Characterization of Brazilian Syrah winter wines at bottling and after ageing

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ABSTRACT: Double pruning extended the harvest season of wine grape (Vitis vinifera L.) to dry winter, enabling production of high quality wines in the southeastern Brazil. Winter harvest allows grapes to fulfill not only technological maturation, but also phenolic ripeness. Winter wines from Syrah grapes harvested from eight vineyards in southeastern Brazil during three harvests were analyzed for their chemical and aromatic composition after bottling and after ageing for 20, 30, and 42 months in bottle. Winter wines have high content of total phenolic compounds, which remained almost constant through ageing, as well as color intensity. Malvidin 3-O-glucoside stood out among anthocyanins, remaining 5-10 % after 39 months of ageing. Moreover, malvidin 3-O-glucoside-pyruvic acid was the main pyranoanthocyanin identified in winter wine. Polymerized pigments index ranged from 54 % at bottling to 80 % after 42 months of ageing. Young winter wines are rich in ester and monoterpenes, as well as alcoholic volatile compounds responsible for ethereal, fruity, flowery, fresh and sweet aromas. Aged winter wines showed higher contents of furfural, geranyl ethyl ether, isomethyl decanoate, α-murolone and α-calcocorene, contributing to sweet, fruity and woody aromas. Syrah winter wines are characterized by high content of phenolic compounds and color stability, and keep good sensorial characteristics after ageing in bottle.

Keywords: double-pruning, composition, color, phenolics, aroma

Introduction

The use of double pruning enables to harvest grapes under climatic conditions that favor grape ripening (Favero et al., 2011; Palliotti et al., 2017; Toda et al., 2019). In southeastern Brazil, this technique allowed vineyard dissemination for high quality fine wine production [Favero et al., 2011].

Wines elaborated from grapes harvested at winter season under low water availability and high thermal amplitude have higher alcoholic and phenols content as well as color intensity than summer wines [Mota et al., 2009]. Similar results were obtained with controlled water deficits in ’Cabernet sauvignon’ vines [Cáceres-Mella et al., 2018]. The authors observed that wines from less irrigated vines exhibited high levels of total phenols, anthocyanins and chroma and therefore showed higher color intensity and sensorial perception of more fullness. Phenolic compounds are the main component of color and mouthfeel in wine, also affecting its ageing ability. Double pruning favors phenolic maturation mainly by high thermal amplitude and low rainfall during autumn-winter season [Favero et al., 2011].

Besides color, aroma is a wine characteristic immediately observed and highly appreciated by consumers. The presence of compounds, such as alcohols, acids, aldehydes, lactones, benzenes, esters, ketones, terpenes, originating from grapes or formed during the fermentation process and ageing, are responsible for the aroma profile of the wine [Vidal and Segurel, 2005; Belda et al., 2017].

Among the cultivars tested under double-pruning management in the southeastern Brazil [Mota et al., 2010, 2011], Syrah wines showed the best adaptation to this management. Winter Syrah wines have been well accepted by consumers, which increased the interest in management of this vineyard in Brazil [Salettes, 2016]; however, there is little information on the composition of these wines and the effect of ageing.

As far as the authors know, there is no information in the literature about aromatic profile of Syrah wines from winter harvest. Therefore, this work investigated the volatile aroma compounds in Syrah wines from winter harvest and the effect of bottle ageing in the composition of these wines.

Materials and Methods

Wine samples

Wines were elaborated from grapes harvested in the 2013, 2014 and 2015 seasons from non-irrigated commercial vineyards in Indaiatuba, SP (23°05’ S, 47°13’ W, altitude of 701 m), Santo Antônio do Amparo, MG (20°55’ S, 44°91’ W, altitude of 990 m), São Bento do Sapucaí, SP (22°41’ S, 45°43’ W, altitude of 886 m), São Sebastião do Paraíso, MG (20°54’ S, 47°06’ W, altitude of 860 m), Três Pontas, MG (21°12’ S, 45°35’ W, altitude of 845 m), Itobi, SP (21°42’ S, 46°55’ W, altitude of 840 m) and Três Corações, MG (21°36’ S, 45°07’ W, altitude of 865 m) in the southeastern region of Brazil. All vineyards were over 6 years old of ‘Syrah’ clone 174 ENTAV-INRA, grafted onto 1103 Paulsen, at vertical shoot position trellis managed under double pruning. The first pruning to induce the vegetative cycle was carried out in September and all bunches at bunch closure stage
were removed to avoid harvest in the summer season. In January of the subsequent year, the lignified shoots were pruned to allow the productive cycle during the autumn-winter season (Pavero et al., 2011).

Grapes were harvested on average with 23.1 °Brix, pH 3.61 and total acidity 5.92 g L⁻¹ tartaric acid. Not all vineyards were represented in the three seasons due to environmental damages or erroneous management that compromised vine production.

Harvested bunches were stored at 4 °C for 24 h at the winery. For each region, 200 kg of grape clusters were destemmed, crushed and placed in 200 L inox fermentation tanks. The musts were inoculated with rehydrated wine yeast Saccharomyces cerevisiae × S. kudriavzevii and added with 80 mg SO₂ kg⁻¹.

Wine density was determined daily during alcoholic fermentation performed at 21 °C. When the density reached approximately 990 g L⁻¹, wines were racked to 100 L stainless steel tanks. Malolactic fermentation was carried out with native bacteria flora at 21 °C and the presence of malic acid was routinely followed by the paper chromatography method (Amerine and Ough, 1980). When malic acid was not detected by paper chromatography, wines were carefully racked to avoid lees, added with 35 mg SO₂ L⁻¹ and kept at 3 °C for 15 d to allow tartaric stabilization. The wines were bottled in 750 mL green glass bottles closed with natural cork and allowed to age in lying position at 15 °C in a dark cell for 20, 30 or 42 months.

**Wine composition**

The physicochemical analyses consisted of alcohol, fixed acidity [g L⁻¹ tartaric acid], pH, residual sugars [g L⁻¹] and ashes [g L⁻¹] (Amerine and Ough, 1980). Color intensity (CI) [A₄₂₀ + A₅₂₀ + A₆₂₀], color hue (A₄₂₀/A₅₂₀), color composition (the contribution of each color component in the overall color expressed by the general equation OD n (%) = OD n/C I × 100) and polymerized pigments were evaluated by spectrophotometry (Ribéreau-Gayon et al., 2006; Harbertson and Spayd, 2006). Total flavonoid content was evaluated by Bate-Smith reaction (Ribéreau-Gayon et al., 2006). Anthocyanins and phenolics were measured by the pH differential method (Giusti and Wroslad, 2000) and Folín-Ciocaltel method (Amerine and Ough, 1980), respectively. Each sample was analyzed in triplicate at bottling and after ageing.

**Monomeric Anthocyanin extraction**

Anthocyanins and polymeric anthocyanins were identified in Syrah winter wines. The identification of the polymeric anthocyanins was performed by HPLC-DAD and LC-ESI-MS/MS analyses. Wines samples (5 mL) were concentrated under vacuum at 40 °C on a rotary evaporator to remove the alcohol, and filtered until to 10 mL with ultrapure water prior to application to a solid-phase extraction polyamide column (1 g) previously conditioned with methanol and ultrapure water. The de-alcoholized sample (2 mL) was loaded into the column and washed with ultrapure water and eluted with 0.3 % HCl in methanol. The eluates were completely dried using a rotary evaporator under vacuum at 40 °C, resuspended in 5 % acetic acid in methanol and filtered through a 0.45 μm PTFE filter. For the polymeric anthocyanin analysis, wine was filtered through a 0.45 μm PTFE and injected directly.

**LC-ESI-MS/MS and HPLC-DAD conditions**

Anthocyanins were identified by LC-ESI-MS/MS using a Prominence Liquid Chromatograph linked to an Ion trap ESquires-LC mass spectrometer with an electrospray ionization (ESI) interface. We used a 5-μm Prodigy ODS3 column (4.60 x 250 mm) with a flow rate of 1 mL min⁻¹ at 25 °C. The mobile phase consisted of solvent A, water ultrapure, formic acid and acetonitrile (95:1:3, v/v/v) and solvent B, water, formic acid and acetonitrile (48:1:51, v/v/v). Anthocyanins were detected at 525 nm (Teixeira et al., 2015). For application to the mass spectrometer after DAD detection, the flow rate was reduced to 0.2 mL min⁻¹ Mass spectrometer operated with collision energies of -3500 V and N₂ like dry gas with ESI in the positive mode using a full scan from m/z 100 to 1500. Compounds were identified according to comparison with the retention time of authentic standards when possible, as well as by absorption spectrum similarity, mass spectral characteristics and by comparison with the literature data. The calibration curve was performed by injecting the standards malvidin 3-O-glucoside, peonidin 3-O-glucoside, petunidin 3-O-glucoside, delphinidin 3-O-glucoside three times at five different concentrations. The acylated form of anthocyanins with coumaroyl and acetyl groups were quantified using the calibration curve of their respective O-glucoside form. The results were expressed as mg 100 mL⁻¹.

**Pyranoanthocyanins analysis by LC-qTOF-MS/MS and HPLC-DAD conditions**

The identification of the polymeric anthocyanins was performed using a Prominence Liquid Chromatograph linked to a qTOF mass spectrometer Compact model. The LC condition was reverse phase Luna 3 μ C18 [150 x 3.0 mm] at 25 °C. The solvent gradient condition was: phase A: 0.5 % formic acid in ultrapure water and phase B: 0.5 % formic acid in acetonitrile at a flow rate of 0.5 mL min⁻¹. The mass spectrometer conditions were: positive mode, N₂ like dry gas, capillary -3500 V, scan m/z 50-1500. The polymeric anthocyanins were identified comparing the mass spectra with data available in the literature [Blanco-Vega et al., 2014].

**Volatile extraction and analysis**

For the isolation and concentration of volatiles, the headspace solid-phase microextraction technique (HS-SPME) was used according to Gürbüz et al. (2006).
with some modifications. All extractions were carried out using a DVB/CAR/PDMS fiber, of 50/30 μm film thickness. An aliquot of 10 g of wine was placed in 20 mL vials closed with Teflon cap. Vials were heated to 30 °C under agitation with a magnetic stir bar for 10 min for headspace equilibrium. Adsorption time was 45 min at the same temperature. The SPME fiber was then injected directly into a gas chromatograph mass spectrometer operating with ChemStation software. The SPME fiber was held for 10 min at 250 °C for desorption of volatile compounds, which were separated in HP-5MS (30 m × 0.25 mm × 0.25 μm) capillary column with helium as carrier gas at constant flow of 1 mL min⁻¹. Initial oven temperature was 40 °C held for 5 min, then increased to 160 °C at 3 °C min⁻¹ and to 250 °C at 10 °C min⁻¹ and kept for 10 min before returning to 40 °C, in a total cycle of 64 min; transfer line temperature at 250 °C; MS detector in SCAN mode 30-500 m/z.

Volatile compounds were tentatively identified by comparison with the NIST library considering 70 % similarity as the cut-off, further confirming the results with the retention indices calculated according to the Kovats Index and compared to data reported on Nist Webbook [https://webbook.nist.gov], Chemspider (www.chemspider.com) or PubChem [www.pubchem.ncbi.nlm.nih.gov] websites. Only aromatic compounds with difference in Kovats Retention Indices lower than 70 units up or down were accepted. All analyses were carried out in triplicate.

Statistical analysis

The Partial Least Squares Discriminant Analysis (PLS-DA) was performed to investigate the trends or group formations of wines from different ageing times on all volatile compounds in the wine samples analyzed by the MetaboAnalyst Program [www.metaboanalyst.ca].

Results

At bottling, winter wine composition was on average 14 % alcohol, pH 4.0, fixed acidity 5.4 g L⁻¹ tartaric acid, residual sugar 3.1 g L⁻¹, ashes 3.9 g L⁻¹, total anthocyanin content 380 mg L⁻¹, total phenolics 2.4 g L⁻¹, total flavanols 2.7 g L⁻¹, color intensity of 13.5, color hue 0.75, and polymerized pigments 54 % (Table 1).

Ageing decreased the total monomeric anthocyanin content and increased color hue and the polymerized pigments index, with no changes in color intensity (Tables 2 and 3). The monomeric anthocyanins identified in the Brazilian Syrah winter wine were the malvidin-3-O-glucoside (m/z 493), peonidin-3-O-glucoside (m/z 463), petunidin-3-O-glucoside (m/z 479) and delphinidin-3-O-glucoside (m/z 465) and the respective acylated form with coumaroyl and acetyl groups. The malvidin-3-O-glucoside was the main anthocyanin for all wine samples (Table 4), remaining 5-10 % of the concentration at bottling after 36 months of ageing.

Contribution of yellow component to the overall wine color was on average 38 % at bottling reaching 41 % after 42 months of ageing, while red color changed from 49 % to 46 % in the same period. Blue component (OD 620) was almost constant during ageing (Tables 1 and 3). Polymerized pigments ranged from 54 % at bottling to 80 % after 42 months of ageing (Tables 1 and 3). Although not all wine samples were analyzed at 30 and 42 months after ageing, it seems that polymerized pigments reached maximum values after 30 months of ageing and remained constant afterwards.

Among polymerized anthocyanins, 14 pyranoanthocyanins were identified in wine samples, mainly carboxy-pyranoanthocyanins [Vitisin type], hydroxyphenyl pyranoanthocyanin and flavan-3-ol pyranoanthocyanin (Table 5). Vitisin A (m/z 561) formed

Table 1 – Physicochemical parameters of Syrah winter wine samples at bottling.

| Parameter                                      | 2013 winter season | 2014 winter season | 2015 winter season |
|------------------------------------------------|--------------------|--------------------|--------------------|
| Alcohol (%) vol                                  | 12 ± 0.3           | 13 ± 0.3           | 14 ± 0.4           |
| pH                                             | 3.83 ± 0.02        | 3.83 ± 0.02        | 3.83 ± 0.02        |
| Fixed acidity (g L⁻¹)                           | 6.57 ± 0.29        | 6.75 ± 0.31        | 7.03 ± 0.31        |
| Residual sugar (g L⁻¹)                          | 3.46 ± 0.29        | 3.46 ± 0.29        | 3.46 ± 0.29        |
| Ashes (g L⁻¹)                                   | 3.75 ± 0.29        | 4.14 ± 0.29        | 4.14 ± 0.29        |
| Total polyphenols (g L⁻¹)                       | 2.41 ± 0.29        | 2.51 ± 0.29        | 2.51 ± 0.29        |
| Total anthocyanins (mg L⁻¹)                     | 540.11 ± 39.21     | 427.18 ± 39.21     | 399.20 ± 39.21     |
| Total flavanols (g L⁻¹)                         | 71 ± 3.5           | 71 ± 3.5           | 71 ± 3.5           |
| Color intensity                                 | 14.32 ± 1.2        | 15.48 ± 1.2        | 15.49 ± 1.2        |
| OD 420 %                                       | 61 ± 3.5           | 61 ± 3.5           | 61 ± 3.5           |
| OD 520 %                                       | 54 ± 3.5           | 54 ± 3.5           | 54 ± 3.5           |
| OD 620 %                                       | 12 ± 0.6           | 12 ± 0.6           | 12 ± 0.6           |
| Polymerized pigments (%)                        | 47 ± 3.5           | 52 ± 3.5           | 52 ± 3.5           |

Average values of three samples per region. *Number represents the harvest season; OD = optical density at 420, 520, or 620 nm; VAR = Vargem (SP); INO = Indaiatuba (SP); SB = São Bento do Sapucaí (SP); SAA = Santo Antônio do Amparo (MG); SSP = São Sebastião do Paraíso (MG); TP = Três Pontas (MG); TC = Três Corações (MG); ITO = Itobi (SP).
Table 3 – Physicochemical parameters of Syrah winter wine samples after 30 and 42 months of ageing in bottle.

| Parameter                  | 2013 winter season | 2014 winter season | 2015 winter season |
|----------------------------|--------------------|--------------------|--------------------|
|                            | VAR13*             | IND13              | SB13               | SAA13             | SSP13             | TP13             | VAR14              | TC14              | SSP14             | IT015             | TC15              | TP15              |
| Alcohol (% vol)            | 14                 | 14                 | 14                 | 14                 | 15                 | 13                | 14                 | 15                 | 16                | 14                 | 15                 | 14                 |
| pH                         | 4.11               | 3.84               | 3.79               | 3.89               | 3.72               | 3.92              | 3.83               | 3.64               | 4.43              |
| Fixed acidity (g L⁻¹)      | 4.99               | 6.03               | 5.86               | 5.37               | 5.58               | 5.77              | 5.84               | 5.57               | 5.67              |
| Ashes (g L⁻¹)              | 4.25               | 3.17               | 4.07               | 3.65               | 2.85               | 2.84              | 3.85               | 3.05               | 2.50              |
| Color intensity            | 14.33              | 14.67              | 14.90              | 15.12              | 12.22              | 12.43             | 12.12              | 14.98              | 12.86             |
| Color hue                  | 0.72               | 0.73               | 0.76               | 0.75               | 0.77               | 0.78              | 0.88               | 0.84               | 0.89              |
| OD 420 %                  | 37                 | 37                 | 38                 | 37                 | 38                 | 38                | 40                 | 40                 | 41                |
| OD 520 %                  | 50                 | 50                 | 49                 | 50                 | 49                 | 49                | 45                 | 48                 | 46                |
| OD 620 %                  | 13                 | 13                 | 13                 | 13                 | 13                 | 13                | 15                 | 12                 | 13                |
| Polymerized pigments (%)  | 69                 | 69                 | 72                 | 68                 | 73                 | 72                | 73                 | 83                 | 78                |

Average values of three samples per region. *Number represents the harvest season; OD = optical density at 420, 520, or 620 nm; IND = Indaiatuba (SP); SB = São Bento do Sapucaí (SP); SAA = Santo Antônio do Amparo (MG); SSP = São Sebastião do Paraíso (MG); TP = Três Pontas (MG); TC = Três Corações (MG); ITO = Itobi (SP).

Table 4 – Mass spectra and concentration of monomeric anthocyanins of Syrah winter wine of five regions at bottling and after 19 and 36 months of ageing in bottle.

| Peak             | RT (min) | [M]+ (m/z) | MS/MS (m/z) | SB13 | TP13 | IND13 | SSP13 |
|------------------|----------|------------|-------------|------|------|-------|-------|
| Delphinidin-3-glu| 12.3     | 465        | 303         | 17.9 | 1.2  | nd    | 10.4  |
| Petunidin-3-glu  | 14.3     | 479        | 317         | 34.3 | 2.1  | 24.6  | 21.7  |
| Malvidin-3-glu   | 15.6     | 493        | 331         | 269.0| 19.3 | 266.0 | 22.9  |
| Petunidin-3-acgly| 21.8     | 521        | 317         | 10.3 | 0.5  | 6.6   | 1.1   |
| Malvidin-3-acgly | 22.2     | 535        | 331         | 22.4 | 1.0  | 20.3  | 1.6   |
| Peonidin-3-cmgl  | 25.6     | 609        | 301         | 22.4 | 1.0  | 20.3  | 1.6   |
| Delphinidin-3-glu| 15.6     | 493        | 331         | 42.1 | 2.3  | 37.8  | 3.8   |
| Petunidin-3-acgly| 21.8     | 521        | 317         | 7.5  | 0.7  | 7.5   | 0.4   |
| Peonidin-3-cmgl  | 25.6     | 609        | 301         | 22.4 | 1.0  | 20.3  | 1.6   |

RT = retention time; glu = glucoside; acgly = 6''-acetyl-glycoside; cmgl = (6-p-coumaroyl) glycoside; nd = not detected; Tₜ = wine at bottling; Tₖ = wine after 19 months of ageing; Petunidin-3-acgly, malvidin-3-acgly and peonidin-3-cmgl were expressed as petunidin-3-glucoside, malvidin-3-glucoside and peonidin-3-glucoside equivalent, respectively. Results expressed as mg 100 mL⁻¹; IND = Indaiatuba; SB = São Bento do Sapucaí; SAA = Santo Antônio do Amparo; SSP = São Sebastião do Paraíso; TP = Três Pontas.
from malvidin 3-O-glucoside and pyruvic acid reaction was the most abundant pyranoanthocyanins (He et al., 2012). Ageing decreased the content of vitisin A on average by 10-30 % in most samples, while 10-HP-pymv-3-gly (m/z 609) increased during ageing (Table 6).

The Partial Least Squares Discriminant Analysis (PLS-DA) accounted for 63 % of the total data variance. The two-dimensional graph showed a clear separation of aromatic compounds from bottled wines to those over 30 months ageing (Figure 1).

Table 7 summarizes all the aromatic volatile compounds tentatively identified in the samples, regardless of vineyard and ageing. Esters represented the principal class of compounds with 40 aromatic volatile compounds identified, followed by terpenes (17 compounds), benzene (14), and alcohol (12). Esters were found mainly at bottling, but their concentration increased slightly at 30 months ageing.

**Discussion**

Winter wines composition resemble that of Syrah wines from traditional regions, such as Australia (Antalick et al., 2015), Italy (Condurso et al., 2016), California (Brillante et al., 2018), and South Africa (Hunter and Volschenk, 2018) confirming the great potential of this technique for Brazilian viticulture.

The anthocyanins identified in the Brazilian Syrah winter wines were 3-O-glucoside and acylated forms of malvidin, peonidin, petunidin, and delphinidin also described in Syrah wines from Spain (Blanco-Vega et al., 2014).

**Table 5** – Mass spectra of pyranoanthocyanins of Syrah winter wine of five regions at bottling and after 19 and 36 months of ageing in bottle.

| Compound                          | RT (min) | MS (m/z) | MS2 (m/z) |
|-----------------------------------|----------|----------|-----------|
| A-type vitisins (10-carboxy-pyranoanthocyanins) |          |          |           |
| 10-Carboxy-pymv-3-glc (vitisin A) | 18.3     | 561      | 399       |
| 10-Carboxy-pymv-3-acglc (ac-vitisin A) | 19.9     | 603      | 399       |
| 10-Carboxy-pymv-3-cmglc (cm-vitisin A) | 23.6     | 707      | 399       |
| 10-Carboxy-pypn-3-glc             | 16.9     | 531      | 369       |
| 10-Carboxy-pypn-3-cmglc           | 22.9     | 677      | 369       |
| 10-Carboxy-pypt-3-glc             | 14.4     | 547      | 385       |
| 10-Carboxy-pypd-3-gl           | 10.4     | 533      | 371       |
| B-type vitisins (pyranoanthocyanins) |          |          |           |
| pymv-3-glc (vitisin B)           | 19.4     | 517      | 355       |
| 10-Hydroxyphenyl-pyranoanthocyanins |          |          |           |
| 10-HP-pymv-3-acglc               | 34       | 609      | 447       |
| 10-HP-pymv-3-cmglc               | 36.5     | 651      | 447       |
| 10-HP-pymv-3-cmgly               | 38.6     | 755      | 447       |
| 10-DHP-pymv-3-glc                | 31.3     | 625      | 463       |
| 10-Flavanol-pyranoanthocyanins   |          |          |           |
| 10-(-)-Epicatechin-pypn-3-acgly  | 28.4     | 817      | 665, 613, 461 |
| 10-(+)-Catechin-pypn-3-acgly     | 30.5     | 817      | 665, 613, 461 |

Table 6 – Relative percentage of polymeric anthocyanins in winter wine of five regions at bottling and after 19 and 36 months of ageing in bottle.

| Compound | SB13 | TP13 | IND13 | SAA13 | SSP13 |
|----------|------|------|-------|-------|-------|
| 10-Carboxy-pypt-3-gly | 34.3 | 34.3 | 41.7 | 34.3 | 41.7 |
| 10-Carboxy-pypt-3-gly | 4.4 | 4.4 | 5.5 | 4.4 | 5.5 |
| 10-Carboxy-pypt-3-gly | 45.41 | 45.41 | 54.54 | 54.54 | 54.54 |
| 10-Carboxy-pypt-3-gly | 5.4 | 5.4 | 6.14 | 5.4 | 6.14 |
| 10-Carboxy-pypt-3-gly | 2.2 | 2.2 | 15.3 | 2.2 | 15.3 |
| 10-Carboxy-pypt-3-gly | 7.8 | 7.8 | 3.8 | 7.8 | 3.8 |
| TOTAL Carboxy- | 68 | 65 | 53 | 68 | 65 |
| 10-(-)-Epicatechin-pypt-3-acgly | 2.2 | 2.2 | 5 | 2.2 | 5 |
| 10-(+)-Catechin-pypt-3-acgly | 6.6 | 6.6 | 10 | 6.6 | 10 |
| TOTAL Flavanol- | 8 | 11 | 7.4 | 8 | 11 |
| 10-HP-pymv-3-gly | 17.17 | 17.17 | 31 | 17.17 | 17.17 |
| 10-HP-pymv-3-gly | 3.2 | 3.2 | 6 | 3.2 | 6 |
| 10-HP-pymv-3-gly | 3.3 | 3.3 | 8 | 3.3 | 8 |
| 10-DHP-pymv-3-gly | 4 | 4 | 8 | 4 | 8 |
| TOTAL Hydroxyphenyl- | 23 | 26 | 37 | 23 | 26 |

glc = glucoside; acglc = 6''-acetyl-glycoside; cmglc = (6-p-coumaroyl) glycoside; pymv = pyranomalvidin; pypn = pyranopeonidin; pypt = pyranopetunidin; pydp = pyranodelphinidin.

**Table 7**

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It is well known that a fraction of the anthocyanin pigments disappears rapidly few months after fermentation. These pigments may be either broken down by external factors (temperature, light, oxygen), precipitated in colloidal coloring matter, combined and condensed with tannins, and also forming stable anthocyanin derived pigments, named pyranoanthocyanins. These pigments are produced by reaction between anthocyanins and acetaldehyde, pyruvic acid or vinylphenols, by-products of yeast, in young wine and also from condensation between anthocyanin and/or flavan-3-ols in aged wine [He et al., 2012]. The elimination of anthocyanins leads to color loss and is detrimental to wine while pyranoanthocyanins production form more stable molecules responsible for color maintenance [Cheynier et al., 2006].

A reduction in total anthocyanins from 490 to 60 mg L\(^{-1}\) followed by an intense reduction in color intensity from bottling to 17 months aged was observed in Italian Syrah wines (Condurso et al., 2016). Color intensity in Brazilian Syrah winter wines, on the other hand, was not affected during ageing as well as total phenolic compounds and flavanols, which remained almost constant through ageing. Moreover, there was an increase in hydroxyphenyl pyranoanthocyanins and

![Figure 1 – Discriminant Analysis of aromatic volatile compounds of Syrah wines at bottling (ENG) and after ageing for 20 months (ENG20), 30 months (ENG30), or 42 months (ENG42).](image)

| Table 7 – Aromatic volatile compounds tentatively identified in the Syrah winter wine samples. |
|---------------------------------|--------------------------------------------------------------------------------------------------|
| **Compound**                    | **Code**   | **CAS** | **Kovats\(^{a}\)** | **Odor\(^{a}\)**                     |
| **Acids**                       |                                                      |                                                  |                                      |
| Hexanoic acid                   | BF         | 142-62-1 | 997                  | Rancid, sour, sharp, pungent, cheesy, fatty |
| n-Decanoic acid                 | BJ         | 334-48-5 | 1374                 | Unpleasant rancid, sour, fatty, soapy, soapy |
| Octanoic acid                   | BC         | 124-07-2 | 1194                 | Fruity-acid                          |
| **Alkanes**                     |                                                      |                                                  |                                      |
| Hexadecane                      | BW         | 544-76-3 | 1599                 | Mild wax                             |
| Tetradecane                     | CH         | 629-59-4 | 1400                 | Mild wax                             |
| **Alcohols**                    |                                                      |                                                  |                                      |
| 1-Decanol                       | AQ         | 112-30-1 | 1275                 | Sweet, fat-like                      |
| 1-Heptanol                      | AM         | 111-70-6 | 977                  | Woody, oily, fatty                   |
| 1-Hexanol                       | AL         | 111-27-3 | 877                  | Herbaceous, woody, sweet, green fruit, banana, flower, grass |
| 1-Hexanol, 2-ethyl              | X          | 104-76-7 | 1035                 | Oily, sweet, flowery, rose, green    |
| 1-Nonanol                       | BH         | 143-08-8 | 1178                 | Rose-orange, fat, floral, green, oil |
| 1-Octanol                       | AO         | 111-87-5 | 1076                 | Fresh, orange-rose, sweet, bitter almond, burnt matches, fat, floral |
| 1-Octen-3-ol                    | CT         | 3391-86-4 | 984              | Sweet, earthy, herbaceous lavender, rose, cucumber, fat, floral, mushroom |
| 2-Heptanol                      | BV         | 543-49-7 | 905                  | Brassy, herbaceous, fruity, green, citrus, earth, mushroom, oil |
| 2-Nonanol                       | CG         | 628-99-9 | 1102                 | Waxy, green, creamy, citrus, orange, cheese, fruity |
| Cis-3-Hexen-1-ol                | CK         | 928-96-1 | 865                  | Grassy-green, herbaceous, leafy      |
| 3-Nonen-1-ol, (Z)               | DB         | 10340-235 | 1158            | Fresh, waxy, green, melon, rind, tropical, mushroom |
| 3-Octanol                       | BY         | 589-98-0 | 998                  | Sweet, oily, nutty, herbaceous       |
| **Aldehydes**                   |                                                      |                                                  |                                      |
| Decanal                         | AR         | 112-31-2 | 1209                 | Sweet, waxy, flowery, citrus, fatty  |
| Furfural                        | N          | 98-01-1  | 841                  | Sweet, woody, almond, fragrant, baked, bread |
| Nonanal                         | BD         | 124-19-6 | 1105                 | Fatty, citrus-like                   |
| Benzeneacetaldheyde             | AV         | 122-78-1 | 1047                 | Harsh, green                         |
| **Benzenes**                    |                                                      |                                                  |                                      |
| Benzaldehyde                     | T          | 100-52-7 | 964                  | Bitter almond                        |

 Continue.
### Table 7 – Continuation.

| Compound | CAS Number | Measurement | Description |
|----------|------------|-------------|-------------|
| Benzene, 1, 2-dimethoxy | G 91-16-7 | 1151 | Sweet, creamy, vanilla, phenolic, musty |
| Benzeneacetic acid, ethyl ester | U 101-97-3 | 1247 | Sweet, floral, honey, rose, balsam, cocoa |
| Benzoic acid | BI 271-89-6 | 995 | Sweet |
| Ethyl salicylate | AT 118-61-6 | 1271 | Sweet, wintergreen, mint, floral, spicy, balsam |
| Ethyl benzate | I 93-89-0 | 1173 | Fruity, dry, must, sweet, wintergreen |
| Benzyl alcohol | S 100-51-6 | 1036 | Fruity, pungent |
| Benzyl nitrile | BE 140-29-4 | 1141 | Bitter almonds, spicy, floral |
| Naphthalene | H 91-20-3 | 1179 | Pungent, resinous |
| 1, 2-Dihydro-1, 1, 6-trimethylnaphthalene | DK 30364-38-6 | 1351 | Licorice (wine off-flavour on ageing) |
| α-xylene | J 95-47-6 | 871 | Geranium |
| Phenylethyl alcohol | A 60-12-8 | 1115 | Flowery-rose, bitter, fruity-peach |
| p-xylene | AF 106-42-3 | 874 | Sweet |
| Styrene | R 100-42-5 | 892 | Sweet, balsam, floral, plastic |

#### Ketones
- 2-nonenone | CJ 821-55-6 | 1094 | Fresh, sweet, green, weedy, earthy, herbal |
- (E)-β-damascenone | DH 23726-93-4 | 1385 | Apple, rose, honey, Tobacco, sweet |

#### Alkyl sulfide
- 1-propanol, 3-(methylthio) | BS 505-10-2 | 983 | Sulphurous, onion, sweet, soup, vegetable |

#### Ester
- 1-butanol, 2-methyl, acetate | CB 624-41-9 | 886 | Over ripe fruit, sweet banana, juicy, fruit |
- 1-butanol, 3-methyl, acetate | BA 123-92-2 | 884 | Fruity – banana, pear, apple, glue |
- Ethyl crotonate | CW 6776-19-8 | 854 | Found in alcoholic beverages. Component of strawberry aroma, guava fruit, pineapple, yellow passion fruit |
- 2-ethylhexyl salicylate | AS 118-60-5 | 1805 | Mild, orchid, sweet, balsam |
- 2-hexenoic acid, ethyl ester | CL 1552-67-6 | 1051 | Fruity – pineapple, apple, green |
- Phenethyl acetate | W 103-14-8 | 1259 | Floral, rose, sweet, honey, fruity, tropical |
- Acetic acid, hexyl ester | BG 123-12-5 | 1019 | Fruity – apple, cherry, pear |
- Octyl acetate | AP 142-92-7 | 1216 | Green, earthy, mushroom, herbal, waxy |
- Diethyl succinate | AX 123-25-1 | 1188 | Mild, fruity, cooked, apple, ylang |
- Ethyl 2-methyl butyrate | CZ 7452-79-1 | 860 | Sharp, sweet, green, apple, fruity |
- Ethyl isovalerate | AH 108-64-5 | 863 | Fruity, sweet, apple, pineapple, tutti frutti |
- Isoamyl butyrate | AB 106-27-4 | 1062 | Fruity, green, apricot, pear, banana |
- Ethyl butyrate | Y 105-54-4 | 808 | Fruity, juicy, pineapple, cognac |
- Ethyl decanoate | AI 110-38-3 | 1399 | Sweet, waxy, fruity, apple, grape, oily, brandy |
- Methyl decanoate | AJ 110-42-5 | 1327 | Oily, wine, fruity, floral |
- Propyl decanoate | DL 30673-60-0 | 1492 | Waxy, fruity, fatty, green, vegetable, woody, oily |
- Ethyl laurate | AE 106-32-1 | 1595 | Sweet, waxy, floral, soapy, clean |
- Methyl laurate | AN 111-82-0 | 1526 | Waxy, soapy, creamy, coconut, mushroom |
- Ethyl 9-decanoate | DU 67233-91-4 | 1390 | Fruity, fatty |
- Ethyl heptanoate | AC 106-30-9 | 1100 | Fruity, pineapple, cognac, rum, wine |
- Ethyl palmitate | CF 628-97-7 | 1917 | Mild, waxy, fruity, creamy, milky, balsam |
- Hexanoic acid, 2-methylbutyl ester | CS 2601-130-0 | 1257 | Ethereal |
- Isobutyl hexanoate | Z 105-79-3 | 1156 | Sweet, fruity, pineapple, green, peach, tropical |
- Hexanoic acid, ethyl ester | AZ 123-66-0 | 1003 | Fruity – pineapple, banana |
- Hexanoic acid, methyl ester | AG 106-70-7 | 933 | Ether-like |
- Hexanoic acid, propyl ester | CD 626-77-7 | 1098 | Sweet, fruity, juicy, pineapple, green, tropical |
- Isoamyl lactate | DF 19329-89-6 | 1073 | Fruity, creamy, nutty |
- Isoeugenyl hexanoate | CF 2198-61-0 | 1254 | Fruity, banana, apple, pineapple, green |
- n-caprylic acid isobutyl ester | CU 5461-06-3 | 1351 | Fruity, green, oily, floral |
- Nonanoic acid, ethyl ester | AY 123-92-9 | 1298 | Fruity, rose, waxy, rum, wine, natural, tropical |
- Nonanoic acid, methyl ester | CM 1731-82-4 | 1229 | Sweet, fruity, pear, waxy, tropical, wine |
- Isoamyl octanoate | CO 2035-99-6 | 1449 | Sweet, oily, fruity, green, soapy, pineapple, coconut |
- Octanolic acid, ethyl ester | AD 106-32-1 | 1204 | Fruity, wine, waxy, sweet, apricot, banana, brandy, pear |
- Octanolic acid, methyl ester | AK 111-11-5 | 1129 | Winy, fruity – orange, oily |
- Isoamyl decanoate | CR 2306-91-4 | 1649 | Waxy, banana, fruity, sweet, cognac, green |

Continue.
flavan-3-ol pyranoanthocyanins in aged wine, pigments probably responsible for the red color of wine.

The polymerized pigment index, applied to define the percentage of free and combined anthocyanins producing color in wine (Harbertson and Spayd, 2006), increased from 54 % at bottling to 80 % after 42 months of ageing, corroborating the contribution of copigmentation reactions to preserve color of winter wines.

The literature does not report aroma compounds in Syrah winter wines. According to Con durso et al. (2016), tipicity and quality of the wine are closely related to volatile aroma compounds from grape and those formed during the vinification process. Syrah wine has been described with spicy, dark fruit, or berry like flavors depending on the terroir. Therefore, studies report different volatile data. For example, rotundone, the sesquiterpene compound responsible for the peppery character of Syrah wines, requires an optimized procedure of extraction and therefore is not always found in Syrah wines samples (Siebert et al., 2008; Cincotta et al., 2015; Condurso et al., 2016).

Freshly fermented wines from vineyards in southeastern Brazil were combined in the left part of the PCA plot while aged wines were displaced to the right part, with positive scores (Figure 1). Loscos et
al. (2010) also observed such tendency. The second component reflects vineyard site importance, which will be discussed in another study.

In an attempt to differentiate wine varieties by their volatile compounds profile, Fabani et al. (2013) selected four ester compounds ethyl caprylate (106-32-1), diethyl succinate (123-25-1), ethyl caproate (123-66-0), and isopentyl acetate (123-92-2), one benzene compound, benzyl alcohol (100-51-6) and one alcohol, 1-hexanol (111-27-3) as representative volatile compounds in wines. All these compounds were also found in Syrah winter wines. As mentioned by these authors, ethyl caprylate was also found through wine ageing, but mainly at bottling and in winter wines aged 20 months.

Volatile esters play a significant role in wine aroma, as they are associated to ‘fruity’ and ‘floral’ flavors. Numerous esters compounds were identified in wine samples from thinned and control plants of Syrah vineyards located in Palermo, Italy (Condurso et al., 2016). The most represented esters identified by these authors, ethyl hexanoate (CAS 123-66-0), ethyl octanoate (CAS 106-32-1), and ethyl decanoate (CAS 110-38-3) were also present in Syrah winter wines from southeastern Brazil. However, those with the most contrasting patterns among ageing were 1-butanol, 2-methyl-acetate [624-41-9], 2-hexenoic acid, ethyl ester [1552-67-6], acetic acid, hexyl ester [142-92-7], ethyl heptanoate [106-30-9], hexanoic acid, propyl ester [626-77-7], n-caprylic acid isobutyl ester [5461-06-3], isoamyl decanoate [2306-91-4] identified as fruity aroma compounds, and hexanoic acid, methylbutyl ester [2601-13-0] and hexanoic acid, methyl ester [106-70-7] with ether-like notes.

Diethyl succinate [123-25-1], an ester mentioned as a chemical marker of wine ageing [Fabani et al., 2013] was found after 30 and 42 months ageing, mainly in winter wines aged for 30 months. Isopentyl acetate [123-92-2] another ester, responsible for the banana bouquet, was present at bottling and after 30 months of ageing. Fabani et al. (2013) reported a tendency to find lower levels with ageing in Syrah wines. As our results are qualitatively, we were not able to measure its content in the samples; however, it was found from bottling throughout ageing, with lower amounts after 42 months in the bottle.

Furfural [98-01-1], an aldehyde responsible for almond and caramel aroma, was found in Syrah winter wines over 30 months of age. This volatile compound is formed from carbohydrates during wine ageing; however, it can also be generated from hemicellulosics of the barrels [Condurso et al., 2016].

Among benzene class, benzyl alcohol (100-51-6) and ethyl benzoate (93-89-0) associated to ‘flowery’ and ‘sweet’ aromas were also found mainly at 30 months of ageing as well as 1, 2-Dihydro-1, 1, 6-trimethyl-naphthalene [30364-38-6], a benzene compound known as off-flavor of ageing. Benzene levels decreased from bottle to 20 months ageing and then increased at 30 months with great loss at 42 months.

The presence of leafy and herbaceous aromas from C6 compounds such as cis-3-hexen-1-ol [928-96-1] released from the enzymatic degradation of lipids from grape cell membrane [Brillante et al., 2018] is related to fresh grape processing. Indeed this compound was found mainly at bottling in Syrah winter wines. Volatile compounds belonging to alcohol, alkyl sulfide, and acids classes were found mainly in young wines.

The volatile phenols associated with smoke, spice, and phenolic aromas [Loscos et al., 2010], guaiacol [90-05-1], and 4-ethylphenol [123-07-9] increased their concentration during ageing.

Terpenes are synthesized during grape maturation. They have pleasant flavor perceived even at low concentrations due to its very low olfactory threshold. The fermentation process has little contribution on terpene levels and therefore their content depends on vineyard management [Condurso et al., 2016]. Syrah winter wines showed an increase in monoterpenes until 30 months ageing with a sharp decrease at 42 months, as observed by Loscos et al. (2010) under accelerated ageing process. Citronellol (106-22-9), the rose-like aroma, was found at bottling while D-limonene [5989-27-5] and p-cymene [99-87-6], both contributing to fresh, citrus-like aroma, increased at 30 months ageing. Pepper and peppermint aromas of terpinen-4-ol [562-74-3] and levomenthol [5989-27-5] were found mainly at bottling and at 30 months of ageing, while l-menthone [14073-97-3] content was higher in wines for 30 months aged.

The monoterpenes linalool [78-70-6] and the ketone β-damascenone [23726-93-4] characterized as ‘floral’ and ‘fruity’ aromas were also present in winter wines, mainly at 30 months of ageing. Norisoprenoids, such as β-damascenone, are formed by an enzymatic reaction of carotenoids that are further subjected to catalytic reactions during wine ageing [Brillante et al., 2018].

Wine health benefits have been attributed to antioxidant, anti-inflammatory, anticarcinogenic, and antibacterial properties of sesquiterpenes [Siebert et al., 2008]. Sesquiterpenes α-Murolene [10208-80-7] and α-calacorene [21391-99-1], which contributes to woody, floral, and herbal aromas, were found mainly after 30 months of ageing.

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