

# Performing sequential harvests based on berry sugar accumulation (mg/berry) to obtain specific wine sensory profiles

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 Associate editor: Fulvio Mattivi

## ABSTRACT

This study aimed to investigate the possible existence of reproducible aromatic red wine styles, focusing on fresh fruit aromas and mature fruit aromas (*i.e.*, with dark, jammy fruit characteristics) and taking into account both vintage and vineyard.

The study was performed on Australian Shiraz and Cabernet-Sauvignon from three different meso-climate areas and two consecutive vintages. Sequential harvests were carried out based on the plateau of the physiological indicator berry sugar accumulation (mg/berry) in order to obtain fresh fruit and mature fruit wine sensory profiles. There was a predictable aromatic sequence during grape ripening at each of these two distinct maturity stages regardless of grape genotype (variety) and environment (vineyard and vintage). The post-plateau period of berry sugar accumulation was found to be crucial for the evolution of wine aromatic profiles. During this period, wine aromatic and phenolic maturity were uncoupled from technological maturity (*i.e.*, berry sugar concentration). Dimethyl sulfide was found to be the most relevant wine aromatic marker for differentiating the fresh fruit and mature fruit stages irrespective of the variety. Specific cultivar markers with potential sensory contribution were also identified; for example, (Z)-3-hexenol, a possible contributor to the aromatic freshness of Shiraz wines from the fresh fruit stage. The evolution of terpenoids appeared to be separate from the dynamics of berry ripening post plateau of fruit sugar accumulation. On the other hand, ester composition was significantly altered during the same ripening period in Shiraz and Cabernet-Sauvignon wines with a marked grape genotype effect. The results showed that yeast metabolism was also affected by berry ripening evolution from the plateau of berry sugar accumulation onwards.

## KEYWORDS

grape maturity, wine style, wine aromas, berry sugar accumulation

Supplementary data can be downloaded through: <https://oenone.eu/article/view/4527>

## INTRODUCTION

One of the most important and difficult tasks for a viticulturist or winemaker is predicting/assessing harvest dates that will ensure the production of wines with preferred styles. More than ever, within a context of global warming, wine producers need objective indicators of grape maturity in order to make informed decisions about when to harvest. The progressive development of grape-derived aromas and flavour precursors during berry ripening has garnered the attention of researchers over recent years (Kontoudakis *et al.*, 2010; Bindon *et al.*, 2013; Cramer *et al.*, 2014; Pascual *et al.*, 2016; Rabot *et al.*, 2017; Böttcher *et al.*, 2018; Boss *et al.*, 2018; Allamy *et al.*, 2018). The decision to harvest grapes for wine production can be determined by measuring grape berry sugar concentration as total soluble solids and expressed as °Brix (technological maturity). Brix degree may be the sole criteria for harvest decision or considered in combination with basic analytical parameters related to berry acidity (pH, titratable acidity) and colour for red cultivars; phenolic maturity is generally assessed by performing analysis of anthocyanins and tannins content in grape skin and seed, and their level of extractability. Wine aroma is one of the most important components of wine quality, but none of the mentioned attributes gives objective information about the aromatic potential of a grape or the resulting wine aromatic profile (DeLoire, 2013; Calderon-Orellana *et al.*, 2014). Up to now, berry tasting is the main method used in the field to assess aromatic maturity. While berry tasting is relevant, it is also highly subjective as the perception of flavours depends on the taster's personal ability, experience and training (Rabot *et al.*, 2017). Therefore, it would be useful for growers and winemakers to be able to objectively predict wine aromatic profile evolution during ripening by measuring simple physiological grape parameters, such as berry sugar accumulation which is dependent on vineyard growing conditions (soil × climate × cultural practices).

Empirically, the aroma of red wines made from grapes from early to later harvests (*i.e.*, grapes of increasing maturity levels) are often described as green/herbaceous, fresh fruit, mature/ripe fruit and jammy/stewed fruit. Sensory studies have demonstrated such aromatic evolution in Merlot, Cabernet-Sauvignon, Petit Verdot and Shiraz wines through sequential harvest (Casassa *et al.*, 2013; Bindon *et al.*, 2013; Longo *et al.*, 2018a; Longo *et al.*, 2018b).

However, in all these studies the choice of harvest dates were based on grape sugar concentration, with harvests being performed from 19 °Brix onwards. A lack of correlation between berry sugar content and aroma development has recently been found in Shiraz wines made from grapes harvested from end of veraison onwards (Boss *et al.*, 2018; Šuklje *et al.*, 2019a). The aromatic profile of red wines made from sequential harvested grapes post plateau of berry sugar accumulation evolves from fresh fruit to mature and jammy fruit; however, in this period, sugar concentration (°Brix) is directly related to berry volume evolution and does not seem to be the most appropriate indicator of aromatic maturity. On the other hand, a recent study using an untargeted analysis was able to demonstrate a coherent evolution of wine volatome in Shiraz wines made from sequential harvested grapes based on the berry sugar accumulation method (Šuklje *et al.*, 2019a). Therefore, the objective of the present study was to demonstrate the existence of reproducible aromatic wine styles by carrying out sequential harvests based on the measurement of grape berry sugar accumulation (mg/berry and not sugar concentration). Wines were made from Shiraz and Cabernet-Sauvignon grapes sourced during two consecutive vintages from nine vineyards located in three different mesoclimate areas. It was hypothesised that genotype wine influences aromatic evolution during berry ripening more than environment; therefore, a variety of vineyards and mesoclimates was accordingly chosen. The evolution of nexuses in grape composition, wine composition and the wine sensory profile were also investigated.

## MATERIALS AND METHOD

### 1. Vineyard

Experimentation was carried out across two consecutive years - during the 2014 and 2015 vintages - in two Shiraz (SH) and one Cabernet-Sauvignon (CS) vineyards (G1\_SH, G2\_SH and G2\_CS respectively) located in the Geographical Indication (GI) Riverina, Griffith (New South Wales, Australia), and one Shiraz and Cabernet-Sauvignon vineyard (O1\_SH and O\_CS respectively) located in GI Orange (New South Wales, Australia). Experiments were also performed in three other Shiraz vineyards in 2015: two located in Griffith (G3\_SH and G4\_SH), and one in Orange region (O2\_SH). Geographical and topographical data of the vineyards are detailed in previously published works (Šuklje *et al.*, 2019b, Schmidtke *et al.*, 2020). The basic vineyard characteristics are presented in Table 1.

Average yield/vine, average number of primary shoots/vine, average number of bunches/vine, average bunch weight and pruning mass were obtained in the 2015 season, and they serve as an indication of differences between vineyards (Table 1). All the vineyards were drip-irrigated, excluding O2\_SH for which no irrigation was applied in 2015.

An experimental plot of 400 vines across 8 rows was established in the middle of each commercial vineyard. Mesoclimatic temperatures, soil moisture profile and vine water status were measured in each experimental plot; mesoclimatic data were previously reported by Šuklje *et al.* (2019b) and Schmidtke *et al.* (2020). Briefly, vineyards were located in areas with three different climates according to the Huglin index (Tonietto and Carbonneau, 2004): warm with temperate nights (all GI Griffith), temperate to warm with temperate nights (O1) and temperate with cool nights (O2). The 2014 vintage was characterised by a series of heat waves late in the ripening season (during veraison and after the plateau of berry sugar accumulation), whereas the 2015 vintage was warmer than long-term median values, shifting all three locations to a warmer classification according to the Huglin index.

## 2. Harvest and winemaking

Harvest dates were chosen using the Sugar Accumulation method as described by Deloire (2013), and they are delineated in Figure 1. A representative 10 bunches were sampled in triplicate per block on a weekly basis from veraison onwards. In the laboratory, 100 berries per replicate were carefully excised with the pedicel to avoid juice loss. Berries were weighed and then crushed for measurements of juice total soluble solids (TSS) content (expressed as Brix degree) and sugar per berry (mg/berry) using sugar concentration (expressed in g/L; 1 °Brix = 10 g/L) and berry fresh mass. Harvest dates linked to potential final wine styles were determined for Shiraz and Cabernet-Sauvignon using the proposed sugar accumulation and wine style models as shown in Figure 1. Two and three successive harvests (H1, H2 and H3) were conducted during the 2014 and 2015 vintages respectively at 12, 18 and 24 days post sugar accumulation plateau for Shiraz and 20, 30 and 40 days post sugar accumulation plateau for Cabernet-Sauvignon. The timing of sequential harvests for both varieties was based on previous studies that suggested there is a relationship between the time after plateau of sugar

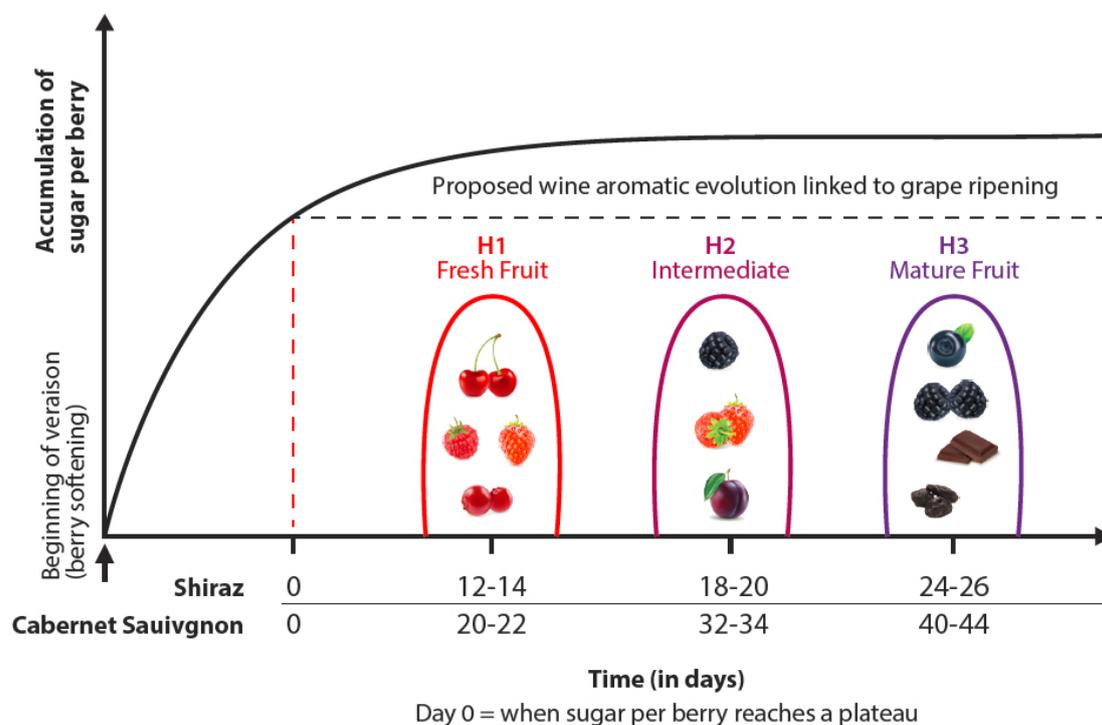
**TABLE 1.** Vineyard and cultivar parameters for sample collection throughout the study.

	G1_SH	G2_SH	G3_SH	G4_SH	G2_CS	O1_SH	O2_SH	O1_CS
Location	Griffith				Orange			
Cultivar	Shiraz	Shiraz	Shiraz	Shiraz	Cabernet-Sauvignon	Shiraz	Shiraz	Cabernet-Sauvignon
Plantation	1995	1997	2008	1997	1997	1995	1989	1995
Clone	Minato	SA1654	BVRC12	SA1654	125	PT23	EVOVS12	G9V3
Spacing (m)	2.5x3.7	2.5x3.7	2.5x3.7	2.5x3.7	2.5x3.7	2x3	2 x 3	2x3
Trellis System	Sprawling	Sprawling	Sprawling	Sprawling	Sprawling	VSP	VSP	VSP
Average Yield/vine (kg)	10.3	14.0	18.6	17.7	8.7	5.1	4.2	4.0
Average No. of primary shoots/vine	86	95	92	92	n.d.	42	21	44
No. of bunches/vine	116	123	149	155	130	84	19	89
Average bunch weight (g)	89	109	125	118	68	62	225	45
Pruning mass (kg)	1.47	1.00			0.93	0.53	n.d.	0.45

Data collected in 2015. G and O vineyards were from Griffith and Orange regions respectively. SH and CS refer to Shiraz and Cabernet-Sauvignon vineyards respectively.

accumulation and the style of the corresponding wines assessed by sensory evaluation ([www.vivelys.com](http://www.vivelys.com)). Harvests did not deviate from these models by more than 2 days. The first harvest (H1), termed Fresh Fruit (FF), was thought to be linked to fresh red fruit notes in wines, while the third harvest (H3),

termed Mature Fruit (MF), was associated with a mature dark fruit style. An intermediate harvest date (H2) was introduced during the 2015 vintage. Dates for sugar accumulation plateaus and harvests are presented in Table 2. Wines were made from 60 kg of grapes in triplicate as described by Šuklje *et al.* (2019a).



**FIGURE 1.** Proposed method for determining optimum harvest dates in relation to the potential wine style based on sugar accumulation per berry for Shiraz and Cabernet-Sauvignon.

**TABLE 2.** Dates of sugar accumulation plateau, TSS at plateau date and harvest dates expressed in number of days after sugar accumulation plateau for Shiraz and Cabernet-Sauvignon vineyards.

Vintage	Vineyard	Plateau date	TSS at plateau date (°Brix)	Plateau-harvest duration for H1 (number of days)	Plateau-harvest duration for H2 (number of days)	Plateau-harvest duration for H3 (number of days)
2014	G1_SH	17/01	21.7	11	No harvest	24
	G2_SH	17/01	21.6	11	No harvest	24
	G2_CS	28/01	19	23	No harvest	42
2015	G1_SH	03/02	20.9	12	17	24
	G2_SH	10/02	20.3	12	19	24
	G3_SH	05/02	19.3	12	18	24
	G4_SH	10/02	19.8	12	19	24
	G2_CS	10/02	20.6	19	30	40
	O1_SH	02/02	20.3	11	17	24
	O1_CS	05/02	19.8	21	32	39
	O2_SH	26/02	20.7	11	18	25

### 3. Grape Juice analysis

Once the grapes had been crushed, the juice was analysed for basic parameters of maturity. TSS (expressed as °Brix), titratable acidity (TA), pH, ammonia and amino acids were determined according to Šuklje *et al.* (2019a) and Schmidtke *et al.* (2020). Yeast assimilable nitrogen (YAN) was calculated from ammonium and free amino nitrogen (FAN) measurements (Illand *et al.*, 2004).

### 4. Grape analysis

Grape berry samples were collected at each harvest date. One hundred berries were randomly collected across the experimental block to obtain three biological replicates. Berries were collected evenly from both sides of the canopy, then immediately frozen in liquid nitrogen and stored at -80 °C until further processing. For the grape berry analyses, a sub-sample of 50 frozen berries was deseeded with a mortar and pestle and ground to a fine powder with an IKA A11 basic analytical mill (IKA, Malaysia). Grape powder was stored at -80 °C until further analysis. The methodology used to analyse organic acids, carbohydrate, amino acids, anthocyanins, polyphenols, carotenoids and volatiles in grape has been previously described by Schmidtke *et al.* (2020).

### 5. Chemical analysis of the wine

#### 5.1. Basic wine and phenolic parameters

The protocol used to analyse ethanol, acetic acid, residual sugar, total anthocyanin, colour parameter, polyphenols and tannin has been previously described by Schmidtke *et al.*, 2020.

#### 5.2. Volatile compounds

The quantification and semi-quantification of around 30 odorants was carried out using a previously developed method of head space solid-phase micro extraction gas chromatography-mass spectrometry (HS-SPME-GC-MS) for analysing esters, higher alcohols, C6 compounds, and lactones (Antalick *et al.*, 2015; Šuklje *et al.*, 2016). Analyses of 10 monoterpenes and 3 norisoprenoids in wines were performed as previously described (Šuklje *et al.*, 2016). Volatile wine sulfur compounds analyses, including H<sub>2</sub>S, methanethiol (MeSH) and DMS were carried out by headspace sulfur chemiluminescence detector HS-SCD as previously described by Zhang *et al.* (2020).

### 6. Sensory analyses

Descriptive sensory analyses (DA) were conducted six months after bottling according to the method outlined by Blackman and Saliba (2009) with further details in Schmidtke *et al.* (2020). The final list of descriptors used for the descriptive analysis is reported in Supplementary Data, SD1.

### 7. Statistical analysis

One-way and two-way analyses of variance (ANOVA) were performed on the chemical data using *STATISTICA*<sup>TM</sup>, Version 12 (StatSoft, Tulsa, OK, USA). The means were separated using Stats-Fischer LSD test and different letters were used to represent different significant differences ( $p \leq 0.05$ ). All quoted uncertainty is the standard deviation of three replicates of one treatment. Principal component analyses were conducted on mean centred concentration profiles of compounds in *STATISTICA*<sup>TM</sup>, Version 12 (StatSoft, Tulsa, OK, USA).

## RESULTS AND DISCUSSION

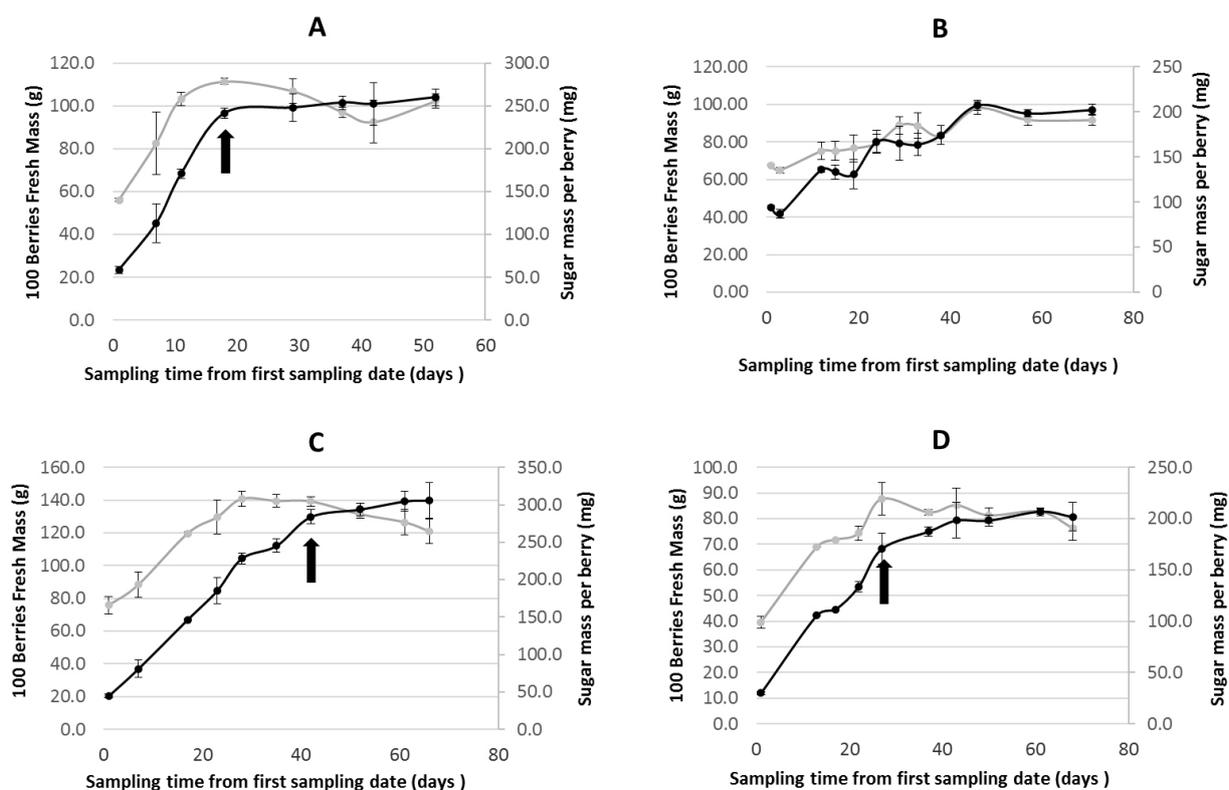
### 1. Berry Sugar accumulation measurements to predict harvest date

Berry sugar accumulation and fresh mass curves were determined on a population of berries from each of the experimental plots in the 2014 and 2015 vintages (Figure 2 and Supplementary Data Figure S4). Irrespective of variety, the plateaus of berry sugar accumulation were evident for most of the vineyards in both regions, excluding O1 site in 2014 (Figure 2A, 2C, 2D and Supplementary Data Figure S4). Differences were observed between vineyards and vintages in terms of the dates when the berry population reached the plateau of sugar accumulation; this reflects the variations in berry ripening dynamics and the asynchrony of berry development (Shahood *et al.*, 2015) linked to climatic conditions, viticultural practices and varieties. The average TSS at plateau was  $20.1 \pm 0.8$  °Brix (Table 2). In contrast, Shahood *et al.* (2020) recently proposed a model of berry ripening based on measurements carried out on thousands of individual berries, whereby the plateau of berry sugar accumulation was reached at 1M sugar (18 °Brix), and further sugar concentration increases were due to berry water loss only. Climatic conditions and vine physiology during flowering usually alter ovule fecundation and the resulting seed number per berry, which is at the origin of the asynchrony of berry development and can also impact berry heterogeneity (Shahood, 2017).

This phenomenon is usually observed in commercial vineyards and has been well-described in the literature (Friend *et al.*, 2009; Gouthu and Deluc, 2015). The present work also confirmed that the evolution of sugar per berry in a population of berries is a relevant physiological indicator which can be used to determine the plateau of berry sugar accumulation and, in turn, the harvest date as previously suggested (Deloire, 2013; Šuklje *et al.*, 2019a). The plateau is generally reached at approximately  $20 \pm 1$  °Brix, and any further increases in sugar concentration are most likely due to berry water loss and ultimately shrivelling (Deloire *et al.*, 2021).

In the 2014 vintage, no clear plateau of sugar accumulation was found in either Shiraz or Cabernet-Sauvignon from the O1 vineyards (650 m) (Figure 2B and Supplementary Data Figure S4). Instead, a slow and unsteady accumulation of berry sugar was observed throughout the ripening period, which was attributed to severe water restrictions as determined by vineyard inspections. The 2014 vintage in O1\_SH and O\_CS vineyards was characterised by severe water stress during the veraison period, followed by several rain

events around time of harvest. A severe vine water deficit inhibited leaf photosynthesis, which in turn inhibited the ripening process by stopping or slowing down berry sugar accumulation (Wang *et al.*, 2003a). Rain events temporarily supplied water in the late maturation stage and may have reactivated the photosynthetic mechanism, resulting in uneven berry sugar accumulation. During the 2015 season, berry sugar accumulation for both cultivars and all vineyards in the Orange region closely followed the predicted model curve (Figure 2D and Supplementary Data Figure S4). The observed plateau of berry sugar accumulation in the 2015 O1 vintage (Figure 2D), in contrast to the 2014 vintage (Figure 2B), can be explained by higher water availability and milder climatic conditions during the veraison and post-veraison periods. Therefore, berry fresh mass and sugar accumulation per berry could be used as relevant morphological and physiological indicators to diagnose vineyards issues such as water shortage (Wang *et al.*, 2003b; Ojeda *et al.*, 2001; Rossouw *et al.*, 2017), in combination with other methods such as  $\delta^{13}\text{C}$  measurement (van Leeuwen *et al.*, 2001).



**FIGURE 2.** Berry fresh mass (grey) and sugar per berry (black) evolution for selected vineyards in Griffith and Orange.

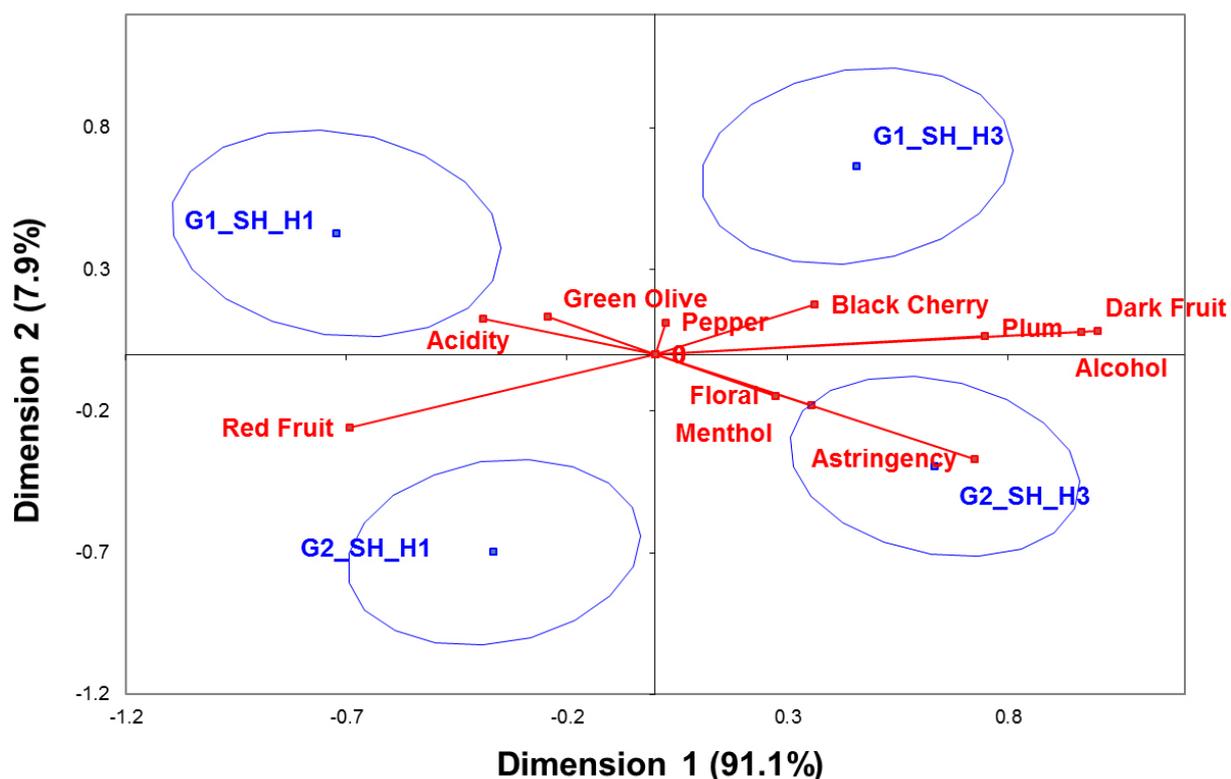
A: G2\_SH\_2014; B: O1\_CS\_2014; C: G2\_SH\_2015; D: O1\_CS\_2015. The black arrow indicates the date of the plateau of sugar accumulation.

## 2. Sensory analysis

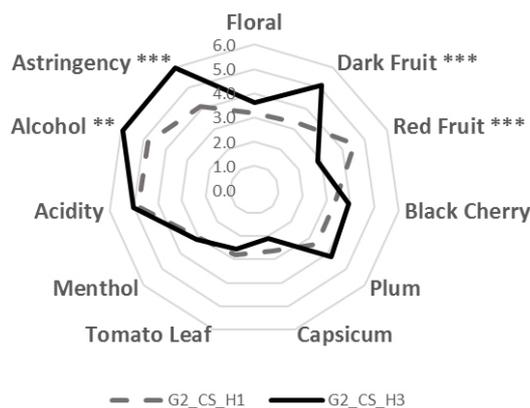
A similar aromatic evolution was observed for Shiraz and Cabernet-Sauvignon wines from Griffith for the 2014 vintage. Wines from H1 were associated with red fruit and herbaceous attributes reminiscent of tomato leaf, green olive and, specifically, capsicum for Cabernet-Sauvignon (Figure 3). Shiraz wines were perceived as being more acidic, but not Cabernet-Sauvignon wines (Figure 4). On the other hand, wines from H3, were characterised by dark fruit, plum sensorial attributes, higher astringency and were perceived as being more alcoholic. In 2015, wines from two other Shiraz vineyards in Griffith (G3 and G4) and from two different climates in the Orange region, as well as an H2, were also evaluated. Once again, H1 wines (FF) were correlated with red fruit and the perception of acidity, whilst H3 wines (MF) were associated with dark fruit, plum, black cherry, astringency and alcohol perception regardless of the vineyard (Figures 5A and 5B). H2 wines were closely grouped with the corresponding “Mature Fruit” wines from the Orange region, but this

grouping was not so evident for the H2 wines from Griffith.

H1 (FF) and H3 (MF) wines showed a similar pattern of aromatic evolution irrespective of the variety, site and climatic conditions across regions and vintages. Descriptors such as red fruit, dark fruit and plum consistently discriminated “Fresh Fruit” (H1) from “Mature Fruit” (H3) stages. In 2015, no selected descriptors could consistently discriminate the intermediate stage (H2) from FF and MF stages (Figure 5A and 5B). H2 wines were perceived differently to wines from H1(FF) and H3(MF) (Figures 5A and 5B), but these differences depended on site, climate and variety (data not shown). While the wine aromatic profile was well-defined for H1 and H3 wines, H2 wines style clearly depended on the vineyard. Therefore, a sequential harvest based solely on grape sugar concentration and maturation time will not guarantee a given aromatic profile of a final wine. Conversely, the number of days after the plateau of berry sugar accumulation (mg/berry) seems to be synchronised with the aromatic maturity perceived in the resulting wines.

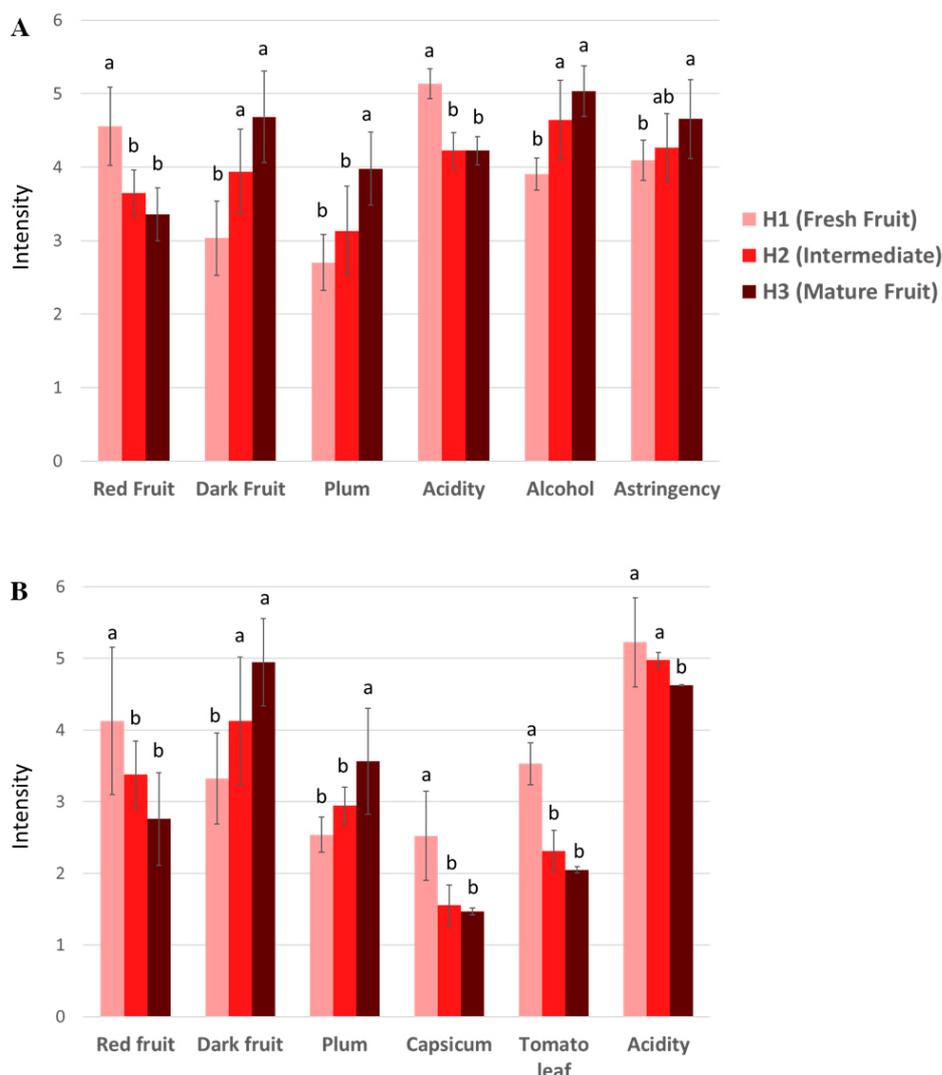


**FIGURE 3.** Principal Component Analysis biplot of sensory data for 2014 G1 and G2 Shiraz wines



**FIGURE 4.** Odour comparison profiles performed on the means of the perceived aromatic intensity of each selected sensory descriptor for 2014 Cabernet-Sauvignon wines.

Significant differences are indicated with stars: (\*), significant at  $p < 0.05$ , (\*\*), significant at  $p < 0.01$ , (\*\*\*) significant at  $p < 0.001$



**FIGURE 5.** Mean rating  $\pm$ SD of sensory attributes intensity showing significant differences assessed in 2015 Shiraz wines (A:  $n = 18$  per harvest date) and Cabernet-Sauvignon wines (B:  $n = 6$  per harvest date) between harvest dates (H1, H2, H3).

One-way ANOVA was used to compare data. Different letters above bars indicate significance at  $p < 0.05$  (Fischer's LSD). All quoted uncertainty is the standard deviation of 18 Shiraz (A) and 6 Cabernet-Sauvignon (B) wines respectively.

### 3. Nexus between wine and grape composition

Here, we discuss the grape and wine composition nexus for harvests carried out at the “Fresh Fruit” and “Mature Fruit” stages, which were specifically defined by sensory analysis

#### 3.1. Parameters related to technological maturity

Delaying harvest resulted in increasing grape fructose concentrations, grape juice TSS and, in turn, the concentration of yeast primary metabolites, such as ethanol and glycerol in the corresponding wines (Table 3 and Supplementary Data Table S2 and S3). However, those variations depended closely on variety, vineyard and particularly vintage. The increase in grape sugar concentration was more pronounced in the 2014 vintage than the 2015 vintage in Griffith. The 2014 season was characterised by several heat waves in January and February at critical periods of berry maturation. The heat waves resulted in late season berry dehydration, which subsequently increased grape juice TSS from an average of 23 °Brix and 22.7 °Brix (H1) to 27 °Brix and 25.6 °Brix (H3) for Shiraz and Cabernet-Sauvignon respectively. Grape berry dehydration did not affect the amount of sugar per berry (Figure 2A and Supplementary Data Figure S4), but only sugar concentration (Table 3 and Supplementary Data Table S2 and S3). Consequently, wine ethanol concentration increased by nearly 20 % from H1 to H3 in Shiraz and Cabernet-Sauvignon respectively, giving a more pronounced alcoholic character to H3 wines. Grape berry shrivelling was observed in Griffith in 2014, being more pronounced for Shiraz, a variety known to be sensitive to late seasonal berry dehydration (Chou *et al.*, 2018). The increase in juice TSS between H1 and H3 observed in the 2015 vintage was lower than in the 2014 vintage (Supplementary Data Table S2), and in one case no significant increase in ethanol content from H1 to H3 stages was observed (G2\_SH). Despite these small variations, the panel perceived H3 wines as being significantly more alcoholic than H1 (Figure 2C), highlighting the complexity of wine composition and the wine sensory nexus. These results also confirmed that wine aroma development in late ripening was not directly linked to grape sugar concentration and the corresponding ethanol content in wine.

The decrease in grape juice acidity is also a component of technological maturity, but the effect on wine sensory profiles was moderated by adjustment of titratable acidity (TA) with the

addition of tartaric acid prior to fermentation. Grape juice TA decreased while pH increased with grape maturity in all of the samples, excluding Cabernet-Sauvignon from Griffith in 2014, for which the values were stable between H1 and H3 (Table 3 and Supplementary Data Table S3). For Shiraz, these variations were more pronounced in 2014, reflecting the impact of heat waves during grape maturation (Supplementary Data Table S2). For Cabernet-Sauvignon, the heat waves occurred before H1, when grape pH and TA values were already high and low respectively. This may explain the relatively small variations in grape juice acidity parameters observed for Cabernet-Sauvignon between H1(FF) and H3(MF) in 2014 (Supplementary Data Table S3).

#### 3.2. Relationship between phenolic maturity and berry sugar accumulation

Phenolic maturity is related to the content of phenolic compounds in grapes and by their level of extractability in wine. Overall, grape anthocyanin concentrations were not significantly altered between H1 and H3 (Supplementary Data Table S2 and S3). The onset of anthocyanin synthesis in grape berries is generally closely related to sugar accumulation (Castellarin *et al.*, 2007). Therefore, the slight variations in grape anthocyanin content which occurred after the plateau of berry sugar accumulation was probably related to temperature conditions, as previously suggested by Mori *et al.* (2007). In contrast, wine colour and total phenolics content tended to increase from H1 to H3 for both varieties. The lack of statistically significant differences between maturity stages was due to a large site effect overlapping the maturity effect, which was particularly evident for the 2015 vintage. Differences were observed between vintages for Shiraz wines: total anthocyanins and red pigment increased in 2015, but these values remained stable in 2014. In Cabernet-Sauvignon wines, total anthocyanins and red pigment increased in both vintages from H1 to H3. Total phenolics, total tannins, colour density and SO<sub>2</sub> resistant red pigment increased for Shiraz and Cabernet-Sauvignon wines in both vintages. These results suggest that while grape total phenolic content was stable after the plateau of berry sugar accumulation (Walker *et al.*, 2007), the extractability of phenolic compounds increased between H1 and H3. The overall increase in phenolic extractability between the H1 and H3 stages may be related to a higher permeability of the grape cell wall, along with later maturity and higher ethanol content (Bindon *et al.*, 2013).

Wine tannins comprised the group of phenolics that was most influenced by grape maturity, with relative increases of 25 to 50 % from H1 to H3. Tannins are the most hydrophobic and the least extractable grape phenolic compounds, especially those located in seeds. Therefore, increasing metabolite extractability from grape to wine strongly favours higher concentrations of tannins in the final wine, which can hence be perceived as being more structured and astringent; nevertheless, the relationship between grape ripening, wine polyphenolic composition and astringency perception is complex (García-Estévez *et al.*, 2017). The higher increase in total tannins between H1 and H3 also tended to improve wine colour stabilisation (Boulton, 2001); wine colour quality generally improved during ripening from Fresh fruit to Mature fruit stages.

### 3.3. Evolution of grape and wine aromatic composition according to the sugar accumulation model

The nexus between grape composition, wine composition and the wine sensory profile is highly complex. The present study revealed a common sensory pattern for Australian Cabernet-Sauvignon and Shiraz in the evolution of wine aromas during ripening, which was synchronised with defined grape harvest time post plateau of berry sugar accumulation (mg/berry), irrespective of grape genotype and environment. Targeted analyses of grape and wine aromatic compounds were performed in order to gain further insight into the evolution of these relationships during ripening. The concentration of about 50 volatile compounds of interest were measured in the grapes and wine samples. Some markers of maturity were common to both varieties whereas other metabolites were genotype-dependent irrespective of the environment (Table 3).

Only ethyl dihydrocinnamate, ethyl propanoate and dimethyl sulfide (DMS) were found to be aromatic markers of the H1 and H3 maturity stages common to Shiraz and Cabernet-Sauvignon irrespective of the environment (Table 3 and Supplementary Data Table S2 and S3). Higher concentrations of ethyl dihydrocinnamate, a grape-derived wine metabolite, were consistently measured in H1 wines compared to those in H3 wines, but the level of variations was about 10-fold lower than the sensory threshold reported in model wine (Ferreira *et al.*, 2000). In contrast, ethyl propanoate and DMS concentrations consistently increased with maturity between H1(FF) and H3(MF). Ethyl propanoate is an

ester produced during alcoholic fermentation, and the influence of grape composition on its synthesis by yeast is still poorly understood. The presence of DMS in wine mainly originates from the hydrolysis of the grape metabolite S-methylmethionine (Segurel *et al.*, 2004). The increase in DMS contents in wine with grape maturity has been previously reported for Petit Manseng and Cabernet-Sauvignon (Dagan, 2006; Bindon *et al.*, 2013).

Concentrations of  $\gamma$ -nonalactone significantly increased from H1 to H3 stages in Cabernet-Sauvignon wines, whereas it was only found to increase in the 2014 vintage Shiraz wines.  $\gamma$ -nonalactone has been associated with plum and cooked fruit aromas being perceived in red wines made with shrivelled berries of late maturity (Pons *et al.*, 2008; Allamy *et al.*, 2018). This compound is formed during alcoholic fermentation from grape-derived precursors related to the oxidation of lipids (de Ferron *et al.*, 2020). The variations and the levels of measured  $\gamma$ -nonalactone concentrations were higher in 2014 and in Cabernet-Sauvignon wines compared to Shiraz wines (Table 3 and Supplementary Data Table S2 and S3). This appears to be the result of a series of late season heat waves in the Griffith vineyards in 2014, which induced the shrivelling of both varieties of grapes, and resulted in a significant increase in  $\gamma$ -nonalactone concentration in H3 wines. Milder climatic conditions in the late ripening period of the 2015 vintage limited late season berry dehydration and shrivelling, and consequently the differences in  $\gamma$ -nonalactone content between H1 and H3 were significantly reduced. This suggests that  $\gamma$ -nonalactone concentrations in wine are related to shrivelling and abiotic stress rather than directly to maturity (Chou *et al.*, 2018). The concentration of  $\gamma$ -nonalactone in wines also seems to be influenced by grape genotype.

Cis-3-hexenol was consistently measured at higher concentrations in H1 stage Shiraz wines, whereas trans-3-hexenol was a consistent marker of the same ripening stage in Cabernet-Sauvignon wines (Table 3 and Supplementary Data Table S2 and S3). Hexanol, cis-3-hexenol, trans-2-hexenol and trans-3-hexenol are the main C<sub>6</sub>-compounds found in wines. They are derived from the reduction of corresponding C<sub>6</sub>-aldehydes during alcoholic fermentation, and they are formed from the enzymatic oxidation of polyunsaturated fatty acids occurring in grapes and during berry crushing.

Interestingly, the variations in C6-alcohols in wines were poorly correlated with the variations in the corresponding precursor in grapes; for instance, there were substantially more variations in cis-3-hexenol in Shiraz wines than in cis-3-hexenal and cis-3-hexenol in grapes (Table 3). These results open up new research opportunities regarding C6-compounds in wines.

The wine composition linked to other grape-derived aromas was not altered significantly between the H1 and H3 stages. The relatively low variations observed for IBMP in the present study indicate that it probably did not directly contribute to the aromatic alteration perceived in Cabernet-Sauvignon wines made from grapes at different stages of maturity (Allen *et al.*, 1994). The concentrations of 10 different monoterpenes and  $\beta$ -damascenone in wine were also not influenced by grape maturity. Some significant variations were measured for  $\alpha$ -ionone and  $\beta$ -ionone between harvest stages, but they depended strongly on genotype  $\times$  environment interactions and did not resemble the trends observed in grapes for the corresponding C13-norisoprenoids and their precursor carotenoids (Supplementary Data Table S2 and S3). It seems that grape and wine monoterpene and C13-norisoprenoids composition was established at the H1 (Fresh Fruit) stage; consequently, these compounds do not directly contribute to the perceived aromatic evolution between the Fresh Fruit (H1) and Mature Fruit (H2) stages.

Paradoxically, yeast-derived metabolites were more affected by grape maturity than the varietal component. The levels of concentration of hydrogen sulfide and methanethiol, which are important contributors to reductive aroma in wines, were affected by grape maturity without consistency across vintages and varieties (Supplementary Data Tables S2 and S3).

The group of metabolites that were the most influenced by grape maturity were the wine esters. Most variations were related to grape genotype, but they were consistent irrespective of the environment, with the exceptions of ethyl propanoate and ethyl dihydrocinnamate, as previously discussed (Table 3 and Supplementary Data Tables S2 and S3). Esters are primarily produced by yeast during alcoholic fermentation and can be classified into three main groups: ethyl esters of fatty acids (EEFAs), higher alcohol acetates (HAAs) and ethyl esters of branched acids (EEBAs). EEFAs were the least affected by grape maturity.

In both vintages, only ethyl butyrate concentration significantly increased in Shiraz wines, whereas the same trend was only observed in 2014 in Cabernet-Sauvignon wines. Bindon *et al.* (2013) reported an increase in most EEFAs with grape maturity in Cabernet-Sauvignon wines, which has thought to arise from the synergistic effects of an increase in grape sugar concentration and general yeast metabolism, leading to a higher production of esters. In contrast, it was not possible to establish a direct link between EEFAs and grape sugar concentration in the present study, which is in line with other observations (Antalick *et al.*, 2015).

EEBAs are also ethyl esters of fatty acids, but they differ from EEFAs in origin. While the latter group is related to yeast lipid metabolism, EEBAs originate from yeast nitrogen and redox metabolism (Antalick *et al.*, 2014, Arias-Pérez *et al.*, 2020). A clear genotype effect related to grape maturity was consistently observed for these esters for both vintages. While all EEBAs concentrations significantly increased from the H1 to H3 stages in Cabernet-Sauvignon wines, their content tended to decrease in Shiraz wines, particularly ethyl isobutyrate, ethyl leucate and, to a lesser extent, ethyl isovalerate. Similar trends have been recently observed in wines from a limited study carried out in the Griffith region in 2013 (Antalick *et al.*, 2015). EEBAs are derived from corresponding branched amino acids, such as valine, isoleucine and leucine. In this study, a slight increase in these metabolites in Shiraz and Cabernet-Sauvignon grapes of greater maturity in both vintages was observed. This trend contrasted with the variations measured for EEBAs in Shiraz wines. Future research on grape maturity and yeast redox metabolism is therefore required.

A high varietal effect was also measured for higher alcohol acetates. The average total HAAs concentrations increased from 250 to 1300  $\mu\text{g/L}$  at the H1 to H3 stages respectively, with higher variability being observed in 2015. The differences were mainly due to isoamyl acetate and, to a lesser extent, phenylethyl and propyl acetate. Conversely, HAAs concentrations tended to slightly decrease in Cabernet-Sauvignon wines (Table 3 and Supplementary Data Table S2 and S3). An increase in HAA concentrations with grape ripening has previously been reported for Australian Cabernet-Sauvignon wines (Bindon *et al.*, 2013) and for Shiraz (Šuklje *et al.*, 2019a). In the present study, neither the slight decrease in HAAs in Cabernet-Sauvignon wines, nor the increases measured in Shiraz wines, were found to be directly related to grape sugar concentration.

Similar observations were reported for Australian Shiraz and Cabernet-Sauvignon wines (Antalick *et al.*, 2015) indicating that a relationship exists between higher levels of amino nitrogen in grape juice and HAAs in wine. In the present study, such a relationship could not be established and the increase of HAAs concentration with grape maturity observed in Shiraz was probably due to more complex interactions between grape juice composition and yeast metabolism.

It would be worthwhile to compare the concentrations of the aromatic compounds measured in the present study with sensory thresholds reported in the literature, as it is probable that some of those compounds contribute to the aromatic evolution perceived between wines from Fresh Fruit and Mature Fruit stages (Table 3). DMS probably enhanced the dark fruit character (Lytra *et al.*, 2014) in both varieties of H3 wines, as previously suggested for Cabernet-Sauvignon wines made

from late maturity grapes (Bindon *et al.*, 2014).  $\gamma$ -nonalactone may have contributed to the sensory profiles in the H3 wines. This seemed to be most obvious in the 2014 vintage and is probably due to grape berry dehydration rather than a maturity effect. In contrast, *cis*-3-hexenol was present at peri-threshold levels in Shiraz wine (Escudero *et al.*, 2007) made from grapes harvested at H1. At such concentrations, this C6-compound may have contributed to the fresh red berry fruit notes (Rowe and Tangel, 1999) perceived in H1 Shiraz wines. Esters are important contributors to the fruity aromas of wine, having a direct impact via complex sensory interactions (Pineau *et al.*, 2009, Lytra *et al.*, 2013). It is possible that some esters (HAAs) contributed directly to wine aromatic evolution between H1 and H3, while EEBAAs and some EEFAAs (*e.g.*, ethyl propanoate and ethyl butyrate) caused aromatic differences due to sensory interactions in aroma perception.

**Table 3.** Shiraz and Cabernet-Sauvignon grape, juice and wine metabolites and analytical parameters that significantly differ between H1(FF) and H3(MF) irrespective of the environment (vintage and regions).

Group of metabolites/parameters	Sample type	H1 («Fresh fruit» stage)	H3 («Mature fruit» Stage)	
Chemical markers of ripening stage irrespective of genotype and environment	Grape		Isoleucine, proline, fructose	
	Grape juice		TSS	
	Wine	ethyl dihydrocinnamate	<b>alcohol, total phenolics, SO<sub>2</sub> resistant red pigment, ethyl propanoate, DMS</b>	
Chemical markers of ripening stage irrespective of environment, but depending on genotype	Grape	Shiraz	chlorophyll b	
		CS	Alanine, aspartic acid, malic acid	
	Grape juice	Shiraz	TA	NOPA, YAN, ratio NOPA/ammonium, pH
		CS	Ammonium, YAN	
	Wine	Shiraz	Lactic acid, <b>cis-3-hexenol</b> , ethyl isobutyrate, ethyl leucate	Glycerol, <b>ethyl butyrate</b> , propyl acetate, butyl acetate, <b>isoamyl acetate</b> , phenylethyl acetate
		CS	Trans-3-hexenol	total anthocyanins, <b>total tannins</b> , red pigment, colour density, <b><math>\gamma</math>-nonalactone, ethyl isobutyrate, ethyl 2-methylbutyrate, ethyl isovalerate, ethyl leucate</b> , ethyl phenylacetate

Metabolites and parameters with potential sensory impact on wines are highlighted in bold.

It is also evident that other chemical markers not analysed in the present study were involved in the aromatic evolution perceived in all the studied wines. Recent studies have emphasised the importance of the interactions between non-volatile and volatile compounds in affecting the perception of red wine aromas (Sáenz-Navajas *et al.*, 2010; Muñoz-González *et al.*, 2014). Therefore, the variations in the non-volatile fraction associated with the different grape maturity stages may also influence the final aromatic perception of the wines. Further research is required to clarify the role of the non-volatile component of red wines in aromatic evolution during grape ripening.

## CONCLUSIONS

The present study has demonstrated the existence of a predictable aromatic sequence during grape ripening in Australian Shiraz and Cabernet-Sauvignon from different meso-climates. Two distinct maturity stages were identified and characterised: i) Fresh Fruit distinguished by fresh/red fruits attributes, and ii) Mature Fruit associated with dark fruit and plum character. Berry sugar accumulation (mg/berry) is characterised by two phases between veraison and harvest: a) pre-plateau of berry sugar accumulation, and b) post plateau of berry sugar accumulation, in which the increase in sugar concentration (°Brix) is mainly due to berry water loss. After the plateau of berry sugar accumulation, the aromatic and phenolic maturity of the wine was separate from technological maturity. Compositional analyses revealed that wine grape and yeast-derived compounds were affected by grape maturity. A few individual compounds can be considered as maturity markers irrespective of grape genotype. The contribution of DMS to the dark fruit aroma specific to Mature Fruit wines was the most important marker for discriminating the Fresh Fruit stages from the Mature Fruit stages. Specific cultivar markers which potentially contribute to aromas were also identified; for example, (Z)-3-hexenol may contribute to fresh fruit aroma in Shiraz wines. While terpenoids were not generally affected by the post plateau ripening process, the composition of esters was significantly altered with a marked varietal effect. The results of the study have contributed to knowledge regarding the nexuses between grape composition, wine composition and subsequent sensory characteristics; however, further research would be required to gain an even greater understanding of these complex relationships.

**Acknowledgements:** The authors would like to thank Campbell Meeks for making the experimental wines for this study and to Australia's grape growers and winemakers for their financial support through their investment body, Wine Australia. The authors would also like to thank the wine producers in Griffith and Orange for allowing us access to their vineyards and for their grape donations.

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