Winemaking supplements: what's inside?

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INTRODUCTION

Tannins and polysaccharides are two key macromolecules present in wine and their composition is linked to important mouthfeel attributes. Tannins are responsible for the astringent sensations that are considered integral to red wine mouthfeel (McRae and Kennedy 2011), while polysaccharides can mediate both astringency and hotness, as well as contribute to palate fullness (Gawel *et al*. 2016). Although these macromolecules are naturally extracted from grapes and yeasts during vinification, it is permissible for tannins and mannoproteins to be supplemented to aid production under the Australia New Zealand Food Standards Code - Standard 4.5.1.

There are two types of commercial tannin products, more commonly known as oenotannins: condensed tannins, which are extracted from grape material (skins and seeds); and hydrolysable tannins, which are extracted from botanical materials such as oak, quebracho and chestnut (Versari *et al*. 2013). According to a survey conducted in selected Australian wine regions, winemakers who made use of oenotannins reported their main objectives were to achieve colour stabilisation, to create specific wine styles, to mask faults and/or for general risk management (Hill and Kaine 2007). However, in reality, whether these desired effects can be achieved or not depends on a range of factors, such as product origin (i.e., grape, oak and/or other material), dose rates, purity, grape variety and the timing of addition (as reviewed by Versari *et al.* 2013). There is no legal limit imposed on the dosage, but the manufacturers' recommendations usually range between 100 and 400mg/L.

Mannoproteins (MP) are polysaccharides present in yeast cell walls which are released during alcoholic fermentation and extended ageing in the presence of lees. MPs are one of the main red wine polysaccharides; for example, MP were found to account for 35% of total wine polysaccharides in a Carignan wine (Vidal *et al.* 2003). The remaining wine polysaccharides were mainly comprised arabinogalactan-protein and rhamnogalacturonan derived from grape cell walls. Early research has shown that low molecular weight MPs are effective in achieving tartrate and protein stability (Waters *et al*. 1994, Moine-Ledoux *et al.* 1997). MPs are, therefore, approved for addition to wine at concentrations of 100 to 300mg/L, giving maximum levels of 400mg/L, taking into consideration the MP levels naturally present in wine (for more information, consult Application A605 at www.foodstandards.gov.au). Subsequent studies found that MPs can also improve colour and tannin stability (Rodrigues *et al*. 2012), as well as enhance palate fullness and reduce astringency (Vidal *et al.* 2004, Rinaldi *et al*. 2012, Quijada-Morín *et al*. 2014). Since the natural release of MP from sur lie practice can be quite a long process, the addition of commercial MP is viewed as an accelerated method for achieving these beneficial effects.

There are myriad tannin and MP products on the Australian market, with various claims regarding product origin and desirable effects. Although product labels generally indicate origin, the method of extraction and approximate content of each ingredient, more detailed information is rarely provided by manufacturers. Product composition undoubtedly influences the oenological outcome and, therefore, winemakers' purchase intention. Evidence suggests grape skin tannins command higher prices than seed tannins (Obreque-Slier *et al*. 2009), and that winemakers may have preferences for different types of tannin (Hill and Kaine 2007). Whereas the molecular weight range and protein content for MPs are likely to affect the outcome of wine stabilisation and sensory consequences. As a consequence, an evaluation of commercial oenotannin and mannoprotein products was conducted in order to determine the variation among supplements available on the Australian market, together with their potential impact on wine sensory properties. Of particular interest was the potential for these products to improve the mouthfeel quality of red wine made from early harvested grapes, since these wines are naturally deficient in tannin and mannoproteins composition.

MATERIALS AND METHODS

Fourteen grape-based tannin products were sourced from five different manufacturers. Twelve products were in powdered form while the other two were in liquid form. Eight MP products were then sourced from five different manufacturers (but not necessarily the same suppliers as for tannin products), five of which were in powdered form, while the other three were liquids. The liquid products were freeze-dried and powdered for ease of comparison. In order to obscure product names, oenotannins were labelled with 'Sk' (for skins), 'Se' (for seeds), or 'SkSe' (for combined skins and seeds), according to the origin of the material information reported by the manufacturers; MPs were randomly numbered. Products were analysed to determine tannin concentration and composition. More detail can be found in Li *et al.* (2017).

Following compositional analysis of all 14 products, two oenotannins (Se4 and Sk5), and one MP (MP7) were selected for a further study. Two Shiraz wines were made from sequential harvests of grapes from the same vineyard, containing 11.5% and 14.5% alcohol (by volume), respectively. Supplements were subsequently introduced to the wines in different combinations and at different concentrations. The supplementation regimes created a series of wines with

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tannin concentrations ranging from 326 to 1067mg/L, and MP concentrations from 68 to 452mg/L, for each harvest date. As a frame of reference, red wine typically contains up to 4000mg/L tannin, while the MP content of wine is usually no more than 200mg/L (Quijada-Morin *et al.* 2014, Smith *et al.* 2015). Wines were then presented to a trained panel of tasters for descriptive sensory analysis.

RESULTS AND DISCUSSION

Study 1: Survey of oenotannin and MP products on the Australian market

In early work, early (sub-optimally) harvested Shiraz grapes were treated with the addition of oenotannin and MP to increase tannin and MP concentrations to levels comparable to red wine made from more mature grapes (Li *et al.* 2017a). Controversially, oenotannin additions did not influence tannin composition, colour parameters or mouthfeel properties of the treated wines, only increased 'red fruit' and 'confectionary' aromas were observed. In contrast, MP addition affected palate coarseness. The significant loss of oenotannins, inconsistent recovery of MPs and absence of expected mouthfeel modification prompted the follow-up study, which aimed to investigate the composition of commercial additives, i.e., 14 oenotannins and eight MPs.

For the analysis of oenotannins, methylcellulose precipitable tannin (MCPT) was measured and calculated as the percentage of dry weight, to represent product purity (Figure 1A). MCPT values were highly variable between products, and the proportion of the major monomeric phenolic compounds present was found to be relatively low across all products. The sub-unit composition (i.e., catechin, epicatechin, epigallocatechin and epicatechin-gallate) and molecular size of tannins were distinctive between skin and seed-derived tannins. This data was then subjected to principal component analysis (Figure 2), which revealed some products exhibited chemical compositions that strongly agreed with the labelled origin of material (i.e., seed vs. skin), for example, Se5, Sk4 and Sk5, whereas other products did not. Furthermore, for certain manufacturers, products marketed under different names, for different oenological purposes, were found to have similar

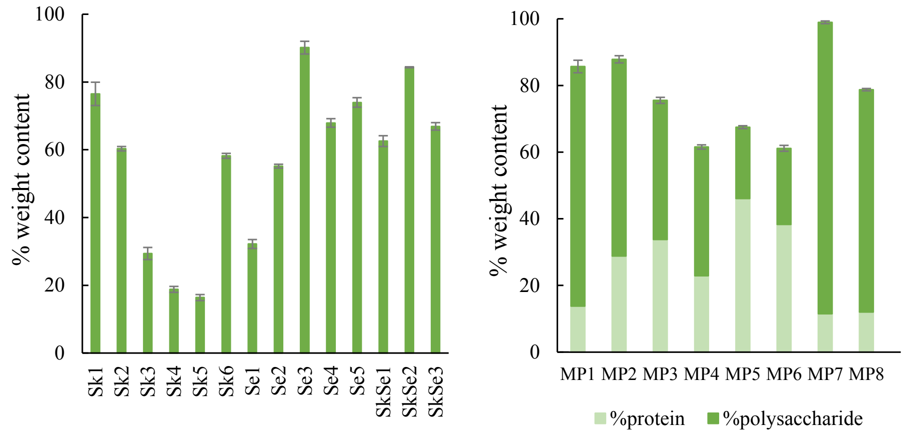

Figure 1. (A) Weight percentage of measurable tannin content (methylcellulose precipitable tannin) in oenotannin products derived from skin (Sk1–6), seed (Se1–5) and skin+seed (SkSe1–3); and (B) total polysaccharide and protein content (%) of MPs. Adapted from Li *et al*. (2017b) AJEV: ajev. 2017.17057.

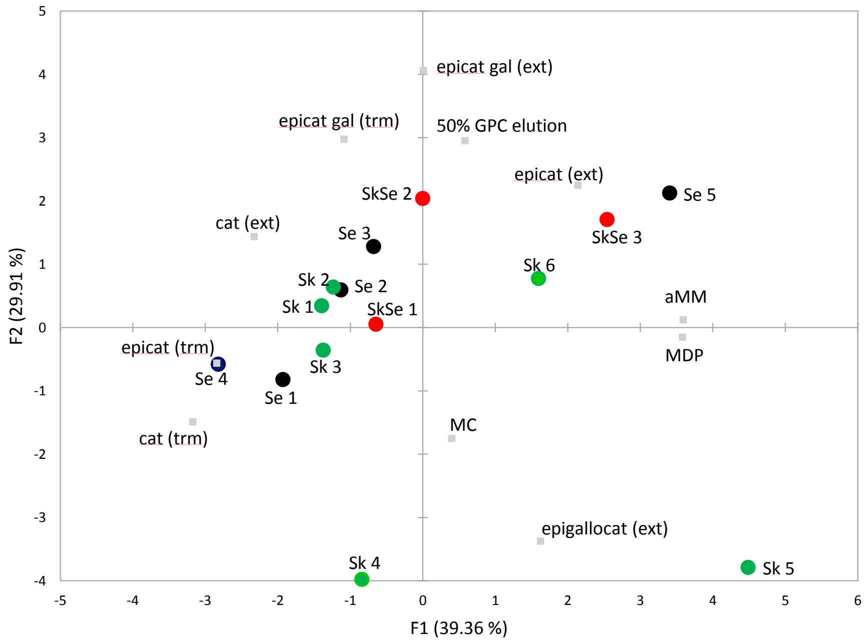

Figure 2. PCA plot of tannin products based on chemical composition. % = percentage of terminal (trm) and extension (ext) units of catechin (cat), epicatechin, (epicat) epicatechin gallate (epicat gal) and epigallocatechin. Sk = skin; Se = seed, SkSe = skin+seed; MDP = mean degree of polymerisation; aMM = average molecular mass; MM = % mass conversion. Adapted from Li *et al*. (2017b) AJEV: ajev. 2017.17057.

compositions. Conversely, products from other manufacturers (sold under different labels) showed significant compositional differences. Some discrepancies have previously been observed between the information provided on product labels and the compositional data measured for oenotannins (Obreque-Slier *et al.* 2009, Harbertson *et al.* 2012) with the majority of oenological tannin products assessed found to comprise less than 50% tannin (Keulder 2006, Harbertson *et al*. 2012). This suggests the addition rates recommended could, in fact, be too little to significantly impact wine composition and quality.

For the analysis of MPs, monosaccharides and proteins accounted for between 60 and almost 100% of the dry weight (Figure 1B). However, the products contained different amounts of mannose and glucose residues (the components of mannoprotein). Some products also contained considerable amounts of arabinose and galactose residues, which indicate the presence of arabinogalactan, a polysaccharide that is not derived from yeast. In the case of MP4, MP5 and MP6, this was due to the presence of gum arabic (which predominately comprises arabinogalactan), a wine supplement permitted for use in Australia mainly for wine clarification and colour stabilisation. The mixed nature of these products was disclosed by manufacturers on the data sheets available for the products. The protein content of products ranged from 10 to 50%. This is likely to have a significant impact on wine phenolic composition, as yeast-derived proteins have higher interactions with wine polyphenolics than with polysaccharide fractions (Mekoue Nguela *et al.* 2016). Furthermore, products containing gum arabic tended towards higher molecular size ranges compared with products containing only MP.

Study 2: Use of selected products to modulate wine mouthfeel

In this study, two oenotannins and one MP were added to Shiraz wine post-vinification. The sensory study revealed panelists perceived wines of 14.5% alcohol as having more 'sweetness', 'body', 'hotness' and 'flavour intensity' than wines with 11.5% alcohol. However, no significant differences were found for any sensory attributes, including 'astringency' and 'body', following supplementation, with the exception that wines supplemented with MP were perceived to be sweeter than wines supplemented with tannins in the series with 11.5% alcohol (Figure 3). However, the same trend was not observed for 14.5% alcohol wines. This finding can, in part, be corroborated by another study that demonstrated a fraction of wine polysaccharides can reduce bitterness in wines of lower alcohol and pH, i.e., early harvest wines.

To make sense of the lack of differentiation amongst wines, a more controlled experiment was performed whereby judges rated: (i) 'astringency' for a series of wines (containing 11.5% alcohol), spiked with seed tannin (at 300, 600, 1000 and 1500mg/L); (ii) 'body' for a series of wines spiked with MP (at 400, 1000, 3000 and 6000mg/L); and (iii) 'body' for a series of wines spiked with pectin, a polysaccharide known to elicit more viscous mouthfeel in wine (at 350, 500 and 600mg/L). The sensory panel could not perceive any intensification of astringency in wines spiked with 300 or 600mg/L of seed tannin (the concentration range comparable to that in wines used in descriptive analysis) relative to the base wines. However, they perceived significantly more astringent sensations in wines dosed with 1000mg/L (or more) of seed tannin. It appeared that the different levels of tannin present in the wines used in descriptive analysis were too subtle for judges to perceive. Higher levels of addition could be used to achieve more pronounced effects, but negative impacts, such as elevated bitterness or undesirable flavours might ensue (Harbertson *et al.* 2012). The judges were also unable to perceive any increase in body in wines with higher MP concentrations, even at 6g/L (Figure 4). However, when presented with wines spiked with pectin, most members of the panel could correctly identify the increase in wine body. These results cast doubt on the extent to which MP supplements can enhance wine body. In this study, wine made from fruit harvested later was perceived to have a fuller body than wines made from fruit harvested earlier. This is likely the result of complex interactions involving flavour and viscosity, as well as other compounding factors, i.e., wines with more mature fruit flavours and less acidity were perceived to have more body. Modification of the macromolecular composition of the wines alone did not achieve similar sensory outcomes. It should be noted that the MP product (MP7) used in this study was of high purity and had a low protein content. The use of other MP products of different compositional profiles may give different results.

CONCLUSION

A considerable diversity among commercial tannin and MP products has been found in this study. The impact on wine chemical and sensory characters from using these products has previously been attributed to concentration, composition (sub unit composition for tannin and protein content for MP) and molecular size. It is, therefore, safe to assume that the choice of product would alter the end result. Bench trials using wines treated with different products are recommended in order to make informed decisions regarding the use of supplements.

In the current study, little effect in modified mouthfeel was achieved by adding oenotannin and mannoprotein products. The mouthfeel of wine is a result of complex interactions between various wine components, such as volatiles, macromolecules, alcohol levels and acids. As such, altering one aspect of the system may have limited outcomes. Applying commercial additives in conjunction with winemaking practices that address the other aspects may achieve more desirable results.

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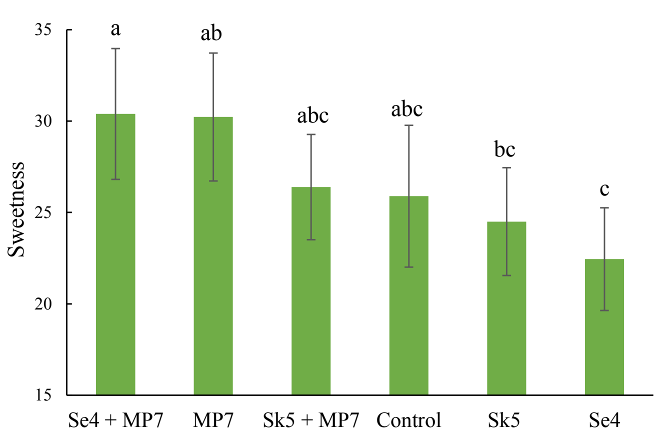

Figure 3. Ratings of 'sweetness' for Shiraz wines containing 11.5% alcohol, with supplementation of skin tannin (Sk5), seed tannin (Se4) and/or mannoprotein (MP7).

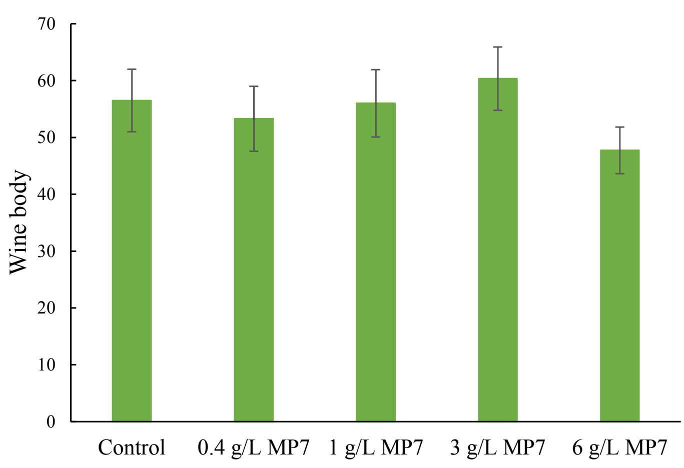

Figure 4. Ratings of 'wine body' for Shiraz wines containing 11.5% alcohol, with different levels of mannoprotein supplementation.