Highlights

- A total of 14 wine sensory attributes were modelled from grape chemical measures.
- Causal and correlational relationships were determined with chemometric modelling.
- Five grape measures were used extensively for modelling.
- Seven grape measures may be redundant in any future objective quality measurements.

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Objective measures of grape quality: From Cabernet Sauvignon grape composition to wine sensory characteristics

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Abstract

In an investigation of objective measures that link grape composition to wine quality, this study sought to identify Cabernet Sauvignon grape parameters that predict the sensory properties of the corresponding wines. Eleven chemical measures comprising volatile and non-volatile compounds, enzyme activity plus standard industry harvest measurements were applied to grape samples obtained from different regions throughout South Eastern Australia over three vintages. Grapes underwent controlled vinification and the resulting wines evaluated with sensory descriptive analysis. The entire multi-vintage data sets were combined and modelled using a combination of partial least squares (PLS) and sequential and orthogonalised (SO) -PLS regression techniques. Optimal models were obtained with single sensory attributes rather than global modelling with the entire sensory profile. Five grape chemical measures, which in the main were harvest parameters, were used along and orthogonalised to model 14 sensory attributes of the Cabernet Sauvignon wines. The seven remaining measures were not used due to their poor ability to model wine sensory attributes, with enzyme activity and tannin by HPLC explaining the least. The study revealed new insights into the relationship between grape chemistry and wine sensory characters, which has implications for developing an objective measurement system for determining grape quality.

Keywords

***Vitis vinifera*, grapes, wine, SO-PLS, chemometrics, Cabernet Sauvignon**

1. Introduction

Measuring the chemical composition of grapes is of primary importance to wine producers so that informed decisions that affect style and quality can be made about harvest timing and vinification. As an extension of this, objective measures of grape quality that can help predict the sensory properties of wines are highly sought after by the industry and actively pursued by wine researchers. Some insight has been provided by discoveries of important varietal compounds in grapes that lead to a direct contribution to wine sensory attributes, with notable examples being methoxypyrazines (green and vegetal) and rotundone (black pepper) (Allen & Lacey, 1998; Wood et al., 2008). Yet the entire grape to wine continuum remains poorly understood due to the complex interplay between grape composition and vinification interventions (i.e., interactions between chemical, biological and human phenomena).

Simplistically, decision-making by winemakers chiefly relies upon tracking changes in basic chemical measures of grapes that include pH, titratable acidity (TA), total soluble solids (TSS), and colour for red grape varieties. Beyond this, grapes may also be assessed for flavour (Niimi, Boss, Jeffery, & Bastian, 2017; Niimi, Boss, Jeffery, & Bastian, 2018) and then wine styles created according to the winemaker's craftsmanship and perceptions. Undoubtedly, winemakers cannot make high quality wines without grapes of a suitable standard, with the difference between high or low quality grapes often being reflected in the price per tonne. Take for example one of the world's great red cultivars, Cabernet Sauvignon, where the price per tonne of grapes purchased in Australia in 2018 varied between AUD$354 to AUD$7300 (Wine Australia, 2019b). However, questions remain, particularly with regard to which chemical constituents differ to justify such large price differences between parcels of grapes, and how any differences impact on wine style and quality.

A wide range of compositional and biochemical factors in grapes are known to influence the chemical constituents of wines in the form of both volatile and non-volatile compounds (Waterhouse, Sacks, & Jeffery, 2016). These ultimately contribute to the holistic perception of wine quality through traits such as flavour, mouthfeel, and colour.

Wine volatile compounds contributing to aroma and flavour are derived from grapes by a number of mechanisms and can be classed as fermentative or varietal. Fermentative compounds such as volatile acids, esters, alcohols and some sulfur compounds such as H_2S arise during fermentation either from glycolysis or metabolism of amino acids in grapes that provide a key component of yeast nutrition, leading to an array of volatile yeast secondary metabolites (Sumby, Grbin, & Jiranek, 2010; Ugliano & Henschke, 2009). In contrast, varietal compounds including terpenoids, methoxypyrazines, sulfur compounds, and C_{13}-norisoprenoids are directly transferred from grapes to wine as free volatiles or are liberated from bound precursors (e.g., glycosides or amino acid conjugates) during fermentation (Ebeler & Thorngate, 2009; Robinson et al., 2014a). With reference to Cabernet Sauvignon, some grape-derived volatiles have been correlated to aroma attributes of the wines: 2-pentylfuran was associated with aroma impact, ethyl acetate with pepper, heptanal with spicy, and 3-isobutyl-2-methoxypyrazine (IBMP) with woody/tobacco attributes (Forde, Cox, Williams, & Boss, 2011).

Wine is of course, more than simply volatile compounds and there are other constituents in the majority such as non-volatile compounds derived from grapes that contribute to taste, colour, and texture. In fact, the wide range of sensory modalities perceived including aroma, taste, colour, and texture all contribute to a better discrimination of wine sensory perception and thereby wine quality judged by experts (Niimi, Boss, & Bastian, 2018). Non-volatile compounds are also prominent in wine, with the most abundant being organic acids and glycerol. Acids primarily contribute to taste and carry through from the grapes to the wine (e.g., tartaric, malic, acetic, and hydroxycinnamic acids) or are formed from yeast (e.g., succinic and pyruvic acids) and lactic acid bacteria metabolism (e.g., lactic acid), whereas glycerol is a by-product of glycolysis (Antalick, Perello, & de Revel, 2012; Cappello, Zapparoli, Logrieco, & Bartowsky, 2017). In the case of red wine in particular, grape skin- and seed-derived polyphenols are an important class of non-volatile compounds that comprise pigmented, monomeric, and polymeric forms, including anthocyanins, flavonols, flavan-3-ols, and tannins. These are extracted during the maceration step of red winemaking and contribute to colour, taste and mouthfeel sensations (Waterhouse et al., 2016). The relative abundance of polyphenolic compounds, in particular anthocyanins and tannins, in grapes appear to be a reliable indicator of their amount in wine (Bindon et al., 2014; Chira, Schmauch, Saucier, Fabre, & Teissedre, 2009).

Due to the complexity, greater understanding of the links between grape chemical composition and the sensory characteristics of resultant wines is required to give producers an enhanced ability to make wines of a targeted style and quality. This approach contrasts with the many studies that have investigated the correlation between wine chemical composition and sensory characteristics (Robinson et al., 2014b). Extending this to examine the impacts of grape composition on wine sensory properties is comparatively less understood (Niimi, Boss, et al., 2017; Niimi, Boss, Jeffery, & Bastian, 2018).

From a sensory perception approach, some key sensory attributes of Cabernet Sauvignon wines including colour, dark fruit aroma and flavour, and mouthfeel can be related to the sensory profile of the berries (Niimi, Boss, et al., 2017). However, berry attributes that contributed to the modelling varied across vintages, which presents a challenge when trying to relate data sets from different years (Niimi, Boss, et al., 2017; Niimi, Boss, Jeffery, & Bastian, 2018). Establishing reliable grape measures that can robustly predict wine sensory attributes stands as a significant challenge in the wine research field.

This study tested the hypothesis that grape chemical measures can contribute to the modelling of wine sensory attributes for Cabernet Sauvignon. Grape samples were harvested over three vintages and 12 different, independent groups of measurements were made on the grapes and used as predictors of the sensory profile of the Cabernet Sauvignon wines produced from these grapes with a uniform winemaking protocol. With multiple blocks and multiple vintages to model, the sequential and orthogonalised-partial least squares (SO-PLS) (Næs, Tomic, Mevik, & Martens, 2011) approach was taken to determine the grape measures that are most important for prediction of the sensory perception of wines.

2. Materials and methods

2.1 Grape samples and winemaking

A total of 75 samples were harvested across the 2013, 2014, and 2015 vintages (25 samples per year) from eight geographical indications (GI) of South Eastern Australia and from identical vineyards across the three years wherever possible (Table 1). GIs are designations to specific regions of Australia that identifies goods and products of particular quality and reputation, in this case grapes and wines (Wine Australia, 2019a). Repeat access to some samples was not possible for various commercial reasons so substitutions were made from nearby vineyards within the same region. Grapes were harvested from February to April of each vintage and involved collecting bunches from all parts of the canopy, from both sides of vines spread throughout the vineyards. Sixty kg of grapes were sampled from each vineyard, and three subsamples of 150 g were taken from the large parcel, frozen immediately in liquid N_2 and stored at -80 °C pending further analysis. Samples were harvested at commercial maturity (between 22 - 25˚Brix) and the 50 kg parcels were vinified separately and identically as described previously (Niimi, Boss, et al., 2017), in order for differences in the grapes to be reflected in the wines. Sampling and data generated from 2013 samples have already been reported previously (Niimi, Tomic, Næs, Jeffery, Bastian, & Boss, 2018). Vinification involved destemming and crushing the grapes, with the addition of 50mg/L Potassium Metabisulphite (PMS). Musts were fermented using *Saccharomyces cerevisiae* at a rate of 300mg/L (EC1118, Maurivin) at 19°C and inoculated with *Oenococcus oeni* (2mg/L of Lalvin VP41, Lallemand S.A.S.) on the second day for malolactic fermentation and the temperature raised to 20°C. Fermentation continued until residual sugars were less than 2g/L, followed by pressing of ferments from the skins into 20 L stainless steel kegs. Ferments were held at 20°C until the completion of malolactic fermentation with malic acid below 0.2g/L. Ferments were adjusted with PMS to free SO_2 levels of 40mg/L, potassium bitartrate added at 4g/L and cold settled at 0°C. The wines were racked off lees and free SO_2 readjusted to 40mg/L. Wines were not adjusted for pH to retain the inherent differences between the samples. Wines were bottled under nitrogen gas and kept at 15˚C for three months to allow for bottle shock, prior to any sensory testing. The produced wines used were the same as those wines reported on previously (Niimi, Boss, & Bastian, 2018; Niimi, Boss, et al., 2017).

2.2 Grape chemical measures

A suite of chemical profiles was determined for the grapes, encompassing volatile and non-volatile compounds, and typical harvest measures according to the analytical methods described previously (Niimi, Tomic, et al., 2018) (Table 2). Briefly, 12 different parameters consisting of a number of variables (analytes) were evaluated: harvest measures (X_{01}), amino acids (X_{02}), targeted volatile compounds (X_{03}), non-targeted volatile compounds (X_{04}), bound volatile compounds (X_{05}), colour (X_{06}), total phenolics and tannins (X_{07}), anthocyanins (X_{08}), tannins (X_{09}), flavonols (X_{10}), fatty acids (X_{11}), and lipoxygenase enzymes (X_{12}). Chemical measures X_{01} by weight, total soluble solids, pH, and TA, $X_{03\text{-}05,\,11}$ were performed by gas chromatography-mass spectrometry, $X_{02,\,08\text{-}10}$ were performed using high performance liquid chromatography (HPLC), X_{06} by CIELab tristimulus, X_{07} by UV spectrophotometry, X_{12}, by spectrophotometry. Every sample from each vintage was subsampled randomly from grape bunches in triplicate from the parcels.

2.3 Wine sensory analysis

The procedures for sensory analyses of wines from the 2013-2015 vintages have been described previously (Niimi, Boss, & Bastian, 2018; Niimi, Boss, et al., 2017) but the subsequent data obtained were subject to different analyses and interpretation in the current study. In short, assessors who had experience in tasting wine or who were screened for sensory performance according to the international standards organisation (ISO) participated in the sensory descriptive analysis of research-scale Cabernet Sauvignon wines. At the beginning of tasting wines of each vintage, vocabularies were developed and refined to list attributes that are relevant to the samples as well as the vintage. This was followed by training in the use of scales, as well as discrimination ability, agreement within the panel, and repeatability. All sensory data were collected in triplicate per assessor. These overall means were utilised for chemometric analyses. Sensory analyses were conducted with the approval of the university human ethics committee (H-2014-057). All wines were assessed within 6 months of bottling.

2.4 Data analysis

Means were calculated from the replicates of each chemical measure in each vintage before further chemometric data analysis. Sensory measures were also calculated as means over the assessors and over the replicates to give an overall sample average for the panel.

Mean measures of each data block within each vintage were checked for systematic variance by inspection of principal component analysis (PCA) plots. One sample was identified as an outlier (14CWA5) based on sensory data and was therefore removed from each data block, leaving 74 samples for further data analysis. Each data block per vintage was analysed with one-way analysis of variance (ANOVA) for sample effects with replicates representing the source of error in the models. Significantly different variables (α = 5%) within a block per vintage were noted for further data analysis. To exclude vintage effects, variables in each data set were standardised within vintage by mean centring and division by the standard deviation prior to further modelling. Having eliminated possible mean differences and differences in variability, the standardised data blocks were stacked vertically with matching variables to give long data blocks. During this process, variables that had missing values in any vintage were removed from the entire combined data set, since the implementation of the SO-PLS algorithm does not handle missing values. To minimise noise in the modelling, this was followed by the removal of variables in each data block that did not differ significantly among the samples for any vintage according to one-way ANOVA as described above. For example, the sensory data block dimensions for each vintage were different, with 28, 32, and 28 attributes being measured in 2013, 2014, and 2015, respectively. Upon stacking and matching the same sensory variables measured across the vintages, followed by removing variables that did not significantly differ in any of the vintages, a table containing 21 attributes remained for the final modelling stage. The resultant number of variables for each data block determined by this method of variable reduction is presented in Table 2.

Data analysis procedures used specifically for SO-PLS (Næs et al., 2011) including partial least squares (PLS) have been described previously (Niimi, Tomic, et al., 2018). This method incorporates X-blocks sequentially after orthogonalization with respect to previously included blocks.

Briefly, when all sensory variables were considered at the same time, a regular PLS2 model was first used to fit each X-block independently (chemical measures) to the Y-block (wine sensory data). Three criteria were implemented for the progression of data analysis. As a first criterion, input blocks that accounted for at least 10% validated explained variance (using full cross-validation) were retained and any blocks that accounted for less were removed from further data analysis. Further analyses with the retained data blocks were performed using SO-PLS2. For the inclusion of block number two in the SO-PLS process, 5% improvement in validated explained variance was used as a second criterion (Menichelli, Almoy, Tomic, Olsen, & Naes, 2014; Niimi, Tomic, et al., 2018). This was realised by modelling the X-blocks with the Y-block using PLS2 with an appropriate number of components. The blocks with the lowest root mean square error of cross validation (RMSECV) were then selected. Holding the optimal model parameters from PLS2 constant, an additional X-block was orthogonally added from the remaining data blocks and modelled with PLS2. The second X-block that gave the lowest RMSECV with an appropriate number of components was chosen. These steps were repeated until no further improvement in models was seen with further orthogonal addition of X–blocks, as determined with RMSECV and validated explained variance values. As the third criterion, the importance of adding X-blocks to the prediction of Y-block/variables was determined using cross validation-analysis of variance (CV-ANOVA) (Indahl & Naes, 1998) as an indicative analysis of block contribution. The CV-ANOVA was tested at α = 0.1 instead of 0.05 due to the large transformations that take place when grapes are vinified into wines, meaning the statistical significances are supposed to be moderate at best.

Finally, Y was predicted from the most optimal model using principal components of prediction (PCP) to yield scores and loadings plots for the series of X-blocks and the Y-block used for the SO-PLS models (Langsrud & Næs, 2003). All models were fitted using a maximum of four components for each X-block (Niimi, Tomic, et al., 2018). The progression of PLS1 for individual variables followed by SO-PLS1 used the same procedures described above for PLS2 and SO-PLS2.

All analyses were performed using the Python programming language (Python version 3.5) utilising the Python packages numpy (Peréz & Granger, 2007), IPython (Oliphant, 2007), pandas (McKinney, 2010), and statsmodels (Seabold & Perktold, 2010). The Python implementation of SO-PLS was coded in-house.

3. Results and discussion

3.1 Data trends due to vintage effects

As an initial approach, similarities in data sets across vintages were evaluated by determining pairwise RV coefficients for each X-block (grape measures) using samples that were common across the 2013-2015 vintages (Table S1). As a general guide, an RV coefficient of >0.7 indicates high similarity between pairs of data sets (Cartier et al., 2006). Many of the pairwise RV coefficients determined across years were low (below 0.7), highlighting that measures between vintages were vastly different. The only exception was seen with data block X_{06} (CIELab) with RV coefficients of 0.63, 0.70 and 0.76 between respective pairs, suggesting these colour-related measures were similar across the vintages (Table S1). Other moderate similarities were seen for X_{02} (amino acids) in all vintages as well as X_{08} (anthocyanins) when comparing 2013 and 2015 vintages. This preliminary evaluation revealed in general the vast differences in each of the data sets across vintages.

The impact of vintage was also evident in the PCA plots of the descriptive sensory analysis data being standardised either across or within vintages, with the first two principal components accounting for 73% and 51% of explained variance, respectively (Fig S1). Standardisation across all samples yielded scores plots that clearly discriminated by vintage, with 2015 segregated in the top left of the plot. The resultant loadings revealed that 2015 wines typically had higher astringency, hue, and body but were lower in some fruity characters, whereas the 2013 and 2014 vintages were characterised by higher scores for sensory attributes other than those in the top left quadrant

This contrasted with standardisation within a vintage, which resulted in discrimination based on region instead of vintage (Fig. S1) as observed when assessing data from a single vintage (Niimi, Boss, & Bastian, 2018; Niimi, Boss, et al., 2017). Overall, the RVL samples were projected negatively on PC1, in the opposite direction of the WBY and McV wines. The majority of the CWA as well as CV samples were projected toward positive PC1 and negatively on PC2 whereas BV wines were projected positively on PC2. These samples possessed higher intensities of mouthfeel, green, dark fruit, and pepper characters alongside taste intensities. The samples LC and EV in contrast varied across vintages. Standardisation within vintage before stacking the data sets together before any modelling was therefore necessary in order to determine differences by region rather than vintage.

3.2 Global modelling of wine sensory profiles using SO-PLS2.

The sensory profiles of the Cabernet Sauvignon wines were modelled using SO-PLS2, with vertically stacked X-blocks of the three vintages, each standardised within vintage. To limit the chances of over-fitting the models, the optimum model (number of components) was determined using a single X-block prior to proceeding with the orthogonal addition of other X-blocks (Niimi, Tomic, et al., 2018), with a maximum of two X-blocks ultimately employed (as described in section 2.4). Colour from CIELab measures (X_{06}) gave the highest validated explained variance as the first block (22.6%, Fig. 1a). The orthogonal addition of the harvest measures data block (X_{01}) increased the validated explained variance to 28.8% (Fig. 1a) with two components giving a lower RMSECV (Fig 1b). Furthermore, modelling the Y-data set using X_{06} as the first block (CIELab colour) followed by X_{01} as the second block (harvest measures) significantly reduced the residual sum of squares through CV-ANOVA at $p<0.001$ and $p=0.006$, respectively. The CV-ANOVA showed that adding a second X-block (harvest measures) provided a significant increase in validated explained variance of the sensory profile, even though the increase was relatively small. Using CIELab and harvest measures met all three criteria required for consideration in modelling sensory profiles (see section 2.4 for the criteria). Orthogonal addition of a third X-block did not improve the model further with any X-block remaining.

The PCP scores and loadings based on the original X-data blocks of X_{06} and X_{01} to model Y showed that most of the RVL samples were projected on negative PC1 (Fig. 2a). These samples characteristically had high scores for confectionery and red fruit sensory attributes, along with light colour and low b* values being correlated (Fig. 2b). In contrast, samples projected positively on PC1 were predominantly from CWA, McV, and WBY and had high a* and Hue (ab) as well as TSS and Brix. Accordingly, these wines were seen to have more depth of colour and dark fruit characters with more intense mouthfeel characters. Differences observed across regions supported previous reports where colour is predominantly driven by the climactic variations in temperature that influence pigment formation within the grape berries (Mori, Goto-Yamamoto, Kitayama, & Hashizume, 2007; Ojeda, Andary, Kraeva, Carbonneau, & Deloire, 2002). The RVL region is known to have a hot climate where the synthesis of anthocyanins is comparatively lower (and thereby lower depth of colour and hue) than the cooler regions such as CWA and WBY (where higher concentrations of anthocyanins lead to deeper colour) (Hall & Jones, 2010). The orthogonal addition of the second X-block predominantly discriminated samples on the second PC, however the loading for °Brix discriminated the samples the most, based on its position near the outer ellipse of the correlation loadings plot (Fig. 2b). Further, the loading for °Brix correlated with both bitterness taste and alcohol mouthfeel. Little discrimination was seen based on the variation of ripeness (std dev Brix), or bunch and berry weights, and the variations in these measures (std dev bunch and berry weights). pH was a variable that moderately discriminated samples on the PCP plots.

In line with a previous report, fitting entire Y-blocks may have compromised the performance of SO-PLS2 evidenced by the low validated explained variance and high

RMSECV (Niimi, Tomic, et al., 2018). Therefore, single sensory attributes were investigated, using a combination of PLS1 and SO-PLS1. By doing so, this provides the opportunity to model attributes with underlying differences across the samples that may not have been otherwise determined with global modelling.

3.3 Modelling single sensory attributes using PLS1 and SO-PLS1

Analyses with PLS1 or SO-PLS1 were used to determine the X-blocks that contributed to the individual wine sensory attributes. During the initial modelling stage using PLS1, optimal models were obtained for each sensory attribute by computation with each X-block. Nineteen sensory attributes that were modelled met the minimum criteria of 10% validated explained variance, and models were determined for each attribute using up to 3 components (Table 3). Two taste attributes (acid and fruit sweetness) did not result in models that satisfied the minimum criteria and will not be interpreted or discussed further.

Seventeen of the 19 attributes were best modelled using a single X-block with PLS1, as orthogonal addition of a second X-block did not further improve the models in terms of increases in validated explained variance and CV-ANOVA. The remaining two attributes were modelled with SO-PLS1 using up to two X-blocks, as the validated explained variance met the minimum required improvement of 5% upon orthogonalisation. Further, orthogonal addition up to three X-blocks did not improve the models of attributes using SO-PLS. CV-ANOVA calculations for the PLS1 and SO-PLS1 models were used to determine whether the modelling with one or two blocks significantly contributed to the explanation of single Y-variables. Twelve PLS1 models showed a significant (p<0.1) contribution by the incorporation of single X-blocks (Table

3). The remaining five PLS1 models of A_Confectionery, A_Savoury, F_Confectionery, F_Green, and T_Bitter did not indicate a significant contribution of orthogonally adding a second X-block to the explanation of Y data blocks due to the models being weak from comparatively higher RMSECV values (Table 3). Only the significant PLS1 models according to CV-ANOVA will be interpreted hereafter. CV-ANOVA calculations on SO-PLS models showed that overall aroma and body mouthfeel were the only attributes that had significant contributions ($p<0.1$) from the two X-blocks (Table 3). Other attributes including colour hue, dark fruit aroma and flavour, and savoury flavour only had a significant contribution of the first X-block (data not shown), thus data analysis was taken as far as PLS1 for these attributes. Positive and negative coefficients were determined for significantly contributing X-variables in each PLS1 and SO-PLS1 model (Table 4.).

Depth and hue of colour attributes were modelled with CIELab colour (X_{06}) measures as expected; depth being modelled with the highest validated explained variance at 66.9% and hue being 48.7% (Table 3). Measures a* (redness) and chroma correlated positively with high intensities of depth and hue of wine appearance, while L* (lightness) correlated negatively for both attributes (Table 4). Dark fruit aroma and flavour were also modelled with the total tannins and phenolics with the same variables positively contributing to the attributes (Table 4). It is likely the case that the dark fruit attribute models were correlative, as total phenolics and tannins themselves are unlikely to directly translate to dark fruit aromas. Likewise, with red fruit attributes, aroma was modelled with flavonols measures whereas flavour was modelled with CIELab colour measures. The contribution of flavonols and CIELab colour measures as a predictor for red fruit perhaps implies correlative rather than causative effects, simply because flavonols and pigments are not volatile for the perception of aroma and flavour perception, respectively. However, it is possible that the differences in colour reflects changes in the expression of *VvMYBA* genes, which are the transcription factors that regulate anthocyanin production, that have been shown to regulate other genes in grape berries (Rinaldo et al., 2015), some of which could affect composition of the fruit and wine. The differences in anthocyanin concentration in the berry skin may also alter the light quality in the berry which, in turn, may alter fruit composition. Despite dark and red fruit characters being most likely a complex mixture of volatile compounds (Robinson et al., 2014b), these attributes could be conceptually driven by the intensity of colour, determined from expectations by colour (Spence, Levitan, Shankar, & Zampini, 2010). This phenomenon has been demonstrated in simple systems (Zellner & Whitten, 1999) and further work would be beneficial to confirm this hypothesis in wine, in that colour may contribute to the difference between perceived red fruit vs dark fruit characteristics. Other mechanisms could however concurrently be at play. It is possible that indirect correlations between colour and red/dark fruit characters are being described by the models, where maceration of skins during wine fermentation can increase intensities of red or black berry aromas (Pineau, Barbe, Van Leeuwen, & Dubourdieu, 2011). Higher levels of polyphenolic constituents in wine has been shown to influence intensities of various aroma attributes in wine (Perez-Jiménez, Chaya, & Pozo-Bayón, 2019).

Astringency mouthfeel was modelled best with CIELab measures, where calculated hue from a* and b*, a*, and chroma measures were positive contributors while b* and L* were negative contributors to the attribute (Table 4). Modelling of astringency could be considered as a direct correlation with pigmented polyphenolics, as there is evidence that anthocyanins and their oligomeric forms can contribute towards astringent mouthfeel characteristics (Gawel, Francis, & Waters, 2007; Sáenz-Navajas et al., 2017).

The attribute was also modelled alternatively with PLS1 using two components, where the X-block was total phenolics and tannin (X_{07}) and this resulted in a validated explained variance of 47.1% (data not shown). The model was comparatively more complicated and perhaps over-fitted compared to CIELab, because of the extra component required whilst yielding a validated explained variance. Nevertheless, total tannin concentrations in grapes can correlate well with that in wine when extracted under wine like conditions (Bindon et al., 2014) and total tannin concentrations in wine are known to positively correlate with astringency (Smith, Mercurio, Dambergs, Francis, & Herderich, 2007), which accords with the current study. On the other hand, tannin profiles (X_{09}) measured by means of HPLC were comparatively poorer at modelling the sensory data, based on the considerably lower validated explained variance (15.8% with one component, data not shown). Thus, despite the relationship between measures of grape total phenolics/tannins with astringency, elucidating the role of specific tannins from grape and astringency perception in wine remains challenging to determine (Vidal et al., 2004).

Pepper flavour and alcohol mouthfeel were modelled best using harvest measures, namely °Brix for both attributes (Table 4). A direct correlation between °Brix and alcohol mouthfeel is to be expected but nevertheless indicated the reliability of the modelling method. Interestingly, the projection of scores in the PLS1 model for pepper flavour was very similar to that of alcohol mouthfeel (Fig S2 and S3) and pepper character has been reported to change with TSS (Heymann et al., 2013).This flavour attribute is characteristic of the grape-derived compound rotundone, a sesquiterpene usually associated with the Shiraz variety, although low concentrations have been measured in Cabernet Sauvignon wines (Wood et al., 2008). However, the relationship of harvest measures with pepper flavour and alcohol attributes in the current study were so similar that they are likely to be linked to ripeness as a common factor. In fact, pepper flavour and alcohol mouthfeel gave a significant positive Pearson correlation of 0.565 (p<0.001). Pepper flavour and alcohol mouthfeel correlation had been seen with two vintages previously (Niimi, Boss, et al., 2017) and the relationship appears consistent when modelling across three vintages (after standardisation within vintage).

Green aroma was explained by targeted volatiles (X_{03}) (Table 3), which included compounds that are known to impart green characteristics (hexanal and IBMP) (Preston et al., 2008). However, X-block X_{03} was not a significant contributor to green flavour based on CV-ANOVA, with a low validated explained variance at 21.7% (Table 3). This suggests that the perception of the green attribute was better modelled as an aroma modality because of greater discrimination through orthonasal perception, which is known to be more sensitive than retronasal aroma perception due to a lower perceived threshold (Diaz, 2004). In contrast to the present work, IBMP in Cabernet Sauvignon grapes did not appear to contribute to green characteristics modelled in the wines (Forde et al., 2011). The differences in these studies may reflect the different descriptors used for the character imparted by IBMP to the wines, which was described as "woody/tobacco" in Forde et al. (2011) and "green" in the current study.

Overall aroma was one of the two attributes that was modelled with two blocks using SO-PLS1 (Table 3). The first block that modelled best was flavonols (X_{10}) with two components giving 35% explained variance. Similar to the model for red fruit aroma attribute, the likelihood for the relationship with flavonols is either correlative or causative. The second data block that significantly contributed to modelling the attribute was harvest measures using one component and improving the model by 14.9%. Positive contributors to overall aroma intensity were °Brix, variation of °Brix, and pH (Table 4).

These results are in agreement with previous work on Cabernet Sauvignon wines produced with grapes harvested as a function of °Brix, which showed increases in the intensity of overall aroma with riper grapes (Schelezki, Šuklje, Boss, & Jeffery, 2018). Those authors reported a decrease in berry weight with later ripening dates, and especially at harvest due to berry shrivel in the hot 2015 season and interestingly, the weight of both bunches and berries were negatively correlated with overall aroma in the current study (Table 4), implying that smaller weight of fruit increases overall aroma. Berry shrivel may have also been one of the causes as some of the samples, for example CV, were consistently observed to have proportions of shrivel at commercial harvest.

The mouthfeel trait of body was the second attribute modelled by SO-PLS1, using CIELab colour measures followed by harvest measures as the two X-blocks. In particular, Chroma, a*, and °Brix correlated highly with this attribute. At first glance, colour and harvest measures do not appear to have any relation to body, where body was a measure of the mouth-filling sensation of wine on the palate. Body has been reported to be influenced by ethanol and glycerol (Gawel, Sluyter, & Waters, 2007). Results were consistent with literature where higher bodied wine was produced from extended grape ripeness (Schelezki et al., 2018). There is also the possibility that body is related to cognitive expectation based on the intensity of attributes from other modalities as wine body was recently found to have little reference to texture but rather more related to holistic perception of flavour and its intensity (Niimi, Danner, Li, Bossan, & Bastian, 2017). It is plausible that body may extend to incorporate colour intensity associations such as colour with more intense body may be unavoidable because of top-down psychological phenomena.

To summarise, the strategy employed in this study has provided insights into the important grape measures for Cabernet Sauvignon that may contribute to the variation in sensory perceptions of wines. A total of 19 wine sensory attributes that were common across three vintages (2013-2015) were assessed and 14 of the attributes were modelled with either one (PLS1) or two blocks (SO-PLS1) of grape measures (X-blocks) from the suite of 12 grape chemistry measurements. Most optimal models were determined using five of the 12 blocks (Table 3), where harvest measures (X_{01}) was used most often (five sensory attributes). This was followed by simple assays giving measures of total phenolics and tannin (X_{07}) as well as CIELab (X_{06}) colour, which modelled three attributes each and flavonols (X_{10}) used to model two attributes. The targeted volatiles block (X_{03}) was used to model one attribute, suggesting the specificity of certain volatiles with the attribute. Notably, the remaining seven X-blocks of grape chemical measures produced suboptimal models, at least from the progressive modelling approach of SO-PLS; those X-blocks were amino acids (X_{02}), non-targeted volatiles (X_{04}), bound volatiles (X_{05}), anthocyanins (X_{08}), tannins (X_{09}), fatty acids (X_{11}), and enzymes (X_{12}). In fact, enzyme activity and tannin measures explained the least amount of validated explained variance during initial modelling stage with PLS1. These seven measures were redundant from the modelling of the data, which therefore suggests that for future studies, the number of grape chemical measures can be minimised to the most meaningful blocks for the prediction of sensory attributes. Leaving out redundant X-blocks would ease the burden of computing many models for SO-PLS and simplify the data analysis process, as well as better focus on the selection of metabolites for measurement. This of course requires validation of the current models with prediction and perhaps further vintage data collection.

Modelling single sensory attributes common to the three vintages gave further details into the contributing chemistry underlying their possible cause of the perceived attribute, providing models with improved validated explained variance that were consistent with the best models from single vintage data (Niimi, Tomic, et al., 2018). Measures related to colour (CIELab or Total phenolics and tannins) were prominent X-block predictors for attributes. Similar observations were made in the current study to previous findings, where F_Dark fruit, MF_Body, C_Depth, and MF_Astringency were modelled with either CIELab or Total phenolics and tannins (Niimi, Tomic, et al., 2018). It was often observed that models using CIELab or Total phenolics and tannins as X-blocks resulted in similar explained validated variances but with slight differences in the number of components used. F_savoury was an attribute that was modelled only with one block (X_{01} harvest measures), which was different from the previous work (which was X_{05}, bound volatile compounds) (Niimi, Tomic, et al., 2018), and therefore this attribute should be interpreted with care. Further studies to reassess the nature of the savoury flavour attribute and the relative importance of measuring it should be considered before deeper investigation of the grape chemical measures that best model this attribute.

3.4 Challenges and limitations

One of the major challenges faced was obtaining identical samples across vintages from all regions. All samples tested were commercially grown throughout South Australia and some samples were not able to be harvested repeatedly year after year, due to vineyards being removed for commercial reasons. Direct comparisons by sample series across years therefore were not always possible.

The choice of the 12 grape measures to model sensory perception of wine was based on the available knowledge of possible metabolomics measurements in grapes at the time. It is possible that other types of useful grape measures exist that may be important for the prediction of wine sensory perception such as berry sensory analysis (Niimi, Boss, et al., 2017). A significant challenge in future is the identification of additional grape metabolome measures that have possible implications for sensory perception in the corresponding wines (Bokulich et al., 2016; Fabres, Collins, Cavagnaro, & Rodríguez López, 2017; Pinu, 2018; Rochfort, Ezernieks, Bastian, & Downey, 2010). The seven grape measures that did not produce optimal models for any sensory attribute of Cabernet Sauvignon does not necessarily imply that these measurements will be redundant for the prediction of other grape varieties. The “redundant” measures may contribute to sensory attribute predictions through complex formation mechanisms that have a direct correlation. Many of these measures are plausible for other varieties and their ability to predict sensory perceptions of those corresponding wines remains to be determined.

The removal of the prominent vintage effect during pre-processing was an important step in order to fulfil the objectives of the study. This made it possible to determine the underlying differences between grape samples rather than by yearly influences. It also meant that data from different vintages can be stacked thereby increasing the number of samples, which is beneficial in determining stable PLS models. A caveat when standardisation of data sets within vintage before stacking into a larger table for analysis is that the values are no longer raw, i.e., to the scale of the original measurements. Therefore, the RMSECV values do not reflect the scale of the original responses and prediction with unknown samples using raw data points e cannot be added to expand the models unless a complete data set in the new vintage is collected and pre-processed with standardisation. Although standardisation will not influence explained variances of the models, future work would benefit from optimised designs to account for confounding and challenging factors that do not require vintage standardisation. This may involve the inclusion of control samples within each vintage to assist in removing vintage as a factor in the data handling stage to eventually allow for prediction of new samples.

For any PLS analyses, models are susceptible to over-fitting and the analyst is required to scrutinise the best number of components required in a model for optimal variations explained. With so many blocks of data there is an added challenge, which is to determine the predictor blocks that give optimal models and to verify that the models make sense. In the case of the current study, data modelling was performed conservatively using full cross-validation and the progressive modelling approach based on limiting the number of components up to four per X-block The number of components was fixed for each stage before going to the next.

An aspect of cross-validation in this case is that for each step in the sequence, a sample is kept out from a geographical area which is already present in the calibration set. Especially for small data sets, this may in some cases lead to somewhat overoptimistic prediction with respect to potential prediction ability in other regions not represented in the data set. However, the focus here is on interpretation rather than universal prediction ability and given that the data set is relatively large, this was not viewed to be an issue here. Nonetheless, to check that the results generally hold for Cabernet Sauvignon outside the regions studied, the model must be tested on data from other locations. In order to shed some light on this issue, segmented cross-validation was performed using year and area of production as segments. The predictions were reasonable in both cases (data not shown), indicating the potential for using a similar model with fruit from other geographical origins.

Minor variation of panel members is at times unavoidable and may contribute to variation in descriptive analysis data, as well as drifts in data across time despite using the same panel. However, it is also possible to yield similar data sets with different members of panels across the same data set, provided that consistent training procedures are undertaken (Drake et al., 2005). The challenge in describing wine is that its complex nature as a product can make it difficult to be certain that different panel members understand the same attributes in the same way across vintages. Further, there may have been unique attributes that were only detected within a single vintage that were not captured in the current study, because the SO-PLS modelling does not handle missing data points.

4. Conclusions

Key grape chemistry measures that correlate with wine sensory attributes have been determined for Cabernet Sauvignon using PLS and SO-PLS modelling. Similar to previous reports, modelling single sensory attributes (PLS1 or SO-PLS1) gave better validated explained variances compared to modelling the entire sensory profiles with SO-PLS2. Harvest measures of grapes most frequently correlated with individual sensory attributes. While some of the attributes appear to be explained appropriately, where they were most likely causation from chemical composition, others may be merely correlations. Simple measures of harvest measures, CIELab colour, and total tannins and phenolics were used to predict 8 of the 14 attributes through either PLS1 and SO-PLS1.

This means that there may still be other possible grape measures that were not captured in the current study that might predict the wine sensory attributes better. The systematic modelling of the sensory attributes revealed that seven X-blocks were not used for modelling and may be removed for future analyses of Cabernet Sauvignon to have a more focused range of grape chemical measures. Confirmation studies are required to validate the refined list of grape chemical measures to correlate sensory perceptions in Cabernet Sauvignon wines.

Overall, the relative similarity of the models determined in the current multiple vintage study with the previous single vintage work demonstrates the promising outlook of the application of PLS/SO-PLS procedures to the prediction of wine sensory attributes from grape chemistry. Work within our group is underway to explore the applicability of the current approach to a white grape variety (Chardonnay), and in future, attention will be turned to the influence of viticultural intervention on grape chemistry and the resulting influence on sensory perceptions of the wine.

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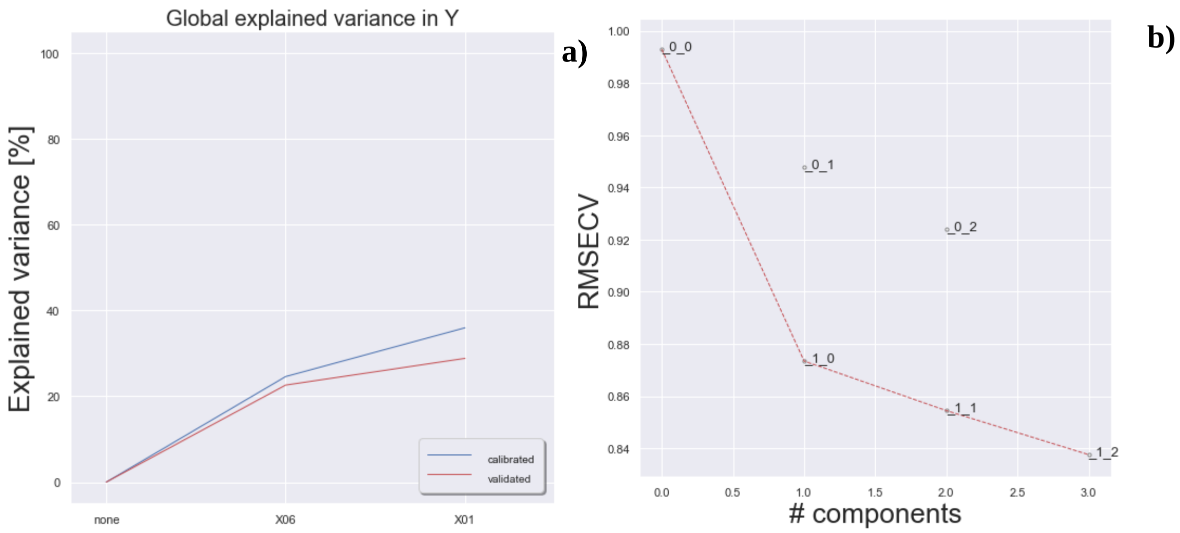

Fig 1. Summary of SO-PLS2 model showing a) validated and calibrated explained variances, and b) Måge plot of RMSECV decrease as a function of total number of model components for 2 block SO-PLS2 using X_{06} (CIELab measures) and X_{01} (harvest measures). Numbers above points denote the number of components for 1st block_2nd block.

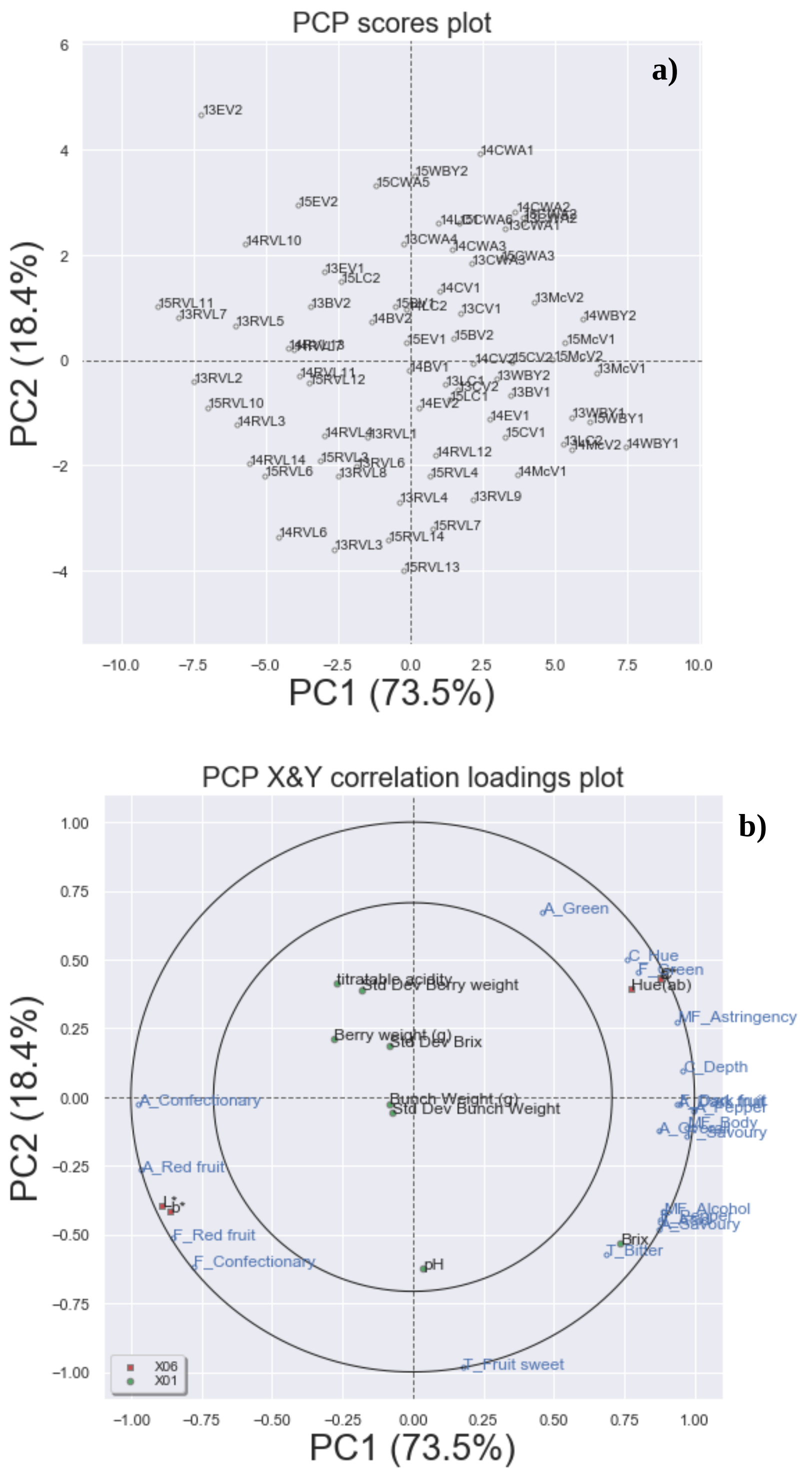

Fig 2. PCP plots from the SO-PLS2 model using X_{06} (CIELab measures) and X_{01} (harvest measures) as first and second blocks, respectively, showing A) scores (as vintage year, sample location and number), and b) correlation loadings plots including X-variables for the two data blocks. Loadings in blue denote those belonging to the Y-block, red loadings are from the first X-block (CIELab), and green loadings are from the second X-block (harvest measures).

Table 1. Samples harvested for each vintage (n = 25) and subsequently used for modelling.

Sample GI	Vintage		
	2013	2014	2015
Barossa Valley (BV)	13BV1	14BV1	15BV1
	13BV2	14BV2	15BV2
Clare Valley (CV)	13CV1	14CV1	15CV1
	13CV2	14CV2	15CV2
Coonawarra (CWA)	13CWA1	14CWA1	15CWA2
	13CWA2	14CWA2	15CWA3
	13CWA3	14CWA3	15CWA5
	13CWA4	**14CWA5**	15CWA6
Eden Valley (EV)	13EV1	14EV1	15EV1
	13EV2	14EV2	15EV2
Langhorne Creek (LC)	13LC1	14LC1	15LC1
	13LC2	14LC2	15LC2
McLaren Vale (McV)	13McV1	14McV1	15McV1
	13McV2	14McV2	15McV2
Riverland (RVL)	13RVL1	14RVL3	15RVL3
	13RVL2	14RVL4	15RVL4
	13RVL3	14RVL6	15RVL6
	13RVL4	14RVL7	15RVL7
	13RVL5	14RVL10	15RVL10
	13RVL6	14RVL11	15RVL11
	13RVL7	14RVL12	15RVL12
	13RVL8	14RVL13	15RVL13
	13RVL9	14RVL14	15RVL14
Wrattonbully (WBY)	13WBY1	14WBY1	15WBY1
	13WBY2	14WBY2	15WBY2

Sample 14CWA5 was later removed due to being an outlier (see Section 2.4).

Table 2. Data blocks arising from different vineyards within GIs for Cabernet Sauvignon grape composition-related measures (X) and wine sensory attributes (Y) assigned for PLS and SO-PLS modelling.

Data block*	Measurement	Data dimensions†	Analysis method
X_{01}	Harvest measures	74 × 8	Weight, TSSǂ, pH, TA#
X_{02}	Amino acids	74 × 24	HPLC
X_{03}	Targeted volatile compounds	74 × 10	GC-MS
X_{04}	Non-targeted volatile compounds	74 × 25	GC-MS
X_{05}	Bound volatile compounds	74 × 56	GC-MS
X_{06}	Colour	74 × 5	CIELab tristimulus
X_{07}	Total phenolics and tannins	74 × 3	UV spectrophotometry
X_{08}	Anthocyanins	74 × 11	HPLC
X_{09}	Tannins	74 × 9	HPLC
X_{10}	Flavonols	74 × 7	HPLC
X_{11}	Fatty acids	74 × 22	GC-MS
X_{12}	Lipoxygenase (LOX) pathway enzyme activity	74 × 3	Spectrophotometric
Y	Sensory analysis	74 × 21	Descriptive analysis

*X-block measurements were made on grapes and the Y block measurement was made on wines.
† Data blocks consist of mean values for 74 samples rather than 75 due to the removal of an outlier.
ǂ Total soluble solids
#Titratable acidity.

Table 3. Optimal models of individual sensory attributes that were common across the three vintages. Optimal models for each attribute were determined using PLS1 when only one block was required and SO-PLS1 when two blocks were required. For each attribute modelled with SO-PLS1, the first row of parameters denotes the first X-block and the second row is the orthogonal addition of the second X-block.

Y-variable(s)	X-block	RMSECV[a]	Comp[b]	Cal[c]	Val[d]	CV-ANOVA[e]
PLS1						
C_Depth	X_{06}	0.572	1	67.7	66.9	**<0.001**
C_Hue	X_{06}	0.712	1	50.2	48.7	**<0.001**
A_Dark fruit	X_{07}	0.705	2	57.6	55.2	**<0.001**
A_Red fruit	X_{10}	0.851	2	33.0	26.5	**0.050**
A_Confectionery	X_{10}	0.900	2	24.2	17.9	0.118
A_Green	X_{03}	0.791	2	47.4	36.6	**0.052**
A_Savoury	X_{01}	0.861	3	38.0	24.9	0.130
A_Pepper	X_{06}	0.860	1	26.9	24.9	**0.025**
F_Dark fruit	X_{07}	0.722	2	55.1	52.4	**<0.001**
F_Red fruit	X_{06}	0.890	1	21.9	19.7	**0.085**
F_Confectionery	X_{06}	0.928	1	15.6	12.7	0.258
F_Green	X_{03}	0.878	1	35.2	21.7	0.234
F_Savoury	X_{01}	0.864	3	38.5	24.3	**0.092**
F_Pepper	X_{01}	0.785	2	49.0	38.1	**0.004**
T_Bitter	X_{02}	0.884	2	30.8	20.7	0.155
MF_Astringency	X_{06}	0.703	1	51.2	49.8	**<0.001**
MF_Alcohol	X_{01}	0.681	2	60.0	53.0	**0.001**
SO-PLS1						
A_Overall	X_{10}	0.854	2	40.4	35.0	**0.019**
	X_{01}	0.703	1	57.7	49.9	**0.066**
MF_Body	X_{06}	0.729	1	47.5	46.0	**0.001**
	X_{01}	0.651	1	62.0	57.0	**0.061**

[a]Root mean square error of cross validation

[b]Components. SO-PLS models are reported as number of components for the first followed by the second blocks.

[c]Calibrated explained variance

dValidated explained variance

[e]Values in bold denote for *p*<0.1.

Table 4. Significantly (*p*<0.1) contributing X-variables in modelling single Y-variables using PLS1 and SO-PLS1 models.

Y variables	X data block	+ve coefficient X variables	-ve coefficient X variables
PLS1			
C_Hue	$\mathbf{X_{06}}$	H(ab); a*, chroma	b*, L*
C_Depth	$\mathbf{X_{06}}$	H(ab); a*, chroma	b*, L*
A_Dark fruit	$\mathbf{X_{07}}$	Colour per berry; Total phenolics	
A_Red fruit	$\mathbf{X_{10}}$	% Quercetin-3-*O*-glucuronide; % Laricitrin-3-*O*-galactoside;	Total flavonols; %[a] Myricetin-3-*O*-glucoside; % Kaempferol-3-*O*-glucuronide
A_Green	$\mathbf{X_{03}}$	Benzyl alcohol; Hexanal; IBMP	2-Pentyl furan
A_Pepper	$\mathbf{X_{06}}$	a*, chroma	b*, L*
F_Dark fruit	$\mathbf{X_{07}}$	Colour per berry; Total phenolics	
F_Red fruit	$\mathbf{X_{06}}$	b*, L*	H(ab); a*, chroma
F_Pepper	$\mathbf{X_{01}}$	°Brix	
F_Savoury	$\mathbf{X_{01}}$	°Brix; Std dev[b] bunch weight; Std dev °Brix; TA[c]	Bunch weight
MF_Astringency	$\mathbf{X_{06}}$	H(ab); a*, chroma	b*, L*
MF_Alcohol	$\mathbf{X_{01}}$	°Brix, pH	
SO-PLS1			
A_Overall	1) $\mathbf{X_{10}}$	Total Flavonols; % Myricetin-3-*O*-glucoside; & % Kaempferol-3-*O*-glucuronide	% Quercetin-3-*O*-glucuronide; % Kaempferol-3-*O*-glucoside
	2) $\mathbf{X_{01}}$	°Brix; Std dev °Brix; pH	Bunch weight; Berry weight; TA[c]
MF_Body	1) $\mathbf{X_{06}}$	a*; chroma	L*
	2) $\mathbf{X_{01}}$	°Brix; pH	

[a] % = percentage of total composition.

[b] Std dev = standard deviation.

[c] TA = titratable acidity

Supplementary materials for Food Chemistry

Objective measures of grape quality: From Cabernet Sauvignon grape composition to wine sensory characteristics

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S1. Data similarity between vintages.

In order to determine the overall data similarity across the three vintages for each data block, RV coefficients were computed. As the analysis requires the data sets to have the same dimensions as well as identical samples for comparison, the data sets were first matched to have identical samples throughout the three vintages. Columns were matched according to that described in the data analysis section.

Table S1. Pairwise RV coefficients between vintages within a data block prior to standardisation.

Data block	**Block identity**	**RV coefficients**		
		2013 vs 2014	**2013 vs 2015**	**2014 vs 2015**
$\mathbf{X_{01}}$	Harvest measures	0.07	0.11	0.06
$\mathbf{X_{02}}$	Amino acids	0.64	0.55	0.54
$\mathbf{X_{03}}$	Targeted volatiles	0.18	0.36	0.11
$\mathbf{X_{04}}$	Non-targeted volatiles	0.13	0.23	0.30
$\mathbf{X_{05}}$	Bound volatiles	0.40	0.27	0.20
$\mathbf{X_{06}}$	CIELab	0.63	0.70	0.76
$\mathbf{X_{07}}$	Total phenolics and tannins	0.58	0.20	0.17
$\mathbf{X_{08}}$	Anthocyanins	0.04	0.65	0.22
$\mathbf{X_{09}}$	Tannins	0.33	0.28	0.27
$\mathbf{X_{10}}$	Flavonols	0.24	0.37	0.38
$\mathbf{X_{11}}$	Fatty acids	0.26	0.36	0.26
$\mathbf{X_{12}}$	Enzymes	0.05	0.05	0.32
Y	Descriptive analysis (wine)	0.09	0.11	0.24

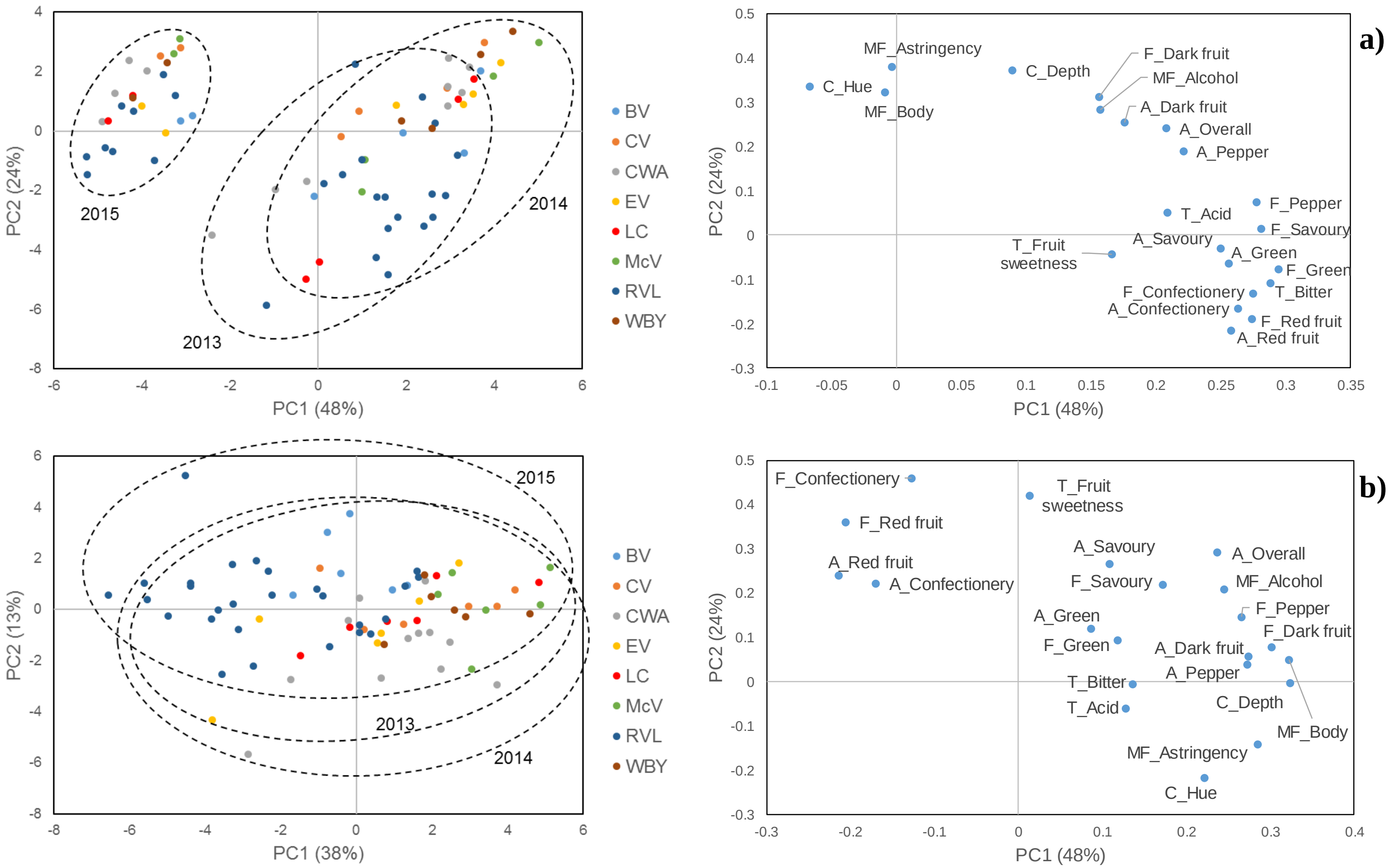

Fig S1. PCA scores and loadings of descriptive sensory analysis of Cabernet Sauvignon wines for three vintages 2013-2015. A) data sets standardised together and B) data sets standardised within vintage Refer to Table 1 for sample abbreviations. C_ = colour, A_ = aroma, F_ = flavour, T_ = taste, and MF_ mouthfeel.

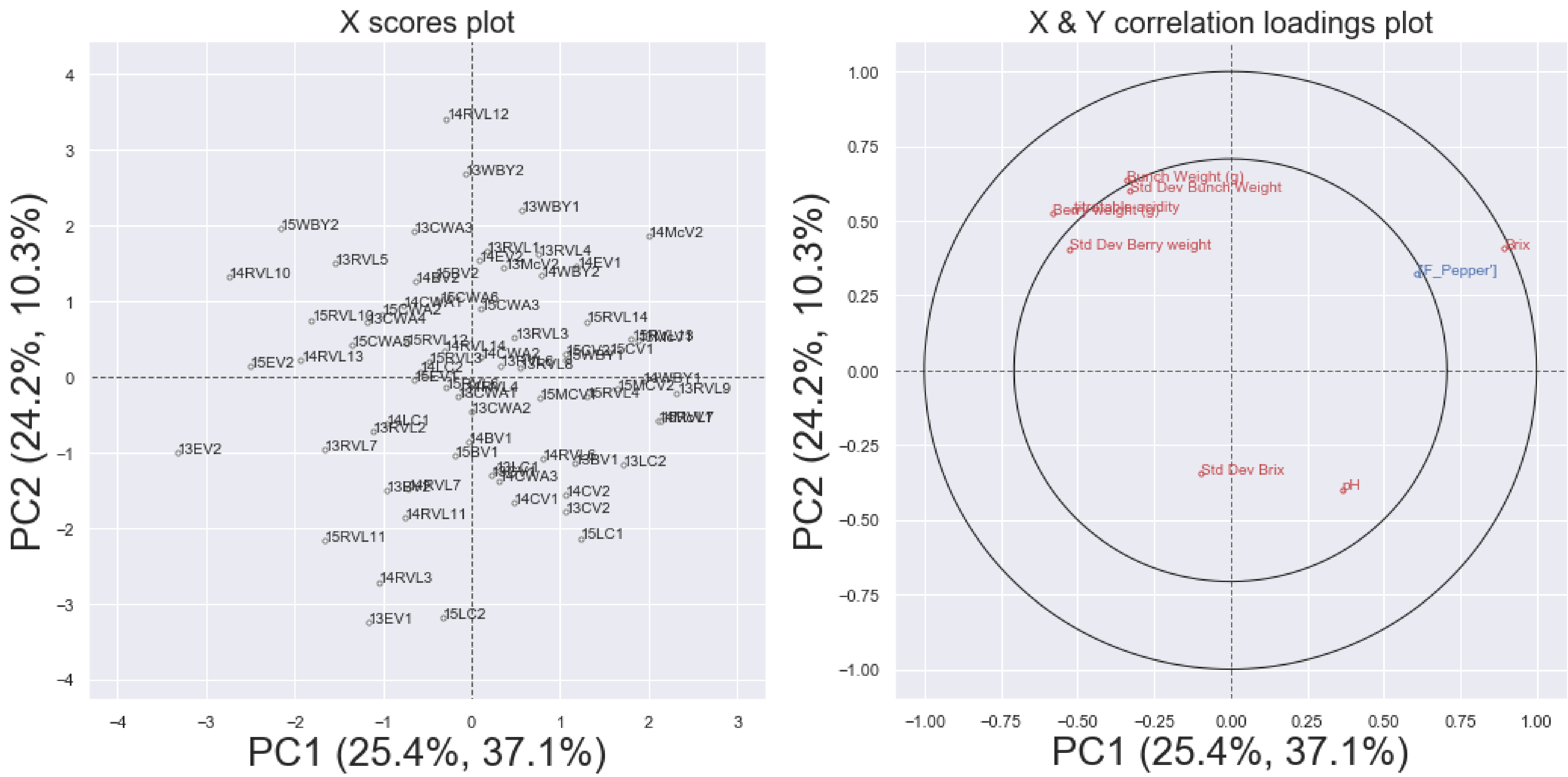

Fig S2. PLS1 scores and loadings of F_Pepper

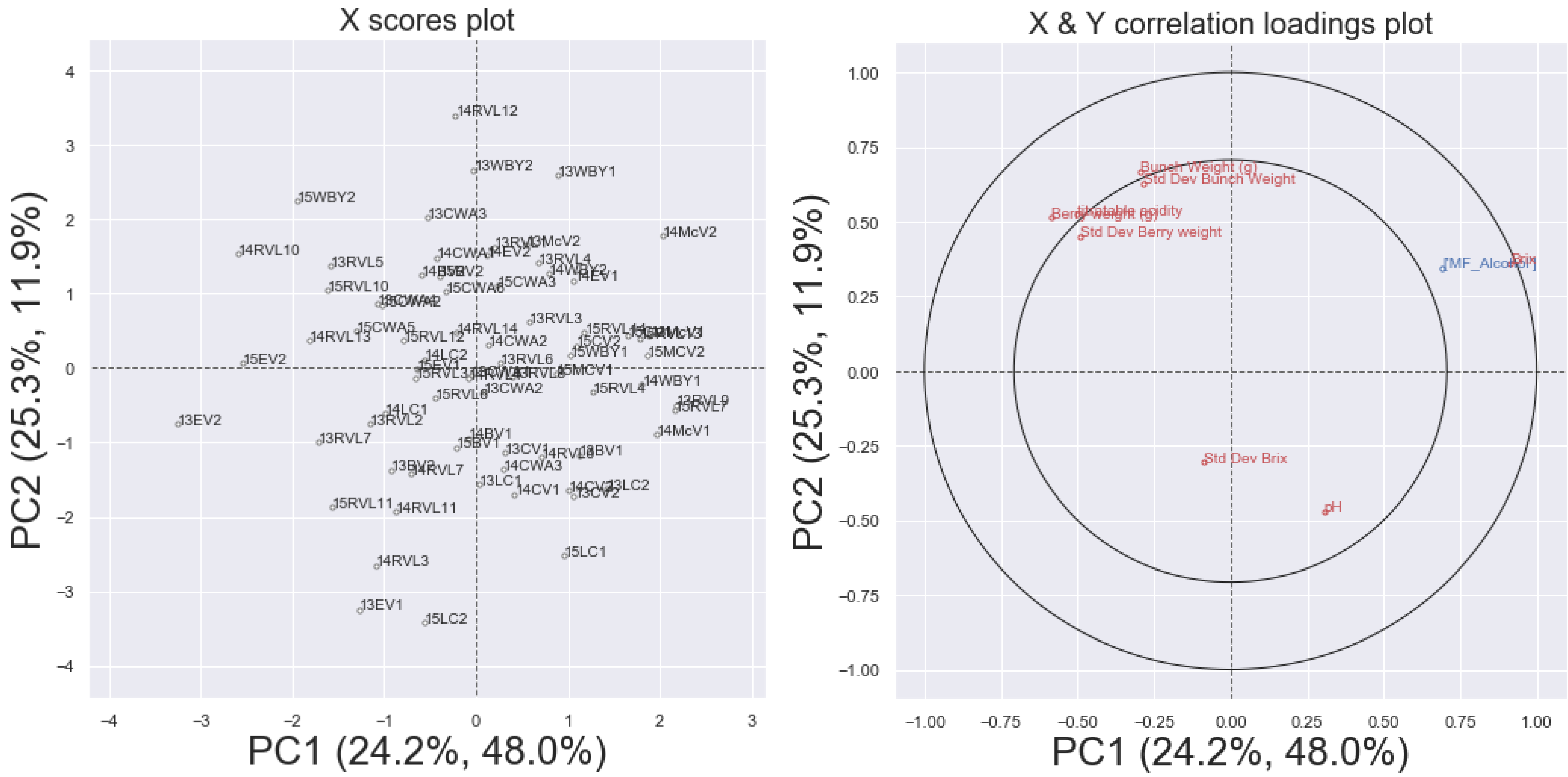

Fig S3. PLS1 scores and loadings of MF_Alcohol