Chemical composition and sensory profile of Syrah wines from semiarid tropical Brazil – Rootstock and harvest season effects

Juliane Barreto de Oliveira\textsuperscript{a,}\textsuperscript{*}, Ricardo Egipto\textsuperscript{a,b}, Olga Laureano\textsuperscript{c}, Rogério de Castro\textsuperscript{a}, Giuliano Elias Pereira\textsuperscript{a}, Jorge Manuel Ricardo-da-Silva\textsuperscript{a}

\textsuperscript{a} LEAP. Linking Landscape, Environment, Agriculture and Food. Instituto Superior de Agronomia, Universidade de Lisboa, Tapada da Ajuda, 1349-017, Lisbon, Portugal
\textsuperscript{b} INIAV, I.P., Pólo de Dois Portos, Quinta da Almoína, 2565-191, Dois Portos, Portugal
\textsuperscript{c} Brazilian Agricultural Research Corporation - Embrapa Grape \& Wine, Rua Livramento 515, CP 130, 95.701-008, Bento Gonçalves-RS, Brazil

ABSTRACT

This study aims to characterise the chemical compositions and sensorial profiles of wines made with Syrah grapes over two harvest seasons (first and second semester), over in different calendar years, from vines on two different rootstocks (1103P and IAC 313). Wine chemical composition and sensory profile were influenced by both rootstock and harvest season. Syrah wines on IAC 313 were favoured with higher concentrations of, petunidin 3-O-acetylglucoside (3.7 mg/L), malvidin 3-O-acetylglicoside (17.8 mg/L), malvidin 3-O-coumarylglicoside (4.4 mg/L), petunidin 3-O-coumarylglicoside (2.0 mg/L), peonidin 3-O-coumarylglicoside (1.4 mg/L), monomeric flavanols (23.6 mg/L), oligomeric tannins (183.0 mg/L), total condensed tannins (1037.7 mg/L), dimer B1 (9.8 mg/L), B4 (5.0 mg/L), trimer C1 (3.1 mg/L) and calcium (80 mg/L). Syrah wines on 1103P had higher concentrations of total anthocyanins (375.6 mg/L), catechin (8.6 mg/L), epicatechin (12.6 mg/L), dimer B2 (21.0 mg/L), B1 3-O-gallate (1.8 mg/L), B2 3'-O-gallate (6.0 mg/L) and total flavanols (53.4 mg/L). The sensory profiles of the Syrah wines were influenced by rootstock followed by, mainly in relation to aromatic attributes. Syrah wines on IAC 313 were scored more highly by the tasters.

ARTICLE INFO

Keywords:
Phenolic compounds
Red wines
\textit{Vitis vinifera} L.
Sensory
Tropical region

1. Introduction

Wine quality is determined as a combination of a large number of factors. Among these, are a range of ‘vineyard’ factors which affect the physicochemical composition of the grapes and thus of the resulting wines. These vineyard factors include: the soil, the weather, canopy management, rootstock, irrigation management (Xu et al., 2015). A number of studies in different regions have compared the effects of different rootstocks on wine quality. These identified significant rootstock effects on wine composition: anthocyanin profile and potassium concentration in Washington (Harbertson & Keller, 2012), volatile compounds and free amino acids in California (Ough, Cook, & Lider, 1968), total polyphenols in Montenegro (Maraš, Kodžulović, Rašičević, Gazivoda, & Perišić, 2016) and anthocyanins and flavanols in Australia and Italy (Mantilla et al., 2017; Suriano et al., 2016).

Traditional winegrowing regions range from warm temperate to cool temperate and these allow only a single crop each year. However, viticulture is also practiced in some tropical regions where seasonal minimum temperatures are not low enough to induce vine dormancy. Here, the vines grow continuously and, with the appropriate interventions, are able to produce two or more harvests per year on the same vines.

The São Francisco River Valley is a tropical, semiarid region of Brazil. Here, viticulture normally extends over two semesters each calendar year – from approximately May to August (semester 1) and from approximately October to December (semester 2). Depending on which season, the wines vary greatly in composition, quality and typicality, mainly due to intra-annual weather variability (Pereira, Araújo, Santos, Vanderlinde, & Lima, 2011). The region is located between parallels 8 and 10’S and is characterised by an annual average temperature of 26.5 °C and about 3000 h of sunshine per year (Pereira et al., 2018). The cultivar \textit{Vitis vinifera} L. Syrah is the main red grape for wine production in this region of northeast Brazil.

The “sub-middle” of the São Francisco River Valley is a very important viticultural region. Hence, it is important to understand the influences of the various viticultural techniques used in this tropical region on the quality of the resulting grapes and wines. The aim of this study was to characterise the chemical compositions and sensory profiles of wines made with cv. Syrah (\textit{Vitis vinifera} L.) during four growth periods - two in the first semester and the others in the second semester.
The wines were made with grapes from vines grafted on one or other of two rootstocks IAC 313 and 1103P. Here, for the first time, it was used an analytical approach to separation and quantify, understand how different kinds of condensed tannins and other chemical components in the wines were affected by the two growth harvest seasons and by the two rootstocks, in this tropical viticulture conditions.

2. Material and methods

2.1. Chemicals and standards

Analytical grade methanol, diethyl ether, ethyl acetate, acetic acid, acetonitrile, sodium metabisulphuric acid, were of the Sigma-Aldrich (St. Louis, USA). Also used were taric acid, potassium hydroxide, methanol, bovine albumin, and sulphuric acid, were of the Sigma-Aldrich (St. Louis, USA). Also used were purified Polyamid DC 6 also referred as TLC 6 (Macherey-Nagel, Düren, Germany).

2.2. Characterisation of vineyards and grapes

The work was carried out in experimental vineyards belonging to a partner winery, Santa Maria/Global wines, located in the municipality of Lagoa Grande, Pernambuco, Brazil, at latitude 8′ 02″S and longitude 40′ 11″W, at an altitude of 350 m. Most soils are podzols. The Syrah grapevines were grafted onto IAC 313 or Paunsen 1103P rootstocks, managed as a vertical trellis, vine spacing was 3.0 × 1.0 m, with drip irrigated with the same volume of water applied to all the treatments of rootstock in the same day. The optimal harvest time was determined by the company on the basis of °Brix, total acidity and pH. The composition of the grapes at harvest is shown in (Table 2, supplements).

Approximately 40 kg of grapes was collected from each of a number of previously, randomly-selected vines. The evaluation of grapes was carried out over four harvests, the first harvest was in December 2014 (semester 2), the second in July 2016 (semester 1), the third in January 2016 (semester 2) and the fourth in July 2017 (semester 1).

2.3. Vinification of monovarietal wines

Wines were made using traditional vinification methods but at experimental scale with each grape sample being of 40 kg. Stems were removed using semi-automatic equipment (Model DH150-DA, Ricefer, Garibaldi, Brazil), then 50 mg/L of sulphur dioxide and 20 g/L of yeast (Saccharomyces cerevisiae, var. bayanus, Ever intec, Venezia, Italy) were added for alcoholic fermentation which occurred at temperatures between 22 and 25 °C, the remontage was carried out once a day in rack and return mode. Maceration time (uniform across all treatments) was for 7 days to maintain uniform the extraction of phenolics. The end of alcoholic fermentation was identified by the stability of the values of density and alcohol content. Malolactic fermentation was made without addition of lactic acid bacteria, using only the native species, with temperatures varying between 16 and 18 °C, the end point was identified using paper chromatography (OIV, 2014). Tartaric stabilisation in the cold (0–5 °C) was for 30 days, sulphur dioxide was corrected and wines were bottled with nitrogen and stored in the cellar at 16 ± 2 °C.

2.4. Physical-chemical characterisation of wines

Wines were analysed after six months for the classic parameters, besides the potassium and calcium. The methodology was based on the International Organisation of Vine and Wine (OIV, 2014).

Colorimetric parameters were analysed as follows: total anthocyanins (Ribéreau-Gayon & Stonestreet, 1965); coloured anthocyanin; total and polymeric pigments (Somers & Evans, 1977); total phenols (Ribéreau-Gayon, 1970); flavonoids and non-flavonoids (Kramling & Singleton, 1969); colour co-pigmentation (Boulton, 2001); colour intensity and tonality (OIV, 2014); tanning power (de Freitas & Mateus, 2001). Separation and quantification of monomeric anthocyanins were made directly in a filtered wine sample, as described by Roggero, Coen, and Raggonet (1986), using a HPLC (PerkinElmer, San Francisco, USA), consisting for a pump Series 200 and detector LC95 Uv/Visible, a column C18 (250 mm × 4 mm), with reverse phase of 5 μm of compaction, protected by a pre-column of the same material (LichroCart, Merck, Darmstadt, Germany). The solvents were: A (40 mL formic acid and 60 mL bi-distilled water), B (acetonitrile PA) and C (distilled water). Methanol:water (50:50 mL/mL) was used to wash the column after the analyses. The initial conditions used were: 25% A, 6% B and 69% C for 15 min, followed by a 25% linear gradient of A, 25.5% B and 49.5% C for 70 min. Finishing with 20 min of 25% A 25.5% B and 49.5% C. The flow was 0.7 mL/min, using a detector with wavelength at 520 nm. Both the samples and the solvents were filtered under the same conditions. The volume injected was 20 μL and the analyses were carried out in triplicate. Quantification of fourteen individual anthocyanin molecules was based in a standard curve using malvidin 3-O-glucoside as the internal standard. Fractionation of low molecular weight flavanoids was by polyamide column chromatography and further quantification was by HPLC following the method of Ricardo-da-Silva, Rosec, Bourzeix, and Heredia (1990). Identification of compounds followed the method of Ricardo-da-Silva, Rigaud, Cheynier, Cheminat, and Moutounet (1991) and Rigaud, Pérez-Izarbe, Ricardo-da-Silva, and Cheynier (1991) and was confirmed using the method of Monagas, Gómez-Cordovés, Bartholomé, Laureano, and Ricardo-da-Silva (2003). The HPLC equipment comprised a UV–Vis detector Waters 2487 (Milford, USA) and a pump Merck L-7100 (Darmstadt, Germany). The separation was carried out on a Lichrosphere C18 reverse phase column (Merck, Darmstadt, Germany) 250 mm × 4.6 mm × 5 μm, at ambient temperature. For monomeric flavan-3-ols, a gradient consisting of solvent A (water: acetic acid, 97:5.2:5.2, mL/mL) and solvent B (acetonitrile/solvent A, 80:20 mL/mL) was applied at a flow rate of 0.9 mL/min as: 7–25% B linear from 0 to 31 min, followed by washing (methanol/water, 50:50 mL/mL) 32–50 min and the rebalancing of the column from 51 to 65 min under the initial gradient conditions. For oligomeric procyani- dins, a solvent gradient A (distilled water) and solvent B (water/acetic acid, 90:10 mL/mL) was applied at a flow rate of 1.0 mL/min as: 10–70% linear B 0–45 min, 70–90%. Quantification of monomeric flavan-3-ol and oligomeric procyani- dins were based on standard curves obtained with (+) catechin for the monomers and B2 for the other compounds.

Separation of proanthocyanidins was carried out using Sep-Pak C18 cartridges ( Waters, Milford, USA) and quantification of the fractions obtained employed the vanillin assay following the method of Sun, Leandro, Ricardo-da-Silva, and Spranger (1998). The wines were dealcoholized by rotary evaporation (BÜCHI Labortechnik, Flawil, Switzerland) at < 30 °C and adjusted to pH 7.0 with phosphate buffer (pH 7.0). This sample was then passed through the two preconditioned neutral Sep-Pak cartridges connected in series: the superior (tC18 Sep-Pak) and the inferior (C18 Sep-Pak). Elution was made with 10 mL of H2O adjusted to pH 7.0 to eliminate phenolic acids, then the carbohydrates were dried with Na2SO4, elutions were carried out first with 25 mL of ethyl acetate to elute catechins and oligomeric procyani- dins, accompanied by some other small phenolic molecules (fractions F I and II), and then with 10 mL of methanol to elute the polymeric procyani- dins and anthocyanins (FIII). For the separation of catechins from...
oligomeric proanthocyanidins (FI + II) was evaporated to dryness under vacuum at 25 °C, dissolved in distilled water, and redeposited onto the same connected cartridges preconditioned with distilled water. After the cartridges were dried with N2, separation of catechins and oligomeric proanthocyanidins was realized by sequential elution with 25 mL of diethyl ether (FI) and then with 10 mL of methanol (FII).

2.5. Characterisation of wine sensory profile

Sensory analysis was carried out by a panel of twelve experienced wine tasters. These evaluated the visual, olfactory, and taste characteristics with Quantitative Descriptive Analysis (QDA), recording 16 attributes: four visual, five aromatic and seven taste. All parameters were quantified on a scale with unstructured intensity of 10 points, with minimum anchorage on the left and maximum on the right. The test room comprised individual, white, illuminated booths. Samples were served individually, coded in tasting glasses (ISO model) containing 50 mL and at a temperature of 18 ± 2 °C (considered ideal for tasting red wines).

2.6. Statistical analyses

All chemical analyses were in triplicate. Analysis of variance (ANOVA) was used to detect significant differences between rootstocks and harvest seasons. Differences between treatments were tested by a multiple means comparison test (Tukey's HSD) (P = 0.05). Principal component analysis (PCA) was used with the data for anthocyanins, fractionation of condensed tannins (flavanols) and small flavanols to evaluate the effects of rootstocks and harvest seasons. Analyses were carried out using the STATISTIX 9.0 analytical software (Florida, USA).

3. Results and discussion

3.1. Classic analysis

Results of the analyses of the classic quality parameters of tropical red wines are presented in Table 1. pH values ranged from 3.84 to 4.02 in the first semester on IAC 313 and from 3.95 to 3.98 on 1103P. In the second semester, the values were 3.91 on IAC 313 and 4.04 to 4.16 on 1103P. There was no significant effect of rootstock or semester on wine pH. According to Pereira et al. (2018) pH values between 3.60 and 4.50 are observed in the region for wines of different varieties, which can be attributed to excessive use of potassium fertilisers, or to naturally high levels of soil potassium in the region.

There is a tendency for higher pH in the second semester grapes.

This may be related to the climatic conditions in this semester which falls over the summer season (higher temperatures, greater insolation, low thermal amplitude day/night), leading to increased acid degradation in the grapes and consequently in the wines.

Total acidity ranged from 4.3 to 5.1 g/L on IAC313 and 4.6–5.7 g/L on 1103P. Higher total acids on 1103P may be related to vigour on this rootstock. This fits with wines from the region of Minas Gerais, Brazil (Dias et al., 2017) where more vigorous rootstocks induced higher total acidity in Syrah wines.

Alcohol content ranged from 11 to 12.9% v/v in the study wines, being lower than that found for traditional regions, and is related to two main factors: first, during the study years (2014–2017), Brazilian legislation required a alcohol content of 8.5–14% v/v in wines made with Vitis vinifera L. (Brazil, 2014). Recently, in 2018, legislation was amended, allowing content between 14.1 and 16% v/v (Brazil, 2018). Another factor is that the grapes from this area of the vineyard were used for production of young wines with low alcohol content and/or for blends with wines from other lots of the Company. In addition, in tropical conditions, companies seek to harvest grapes and produce wines with different alcoholic potentials and total acidity, then mix to correct and reduce the pH, which are generally high. Thus, they mix with more or less acidic wines, more or less alcoholic, to keep the pH between 3.6 and 3.8, naturally, without adding tartaric acid, which is common and allowed by Brazilian and worldwide legislation (OIV, 2014).

3.2. Potassium and calcium

Potassium values are considered high in the wines made from grapes of the two rootstocks (Table 1). The wine potassium content on IAC 313 ranged from 1700 to 2423 mg/L and on 1103P it ranged from 1960 to 2068 mg/L. When evaluating red wines from several regions of Brazil, Miele, Rizzon and Zanus (2010) also found high levels of potassium in their wine samples from the São Francisco Valley. There is a tendency for higher potassium concentrations in the second harvest season. This is possibly related to higher temperatures during both day and night, which increases photosynthesis, growth, enzymatic activity and vine water usage. According to some authors, potassium regulates these processes (Silva et al., 2014).

The highest calcium levels were in wines from grapes on IAC 313. In semesters 1 and 2, calcium concentrations were 80 mg/L and 62 mg/L, respectively. The rootstock influenced calcium concentration of Syrah semiarid tropical wines. Rizzon and Miele (2017) when evaluated the effect of fifteen rootstocks on the mineral composition of Cabernet sauvignon wines, also verified a significant effect on the calcium concentrations.
Higher wine calcium on IAC 313 may be related to higher soil calcium uptake rates by this rootstock. Other authors have noted calcium accumulation can be related to scion and also to rootstock (Wooldridge, Louw, & Conradie, 2010). The highest wine calcium concentrations were found in the first semester. This may be due to greater use of phytosanitary treatments against fungal diseases in the first semester when temperatures are around 27°C and rainfall is greater. A factor that may relate to the higher calcium concentration in wines in the second semester is the higher pH that favours calcium precipitation (Mckinnon, Scollary, Solomon, & Williams, 1995).

3.3. Global phenolic compounds

Table 2, expressed in gallic acid, wine from vineyards on IAC 313 presented higher concentrations of phenolics. Total phenols were of 2313.4 mg/L; flavonoids 2142.2 mg/L and non-flavonoid phenols 1840.4 mg/L. Total phenols were lower than reported by Gris et al. (2013) for Syrah wines (1103P) in the Santa Catarina region, where they found 2732.2 mg/L and 2790.5 mg/L in two consecutive years. Variation in the overall levels of phenolic concentration was significant, clearly the rootstock is not the only source of such variation. The amounts and types of the family of flavonoids (the largest group of total phenols) and non-flavonoid are also involved in reactions during vitification and wine aging (Balga, Leskó, Ladányi, & Klály, 2014; Fang et al., 2008), which may be related to lower concentrations of these compounds in the studied wines when compared to other wines of the same variety.

The effect of the semester was more significant for the non-flavonoids, with a trend towards higher concentrations in the second semester. Concentrations ranged from 205.8 to 375.6 mg/L both expressed in malvidin 3-O-glucoside. These concentrations were lower than those reported by Harbertson and Keller (2012) and Condouris et al. (2016) for Syrah wines in regions of traditional viticulture. The coloured anthocyanin concentrations ranged from 19.3 to 41.5 mg/L of malvidin 3-glucoside in wines 1103P. These compounds include phenolic, benzoic and cinnamic acids and also other phenolic derivatives such as stilbenes. The higher concentrations in the second harvest season may be related to the higher temperatures during this period (Table 1, supplementary material), that promote greater synthesis of hydroxybenzoic acids and stilbene as a wine response to climate stress. Increases in these compounds as a defence response to stress have also been noted by Teixeira, Eiras-Dias, Castellarin, and Gerós (2013).

3.4. Colour, anthocyanins and other pigments

Concentrations of total and coloured anthocyanins in the wine were higher onto 1103P (Table 2) but with a greater influence of semester than of rootstock. The concentrations of total anthocyanins in Syrah wines on IAC 313 varied from 190.8 to 316.5 mg/L while on 1103P the range was from 205.8 to 375.6 mg/L both expressed in malvidin 3-O-glucoside. These concentrations were lower than those reported by Harbertson and Keller (2012) and Condouris et al. (2016) for Syrah wines in regions of traditional viticulture. The coloured anthocyanin concentrations ranged from 19.3 to 41.5 mg/L of malvidin 3-O-glucoside and from 19.5 to 46.4 mg/L of malvidin 3-O-glucoside in wines from plants on IAC 313 and 1103P, respectively.

The polymerised pigments were higher in the second harvest season, possibly due to a higher concentration of monomeric anthocyanins and proanthocyanidins. A reaction between anthocyanins and tannins extracted during fermentation may contribute to the formation of polymeric pigments (Bindon, Kassara, Hayasaka, & Schulkin, 2014; Es-Saffi, Fulcrand, Cheynier, & Moutounet, 1999).

Percentage of co-pigmentation (Table 2) varied between rootstocks and semesters. Wines from IAC 313 showed higher co-pigmentation in the second semester, while those from IAC 310 were higher in the first semester. This may be related to a greater synthesis of cofactors (phenolic acids, flavonoids, flavones, amino acids and anthocyanins) in the grapes from each rootstock and in the different semesters but further investigation is required.

Concentrations of anthocyanins varied between rootstocks and harvest seasons, with no significant differences in total wine pigments, polymerised pigments, hue or colour intensity (Table 2). For wines on self-rooted Syrah vines and on Syrah vines grafted on 110 Richter, Mantilla et al. (2017) found higher concentrations of anthocyanins and pigments on the grafted vines. Dias et al. (2017) evaluated Syrah wines on different rootstocks and found wines from vines with the more vigorous rootstocks had slightly improved phenolic composition.

3.5. Monomeric anthocyanins

Among the fourteen anthocyanins measured (supplementary material – Table 3), five were significantly higher in wines from IAC 313: petunidin 3-O-acetylglucoside (3.7 mg/L), malvidin 3-O-acetylglucoside (17.8 mg/L), pelargonidin 3-O-coumarylglucoside (1.4 mg/L), petunidin 3-O-coumarylglucoside (2.0 mg/L) and malvidin 3-O-
The second semester of 2014, wines from grapes onto 1103P had higher levels of cyanidin 3-O-glucoside (2.2 mg/L) and cyanidin 3-O-acetylglucoside (2.6 mg/L). The highest concentrations of malvidin 3-O-glucoside in the second semester of 2016 were 36.1 mg/L (IAC 313) and 34.4 mg/L (1103P), these concentrations were lower than the reported by other authors for Syrah wines from traditional regions, for example, Lingua, Fabani, Wunderlin, and Baroni (2016) detected 87.4 mg/L for Argentine wines and Gil-Muñoz Bautista-Ortíz, Ruiz-García, Fernández-Fernández, and Gómez-Plaza (2017) found 448.2 mg/L in Spanish wines. There were no significant differences between samples for the other anthocyanins. Here, the effects of rootstock on anthocyanin composition were similar, variable and non-significant, in line with the findings of Harbertson and Keller (2012) for Syrah wines, five rootstocks (5C, 140 Ru, 1103P, 3309C, and 101CU) on Syrah wine composition in the Yakima Valley (USA).

Total monomeric anthocyanins ranged from 37.3 to 71.9 mg/L (IAC 313) and 41.1–71.3 mg/L (1103P). There was a trend for higher concentrations in the second harvest season, for wine samples (1103P). In general, the classes, proportions and quantities of anthocyanins in red grapes depend on cultivar, weather and viticultural practice, rather than on rootstock (Cortell, Halbleib, Gallagher, Righetti, & Kennedy, 2007; Revilla, Garcia-Beneytez, Cabello, Martin-Ortega, & Ryan, 2001).

### 3.6 Condensed tannins

Concentrations of monomeric, oligomeric and polymeric tannins are shown in Table 3. These varied between semesters and rootstocks. It is reported that condensed tannin concentration of the wine depends on: the composition and amounts of tannins in the berries at harvest (Kennedy, Matthews, & Waterhouse, 2000), on extraction processes and must composition (Sacchi, Bisson, & Adams, 2005) and on interactions with polysaccharides (from grape skins) and mannoproteins and other polysaccharides from yeast (Bindon & Kennedy, 2011; Hanlin; Hrmova, Harbertson & Downey, 2010; Rodrigues, Ricardo-da-silva, Lucas, & Laureano, 2012).

Monomeric flavanol contents of wines varied from 7.4 to 23.6 mg/L.

<table>
<thead>
<tr>
<th>Variety vs. Rootstock</th>
<th>Syrah – IAC 313</th>
<th>Syrah – 1103P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Harvest season</td>
<td>I semester</td>
<td>I semester</td>
</tr>
</tbody>
</table>

#### Condensed tannins

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Monomeric</td>
<td>20.2±1</td>
<td>23.6±0</td>
<td>16.7±4</td>
<td>4.5</td>
<td>7.4±0</td>
<td>22.4±0</td>
<td>16.3±4</td>
<td>0.4</td>
<td>11.7±4</td>
</tr>
<tr>
<td>Oligomeric</td>
<td>35.8±5</td>
<td>25</td>
<td>183.0±5</td>
<td>5.9</td>
<td>45.8±1</td>
<td>41.1±1</td>
<td>52.2±4</td>
<td>14.4±1</td>
<td>87.3±1</td>
</tr>
<tr>
<td>Polymeric</td>
<td>387.8±5</td>
<td>2.3</td>
<td>787.1±3</td>
<td>3.1</td>
<td>579.3±1</td>
<td>531.5±1</td>
<td>543.2±7</td>
<td>7.7</td>
<td>665.4±1</td>
</tr>
<tr>
<td>Total tannins</td>
<td>443.5±3</td>
<td>3.1</td>
<td>1037.7±6</td>
<td>7.7</td>
<td>641.8±8</td>
<td>580.0±3.2</td>
<td>617.8±7.9</td>
<td>7.9</td>
<td>824.2±1.5</td>
</tr>
</tbody>
</table>

Means followed by the same letter in the lines did not differ by Tukey test at 5% (p<0.05). Legend: concentrations in mg/L, I (< 0.05). Findings agree with Oliveira et al. (2018) in the same region, for wines cv. ‘Touriga Nacional’. It would seem these differences are related first to the extraction of condensed tannins and then to their subsequent re-arrangements during and after vinification and during aging. The value of total tannins in wines from IAC 313 in the second semester of 2014 was so high, as compared to other treatments. IAC 313 rootstock, produced by Campinas Agronomic Institute (IAC), in Brazil, is a very vigorous rootstock and in that condition presented highest values, with high amounts of leaves and physiological activity (data not measured) when compared to the Paulsen 1103 in under the same conditions. In other vintages the values have also presented differences but not too much, even were significant.

Table 3 shows a relationship between total condensed tannins and tanning power (the aggregation of the tannin with protein). The more tannins in a wine the greater the tanning power (de Freitas & Mateus, 2001).
3.7. Monomeric flavonols and small oligomeric procyanidins

Monomeric and small oligomeric flavanol concentrations are shown in supplementary material, Table 3. The highest concentrations of the (+)-catechin (6.6 mg/L) and (−)-epicatechin (12.6 mg/L) monomer fractions on 1103P in the second semester. The (−)-epicatechin 3-O-gallate compounds ranged from 0.2 to 1.0 mg/L, there are no differences between rootstocks or semesters.

Wines on IAC 313 had higher concentrations of B1 (9.8 mg/L) and B4 (5.0 mg/L) while those on 1103P had higher concentrations of B2 (21.0 mg/L), B1 3-O-gallate (1.8 mg/L) and B2 3′-O-gallate (6.0 mg/L). Among the procyanidins trimers, C1 was higher on IAC 313 (3.1 mg/L). The concentration of trimer 2 (0.9–3.0 mg/L) was not significantly different between rootstocks or semesters.

Total flavanols were higher on 1103P (53.4 mg/L) and values were significantly higher in semester 2. This is possibly related to the higher temperatures and lower day/night temperature differentials over this period. It resulted in a divergence between phenolic and technological maturation (mainly in seeds), providing a possible increase of tannins in wines. With the rapid technological maturation in the second semester, grapes are harvested with green seeds colour, which may favour the extraction of procyanidins for into wine. Further study is required to better understand tannin extraction in this terroir.

3.8. Principal component analysis (PCA)

Fig. 1A and B shows differences between wines from four harvest seasons and two rootstocks. Results are from monomeric anthocyanin analyses carried out using HPLC (supplementary material, Table 3). In addition to total phenols, the flavonoids, non-flavonoids, total and coloured anthocyanins and total and polymerised pigments, were all analysed spectrophotometrically (Table 2). The first two principal components explain 63.08% of total variability (PCI vs. PC2), where PCI explained 34.79% of variability and PC2 explained 28.29%.

The first principal component separated samples in relation to semester 1 and 2 for all years. On the positive side of the x-axis are the samples from the first semester, except for wines on IAC 313 in 2017, and on the negative side those on 1103 P from the second semester of 2014 and 2016 vintages, those from both rootstocks. Separation was most influenced by total and polymeric pigments, flavonoids, total phenols, malvidin 3-O-coumarylglucoside and peonidin 3-O-acetylglucoside, which characterised wines from the second harvest season, of the 2014 and 2016 vintages.

In second principal component, on the positive side of the x-axis in 2014, discriminated the samples in the second semester in both rootstocks. On the negative side of PC2 x-axis were wines from the second semester in 2016, also for both rootstocks. This evidenced a ‘vintage effect’, between years but in the same semester. This separation was most influenced by higher concentrations of cyanidin 3-O-glucoside, petunidin 3-O-acetylglucoside, cyanidin 3-O-acetylgalactoside, petunidin 3-O-coumarylglucoside and non-flavonoids phenols in 2014. Wines from 2016 were characterised by higher amounts of petunidin 3-O-glucoside and malvidin 3-O-glucoside.

Fig. 2A and B shows discrimination among samples from the four vintages and the two rootstocks. Results are based on fractionation of condensed tannins and small oligomeric flavanols, analysed by HPLC (Table 3). The first two principal components (PCI and PC2) explained 55.64% of total variability, where PCI was responsible for 31.65% and PC2 for 23.99%.

The PCI separated samples mostly according to rootstock. In the
positive side of the x-axis are the samples of Syrah wines on IAC 313 in the second semester of 2014, these being influenced by the monomeric tannins, B4 and B2 procyanidin dimers and trimer 2. On the negative side of the x-axis of PC1 are samples wines from vines on 1103P, in the second semester of 2014 and samples on 1103P, in the second semester of 2016. The separation of these samples was influenced mostly by catechin, epicatechin and tanning power.

The second principal component separated the samples in relation to the harvest season, with wine samples on 1103P, in the second semester of 2014, and on 1103P, in the second semester of 2016. The separation of these samples was influenced mostly by catechin, epicatechin and tanning power.

In the tropical conditions of the São Francisco Valley, harvest date is an important determinant of stability of the phenolic compounds. For example, red wines from grapes harvested between May to August can have more stable colour than those from grapes harvested between October to December. Wines from semester 2 can suffer earlier loss of colour and lower stability, browning just few months after bottling and thus having a shorter shelf life (unpublished data).

3.9. Sensory characterisation

The taster scores indicate an influence of rootstock on sensory profile (Table 4). From the 16 attributes evaluated, wines from grapes onto IAC 313 scored higher in 11 attributes, the other attributes were scored higher onto 1103P.

Fruity and spicy aromas scored higher on IAC 313, while floral, herbaceous and empyreumatic aromas scored higher on 1103P. A fruity aroma is characteristic of a young Syrah wine as mentioned by Zhao, Gao, Qian, and Li (2017) when evaluating wines in two regions of China - they reported more fruity aroma in Syrah wines from the north than from the south. Oliveira et al. (2011) also identified fruity aromas in Syrah wines of different clones, in the northeast, semiarid region of Brazil. Spicy aromas (mainly pepper) were also mentioned by Mayr et al. (2014) in characterising two premium Syrah wines from Australia using gas chromatography.

The Syrah wine onto IAC 313 scored high for sweetness, acidity, alcohol and astringency Table 4. For other taste attributes, such as sweetness, acidity and alcohol, it was not possible to correlate these with chemical and physicochemical factors such as pH, total acidity, alcohol content, and reducing substances. This demonstrates how difficult it is to characterise a wine solely on chemical analyses, it being critical to include sensory analyses. This observation was made also by Sivilotti, Zulini, Peterlunger, and Petrussi (2007) when evaluating Cabernet Sauvignon wines from grapes and vines on various rootstocks.

Wine astringency is related to the quantity and types of tannins present. According to the chemical analyses, the wines scoring highest for astringency, Syrah onto IAC 313, are those with high concentrations of oligomeric tannins, total tannins and tanning power (Table 3). In particular, the astringency of tannins, which affects palatability, is reported to be related to the formation of complexes with salivary proteins. These may result in a decrease in lubricating properties of saliva and greater friction on mouth surfaces (Gawel, Oberholster, & Leigh Francis, 2000).

As for the effect of semester on wine sensorial profile (Table 4) the notes varied among attributes according to year, there was no specific semester effect but there was a vintage effect. Especially for the first harvest season in 2017, with higher notes for fruity aroma, alcohol and persistence, regardless of rootstock; also for the second harvest season in 2014, with fruity aromas, spices and alcohol, regardless of rootstock.

4. Conclusions

Some compounds in Syrah wines from tropical semiarid region were influenced by rootstock and harvest season. In the classic physicochemical analyses, rootstock effects were not significant, with only small variations occurring between semesters.

Semester did influence wine composition with respect to calcium (semester 1), and with respect to alcohol content, total monomeric anthocyanins, non-flavanoids, polymerised pigments and total
flavanols (semester 2).

Syrah wines on IAC 313 were favoured with higher concentrations of anthocyanins 3-O-acetylgalactoside (petunidin and malvidin), anthocyanins 3-O-coumarylglucoside (malvidin, petunidin and peonidin), monomeric flavanols, oligomeric tannins, total condensed tannins and flavanols (B1, B4 and C1). Syrah wines on 1103P had higher concentrations of anthocyanins, flavanols (catechin, epicatechin, B2, B1 3-O-gallate, B2 3'O-gallate) and total flavanols.

The sensory profiles of the Syrah wines were influenced by rootstock followed by, mainly in relation to aromatic attributes. Syrah wines on IAC 313 were scored more highly by the tasters. The vintage effect was more significant than the semester effect for all samples, wines of the years of 2014 and 2017, with higher scores.

In tropical regions, such as the “sub-middle” of the São Francisco River Valley, the IAC 313 rootstock is more indicated than the Paulsen, even though the IAC is a more vigorous rootstock. Therefore, the opposite is recommended for temperate zones. Actually, to produce quality wines in temperate zones, rootstocks having less vigour are highly used.

The results indicate that the two different rootstocks can be used for the elaboration of different types of wines, such as the IAC 313 for guard red wines (with higher aging potential), and the Paulsen 1103 for young wines.

Acknowledgments

This research was supported by Brazilian companies: CAPES by scholarship of Oliveira, J. B. (Capes – 6070/1302); Embrapa Grape & Wine and Semiárid; project CNPq (403438/2013-6) and the wine company “Santa Maria/GLOBAL Wines” (Lagoa Grande Municipality, Pernambuco).

In Portugal, we thank the research center in Instituto Superior de Agronomia: Linking Landscape, Environment, Agriculture and Food – LEAF (UID/AGR/04129/2013) and FCT by scholarship of Egípito, R. (SFRH/BD/128847/2017).

Appendix A. Supplementary data
Supplementary data to this article can be found online at https://


Further reading


