be offset by the lower % tannin fragmentation.

Conclusions

Red wine texture softens with ageing due largely to a decrease in tannin concentration and tannin size. Lower wine pH and a closure that allowed a slight ingress of oxygen resulted in more rapid 'ageing' of wine colour with fewer anthocyanins and more pigmented polymers and, potentially, a greater reduction in wine astringency caused by a more rapid decrease in % tannin fragmentation. Decisions about wine pH and oxygen exposure in bottle can therefore give winemakers some control over tannin and colour development during ageing. Future studies will investigate the impact of tannin structural changes on mouth-feel and will delve further into the other components of wine that contribute to the softening of wine astringency with ageing.

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