Struck match, freshness and tropical fruit: thiols and Chardonnay flavour

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Chardonnay is the most planted white grape variety in Australia, but understanding of its flavour and aroma chemistry has been limited. Recent research at the AWRI has highlighted the importance of 'thiols' (a class of sulfur-containing compounds, previously thought to be important mainly in Sauvignon Blanc) in Chardonnay flavour. These compounds can contribute to overall wine freshness, 'fruity' characters, 'flint/struck match' notes and less desirable 'box hedge/cat pee' characters.

BACKGROUND

Chardonnay is the most planted white grape variety in Australia, with more than 360,000 tonnes harvested in 2017 (Wine Australia). Understanding of the compounds responsible for its aroma and flavour is, however, still quite limited. This is partly due to the subtlety of many wines of this variety, and also the wide range of winemaking options used in Chardonnay production, from low temperature fermentation in stainless steel, to inclusion of solids, barrel

AT A GLANCE

- Thiols are a class of flavour compounds known for their contribution to the aroma and flavour of Sauvignon Blanc wines.
- A survey of thiols in 106 commercially available Chardonnay wines found levels of four key thiols that were well above their sensory thresholds.
- A winemaking trial using Chardonnay juice from 16 vineyards across five states also found high levels of thiols and showed that wine sensory characteristics were correlated with thiol concentrations.
- Simple steps are available for grapegrowers and winemakers to increase or decrease thiol concentrations to influence wine style.

fermentation, malolactic fermentation, and ageing on lees. In recent years many Australian Chardonnay producers have been focussing on finer, more complex and restrained styles and the AWRI has worked to improve knowledge of Chardonnay aroma and flavour chemistry to assist with this goal. Many producers are working to optimise the profile of 'fruity' flavours such as 'stone fruit' and 'citrus', while allowing complexing characters such as 'struck flint/match' to play a role. And as with virtually all wine types, one of the features of a desirable wine, especially when relatively young, is the degree of general fruit 'freshness' and overall intensity and length of flavour. Understanding this aspect of wine quality has been another area of active work for AWRI flavour researchers.

Recent efforts have focussed on exploring the role of several sulfur compounds known as thiols in Chardonnay flavour. These thiols are highly potent flavour compounds known to give many Sauvignon Blanc wines their 'tropical fruit/ passionfruit' character. They can also contribute a less desirable 'cat pee/ sweaty/box hedge' or 'green' aroma to Sauvignon Blanc when at high concentrations. There are three main compounds: 3-mercaptohexanol (3-MH), 3-mercaptohexyl acetate (3-MHA), and 4-mercapto-4-methylpentan-2-one (4-MMP), each with very low sensory detection thresholds, so that even at sub-part per billion concentrations they can have a dominating effect on wine flavour (King *et al.* 2011). The aroma of 3-MH is described as 'grapefruit-like', while 3-MHA can contribute 'passionfruit/tropical fruit' flavour, and at higher concentrations a 'cat pee' character. A further thiol compound called benzyl mercaptan (BM) has also been assessed. This compound is also known to contribute to 'gunflint/struck match/mineral' aromas in, for example, Sauvignon Blanc wines produced in the Loire Valley in France. Multiple factors can influence the formation of thiols in wine. Generally, they are formed by enzymes from yeast metabolism acting on precursors in grape juice and there are several practical avenues that can be taken to enhance or reduce their levels in the wine.

HOW COMMON ARE THIOLS IN AUSTRALIAN CHARDONNAY?

One of the obstacles in flavour research is often the speed and ease of use of the analytical methods needed. Previous methods for thiol analysis were slow, difficult and used toxic materials, meaning that progress in knowledge of these compounds was also slow. A highly sensitive and accurate analytical method was recently developed with colleagues from The University of Adelaide (Capone *et al.* 2015), which is relatively straightforward to apply to large sample sets. This method was applied to a survey of more than 100 commercially available Australian Chardonnay wines, with a range of ages and prices, including some of the top selling wines in the country.

Figure 1 shows the results from the analyses of these 106 wines. The initial surprise was the number of wines that contained concentrations of each of the four thiols above their aroma detection thresholds. For the compounds 3-MH and 3-MHA, all wines were well above the reported sensory threshold, strongly suggesting that these highly potent aroma compounds were contributing flavour to the wines.

Almost all wines were also above the threshold concentration for 4-MMP and BM. A previous report (Mateo-Vivaracho *et al.* 2010) provided a guide as to whether the compounds at a certain concentration were likely to contribute general 'fruity' flavour or 'fruit freshness', or a clear dominating sensory effect. In Figure 1, when the concentration is above the aroma detection threshold value (dashed red line) but below the dashed blue line, these compounds are likely to be enhancing 'fruit' flavour, but when concentrations are above the blue line there may be dominant 'grapefruit', 'tropical fruit' or 'cat pee' aromas. For 3-MH there were numerous wines with concentrations above this indicative line, while only one wine had a 3-MHA concentration above the blue line. No wine was above the blue line for the 4-MMP compound, while almost all were above the blue line for BM.

Also of interest was the number of wines from Western Australia

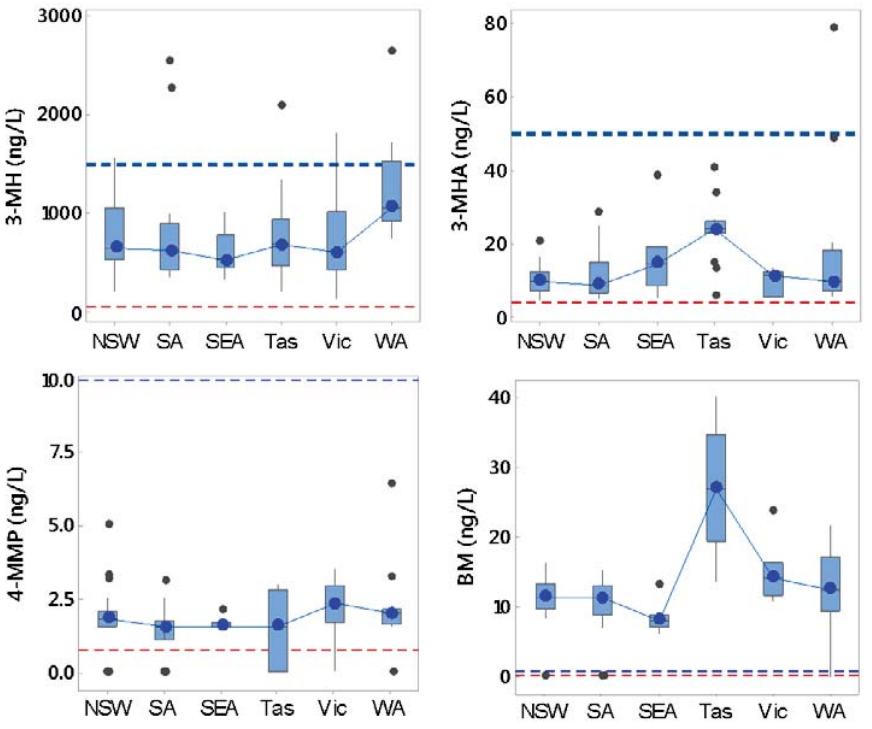

Figure 1. Concentrations of the thiol compounds 3-MH, 3-MHA, 4-MMP and BM for a set of 106 commercially available Chardonnay wines, grouped by state (SEA: South Eastern Australia). Median values are shown by the connected symbols and the outlier wines by the black circles. The sensory threshold for each compound is shown as the dashed red line, while the blue line represents the concentration where the compound may start to dominate the aroma.

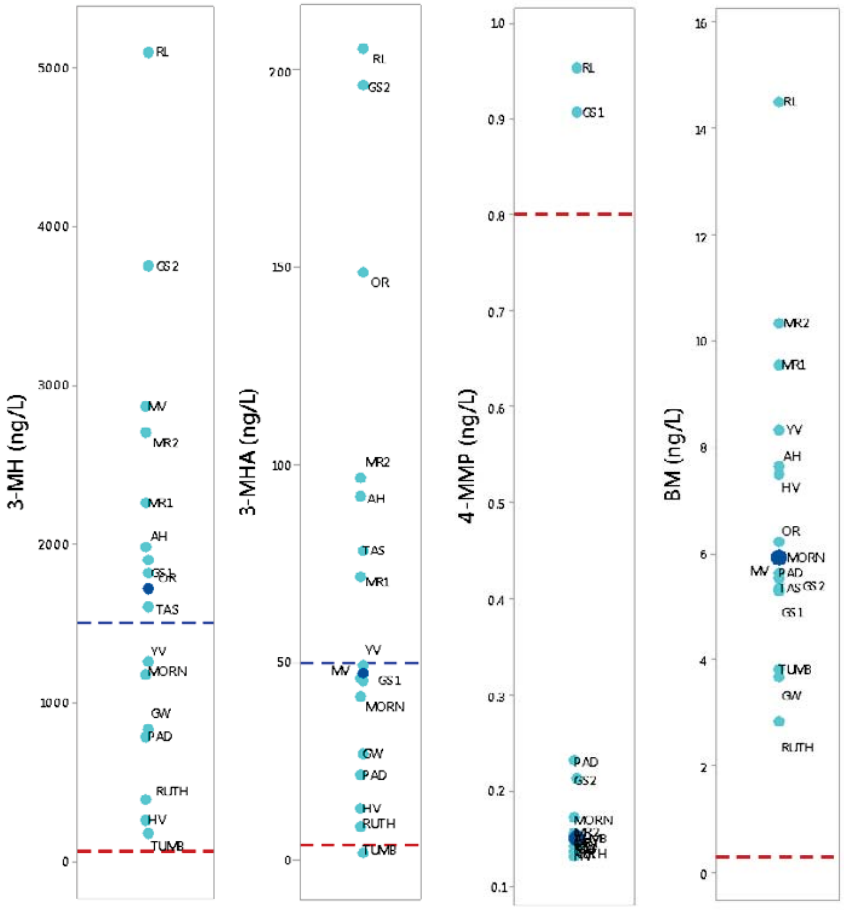

Figure 2. Concentration of the four thiol compounds (3-MH, 3-MHA, 4-MMP and BM) for a set of 16 wines made from juices sourced from vineyards across a wide range of Australian regions. RUTH: Rutherglen; HV: Hunter Valley; TUMB: Tumbarumba; PAD: Padthaway; GW: Great Western; MORN: Mornington Peninsula; GS: Great Southern; MV: McLaren Vale; YV: Yarra Valley; MR: Margaret River; TAS: Tasmania (Coal River Valley); AH: Adelaide Hills; OR: Orange; RL: Riverland. The median values are shown by the dark blue symbols. The sensory threshold for each compound is shown as the dashed red line, and the dashed blue line shows the indicative concentration where the compound may start to dominate the wine's aroma.

with relatively high concentrations of 3-MH. The wine with the highest level was a well-known and highly regarded premium oaked Chardonnay from Margaret River, considered one of the 'new wave' of Australian Chardonnays with a retail price of $80. Tasmanian wines had the highest median concentration of 3-MHA, while the highest individual concentrations were found in two large-volume selling Western Australian Chardonnays, previous vintages of which were assessed by a trained AWRI sensory panel as being high in 'passionfruit' aroma. Tasmanian wines were high in BM and, overall, higher priced wines were more likely to have higher concentrations of this compound, probably reflecting the propensity of barrel fermentation and use of time on lees and time in barrel in producing higher-priced wines, which are factors that can affect the formation of this compound. The high values of 3-MH for wines from Western Australia might reflect the use of the Gin-Gin Chardonnay clone, which is known for its 'tropical fruit' character. A recent Chardonnay clonal project led by Dr Mike McCarthy, from SARDI, showed that over several vintages wines made from this clone can be rated significantly higher in 'tropical fruit' character than wine from other clones made in an identical fashion (Whiting *et al.* 2017).

The results showed clearly that these four thiols are part of the complex flavour story of Chardonnay wines. However, there was no sensory data collected from these wines, and as they were commercially available wines, there is the possibility of a percentage of other varieties being included. There would also certainly have been a wide range of viticultural and winemaking variations in their production.

YOUNG UNWOODED CHARDONNAY: DO THIOLS CONTRIBUTE IMPORTANT FLAVOUR WHEN WINEMAKING IS IDENTICAL?

To further study the effect of thiols in Chardonnay, a set of free-run whole-bunch pressed juices were sourced from major Chardonnay-producing regions in Australia (16 vineyards across five states), and wines were made from them under controlled conditions without the use of oak. The sensory attributes of the wines were quantified by a trained AWRI sensory panel, and more than 70 aroma compounds were analysed, including the thiols. The results of the chemical analysis showed a high concentration of thiols, with an even wider range of results than seen in the commercially available wines (Figure 2).

The concentration of 3-MH in each wine was well above the sensory threshold (up to 80 times) and the concentration of 3-MHA was above the threshold in all but one of the wines (up to 50 times the threshold in two wines). Benzyl mercaptan was similarly well above the reported aroma threshold in all wines (up to 48 times), while 4-MMP was only slightly above the threshold in two wines. Interestingly, the wine made from Riverland juice was highest in all thiols, which is consistent with the data from the commercially available wines, where some wines from warm inland regions were relatively high in thiols. There was some variation in the ripeness of the grapes, with alcohol concentration ranging from 12.5 to 14.7%v/v, but there was no correlation of alcohol and thiol concentration. The high levels of thiols in some warm inland region wines may reflect differences in irrigation regime or nutrient status of the fruit, as these have been shown previously to affect thiols in wines, and this is an area of active research. ▸

Figure 3 shows a representation of the sensory differences among the wines, with the degree of correlation of the four thiols with the sensory attributes also shown. Of the 16 wines assessed, the Great Southern 2 wine (GS2) was rated highest in 'passionfruit' and 'lime' aroma, with the other wines plotted in the upper half of the figure also rated highly in these descriptors. The 3-MHA and 3-MH concentrations were closely correlated with 'passionfruit' and 'box hedge' aroma. The wine made from Riverland juice (RL) was rated highest in 'box hedge/cat pee' as well as 'flint' aroma, and these attributes were related to 4-MMP and BM, respectively.

When the relationship of thiol concentrations with wine sensory properties was more closely investigated (Figure 4), a non-linear relationship was seen between 3-MHA concentration and 'citrus' flavour, with a peak at 100ng/L, followed by a decline. The sensory scores for 'passionfruit' or 'box hedge/cat pee' aroma, on the other hand, continued to increase with increasing concentration of 3-MHA, providing further evidence that these compounds can contribute different characters as they change in concentration, moving from general 'citrus/fruit' to 'tropical fruit' to 'cat pee/box hedge/sweaty'.

It is important to note that the wines in this study should not be considered representative of the different regions, as only a single juice was obtained from each region in most cases. The intention of this investigation was to achieve a diverse range of wines, not to define differences between regions. As a final aspect of this study, a group of 156 white wine consumers gave liking scores for a subset of these wines, and those wines with higher thiol concentrations were found to be well liked by two identified clusters of consumers, comprising 60% of those tested.

CONCLUSION

This study has shown that Chardonnay wines can gain flavour from the thiol compounds previously thought to be mainly involved in Sauvignon Blanc varietal character, and that these compounds are much more prevalent and important for Chardonnay as a variety than previously thought. With concentrations comparable to those observed in some Sauvignon Blanc wines, the fact that most Chardonnay

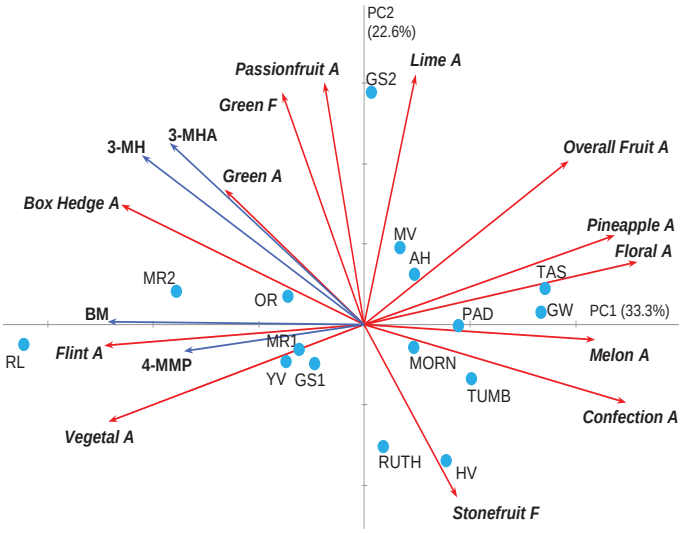

Figure 3. The sensory properties of the wines made from the 16 juices sourced from multiple regions across Australia. Correlation of the concentrations of the four thiols measured with sensory attributes is shown with blue arrows.

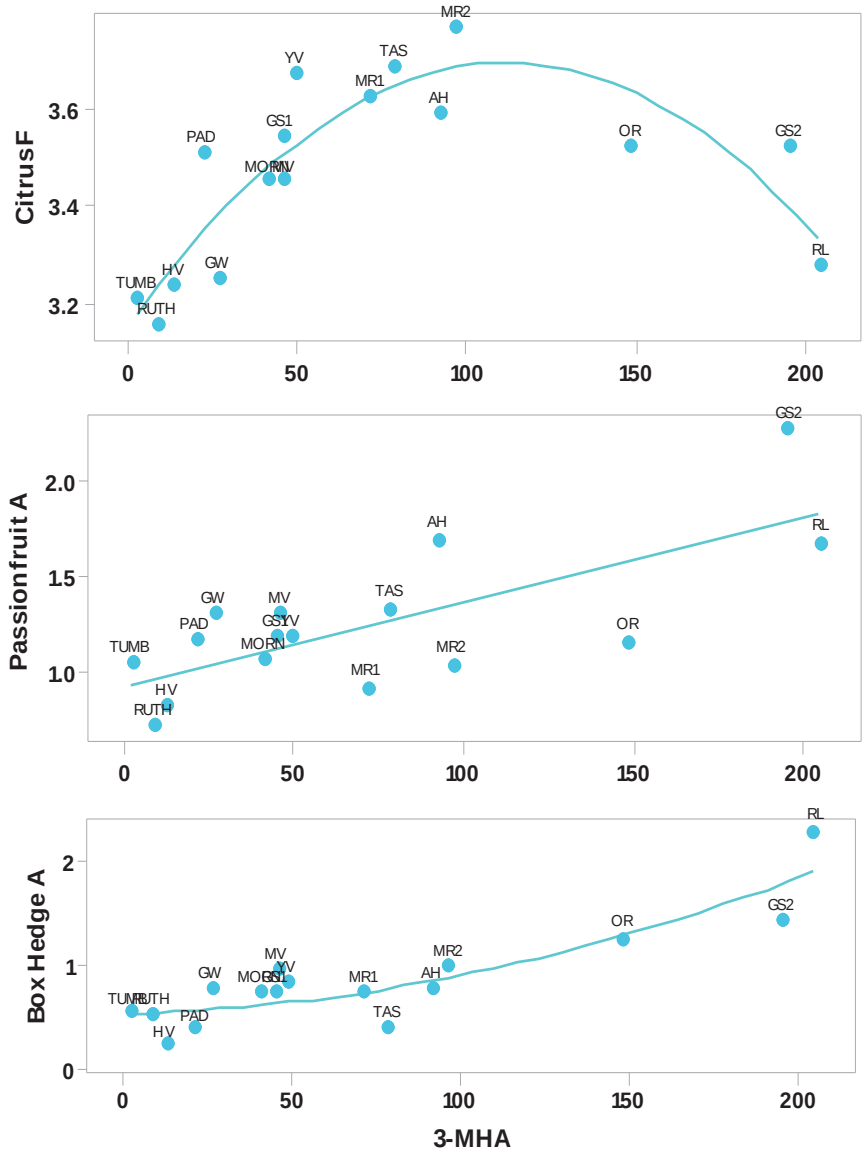

Figure 4. Relationships between 3-MHA concentration and 'citrus' flavour, 'passionfruit' aroma and 'box hedge/cat pee' aroma intensity scores from a trained sensory panel, for a set of 16 wines made from juices sourced from vineyards across a wide range of Australian regions.

wines do not taste highly aromatic is likely due to complex interactions among the multitude of compounds present suppressing the strong 'passionfruit' or 'box hedge' characters that are so evident in many Sauvignon Blanc wines. While the thiol compounds may be partially suppressed by other compounds, the sensory study showed that they certainly make a contribution to wine aroma and flavour. From previous research at the AWRI, variables such as post-harvest skin contact, including time from machine harvesting to delivery at the winery, and choice of yeast strain are known to have a large effect on thiol concentration in finished wines, allowing the 'dialling up or down' of their concentration by wine producers in a fairly simple, efficient manner. The current research has shown that thiols and their precursors in grapes are important components to consider in viticultural and winemaking trials for Chardonnay, being well accepted by the majority of white wine consumers, and may provide a target for winemakers and viticulturists in influencing wine style. For more details on this study see Capone *et al.* (2017).

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