



Wine composition of Merlot and Cabernet Sauvignon vine clones under the environmental conditions of Serra Gaúcha, Brazil

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Abstract

This study aimed to evaluate the wine composition from vine clones of Merlot (181, 346, 347, 348) and Cabernet Sauvignon (R5, 18A, 163, 338, 341). The grapes were harvested between 2010 and 2012, then on the same day, taken to the winery facility for winemaking. After crushing and destemming the grapes, the musts were transferred to glass containers, where the alcoholic and later malolactic fermentations occurred. Next, the wines were bottled and analyzed, where the classical variables were determined by physicochemical methods, volatile compounds by gas chromatography, and minerals by atomic absorption spectrophotometry. Data were submitted to ANOVA, Tukey test, correlation analysis, and Principal Component Analysis. The clone effect was significant for some variables; however, year and varietal group exerted greater effects. The Merlot group generally had higher values of ethanol, absorbance at 520 nm, color intensity, total polyphenols index, and methanol. On the other hand, the Cabernet Sauvignon group presented higher pH, ashes, alkalinity of ashes, hue, and potassium. Therefore, the three-year average data demonstrate that the evaluated Merlot and Cabernet Sauvignon clones are suitable to produce quality wines in the region, especially Merlot 181, 346, and 348 and Cabernet Sauvignon 18A and 163.

Keywords: *Vitis vinifera*; grape; minerals; volatile compounds.

Practical Application: The evaluation of wines from different Merlot and Cabernet Sauvignon vine clones in Serra Gaúcha provides subsidies to define the clone to be cultivated according to the winery's objective.

1 Introduction

The vine is currently cultivated in many Brazilian regions, with Rio Grande do Sul the largest producer. In this state, the grapes are mainly used for wine and juice production, which are commonly made from *Vitis labrusca* L. cultivars. However, some wines are made from *Vitis vinifera* L. grapes, where Merlot and Cabernet Sauvignon are two important cultivars of this species. They are cultivated in many viticultural regions worldwide, such as France, Australia, Argentina, California, Chile, and Brazil (Serra Gaúcha), which have different soil types and climatic characteristics.

A Cabernet Sauvignon boom in Serra Gaúcha took place a few decades ago. However, it is a long cycle variety requiring high heat summation from budbreak to grape maturity and low rainfall in the last days of the fruit ripening (Miele, 2019). For this reason, the grapes do not ripen properly in some years, with most wines having a vegetal note (green pepper), which is not well accepted by the consumers. Therefore, it has been partially replaced by Merlot, whose grapes ripen earlier and wines usually do not have such vegetal note.

Generally, the vineyards are established by planting the rootstocks in the field and grafted a year or two later; however, this practice is being replaced by selected clones produced by specialized nurseries. A clone can be defined as a group of individuals with the same genetic characteristics as the parent plant that is made asexually. By doing this, growers should have specific targets related to vine characteristics and wine

composition, typicality, and quality. Therefore, the genetic material, soil characteristic, and climate conditions should be taken into account in choosing a new clone, which may not be better than the one currently grown.

The performance of Merlot (Fidelibus et al., 2007; Rizzon & Miele, 2003) and Cabernet Sauvignon grapevine clones had been studied for agronomical and/or fruit composition (Brighenti et al., 2012; Burin et al., 2011; Fidelibus et al., 2006; Marcon Filho et al., 2019; Rizzon & Miele, 2002; Stefanini et al., 2000; Wolpert et al., 1995). However, studies on Merlot and Cabernet Sauvignon wines are scarce (Visser, 2003).

Due to the deficiency of wine parameters from clones of Merlot and Cabernet Sauvignon vines in Serra Gaúcha, this experiment aimed to evaluate their composition, through classical, volatile compounds, and mineral variables, which may allow comparison between them and suggest to growers the best choice of the clone to grow.

2 Material and methods

2.1 Vineyards

The experiment was carried out over three years, on the 2010 to 2012 vintages, in Merlot and Cabernet Sauvignon vineyards. Some were grown in Tuiuty (29°04' S; 51°33' W; 616 m high)

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and others in Vale dos Vinhedos (29°10' S; 51°34' W; 467 m high), two viticultural regions of Bento Gonçalves, RS, Brazil. The vineyards were established with grafted vines considered free from viruses. Control of diseases, pests, and weeds, as well as canopy and soil management, was performed according to the cultural practices carried out in the vineyards of the two partner wineries.

2.2 Grapevine clones

The Merlot (M) grapevine clones were 181, 346, 347, and 348, and the Cabernet Sauvignon (CS) clones were R5, 18A, 163, 338, and 341.

The grapes were harvested when ripe, by decision of the wineries to make quality wines, whose dates varied with the year. In general, for the nine clones and three years, the grapes ripened earlier in 2012 (February 28th) and later in 2011 (March 14th), being intermediary in 2010 (March 5th), where Merlot ripened from 3 to 5 March and Cabernet Sauvignon from 3 to 17 March. After harvest, the grapes were placed in two 20-kg plastic boxes and taken to the winery to make wine on the same day.

2.3 Winemaking

The grapes were crushed and destemmed, transferring the not-chaptalized musts to 20-L glass containers, from which samples were taken for analysis. Then, 50 mg/L of SO₂ was added to each container. In addition, 0.20 g/L of commercial dry active yeast (*Saccharomyces cerevisiae*) was supplied, and the containers were closed with rubber stoppers and water-filled airlocks. After eight days of maceration, in a 25 °C controlled-temperature room, the liquid phase was pressed off the skins. Next, they were transferred to 9-L glass containers also fitted with rubber stoppers and water-filled airlocks, kept at 24 °C until sugar concentration was less than 4.0 g/L. Malolactic fermentation occurred naturally, which was regularly evaluated by paper chromatography, adjusting total SO₂ to 50 mg/L. The wines were then transferred to 750-mL glass bottles, which were each sealed with a cork and stored at 15 °C in a temperature-controlled room.

2.4 Must analysis

The grape musts were centrifuged, and analyses were performed on the supernatants. Total soluble solids were determined by an Abbe refractometer (American Optical Corporation), with temperature correction; titratable acidity, by titration; and pH, by a Corning pH meter.

2.5 Wine analysis

The wines were analyzed in the same year they were made for classical, volatile compounds, and mineral variables. Most of them were determined by physicochemical methods (Rizzon, 2010); anthocyanins, by pH difference; tannins, by acid hydrolysis; absorbance at 420, 520, and 620 nm, by UV/VIS spectrophotometry using a 1-mm path length cell (Ribéreau-Gayon & Stonestreet, 1965, 1966); tartaric and malic acids, by liquid chromatography; and lactic acid, by paper chromatography.

The volatile compounds were performed by a Perkin Elmer GS AutoSystem XL gas chromatograph with flame ionization detection, equipped with a 50-m length capillary column, polyethylene glycol CP-WAX 57 CB stationary phase. The wine samples (3 µL) were directly injected into the chromatograph, the internal standard was a 10% solution of 4-methyl-2-pentanol at 1 g/L.

Minerals were determined on a Perkin Elmer (2380 model) and a Varian (240 FS model) atomic absorption spectrophotometers, where K was analyzed by flame emission and Ca and Mg by atomic absorption (Rizzon, 2010). Recommended proportions of acetylene/air mixtures were used for each chemical element. Mg and K were diluted in deionized ultra-pure MilliQ water prior to their determination; for Ca analysis, wines were diluted in a solution of lanthanum oxide and hydrochloric acid provided by Merck; and P, determined by UV/VIS spectrophotometry. The atomic absorption standards were from Merck and mineral concentrations were determined based on the curve for each element.

2.6 Statistical analysis

The wine data from Merlot and Cabernet Sauvignon vine clones were submitted to the ANOVA and Tukey's multiple range test. Correlations were made between the wine variables and those of wine and must, as well as the Principal Component Analysis (PCA) to discriminate wines. These analyses were performed in the Statistica program.

3 Results and discussion

The composition of Merlot (M) and Cabernet Sauvignon (CS) wines are presented in Tables 1 and 2 (classical variables), Table 3 (volatile compounds) and Table 4 (minerals).

3.1 Classical variables

In 19 of 22 variables, no significant difference ($p > 0.05$) between wines was found (Tables 1 and 2), but there was an effect on ethanol, pH, and hue ($p < 0.01$). The ethanol content of M 181 (12.8% v/v) was 24.3% higher than CS 338, 21.9% than CS R5, and 19.6% than CS 341, but it did not differ from other treatments. The pH of CS R5 and CS 163 (4.04 and 4.03, respectively) were on average 8.9% higher than M 346 and M 347 (3.70 and 3.71, respectively). The hue of CS R5 (0.810) was 32.6% and 27.4% greater than M 346 and M 347, respectively.

However, the vintage affected the wine composition much more than the clone itself (Tables 1 and 2). Indeed, 15 of 22 variables were affected by the vintage, mainly those related to ethanol, organic acids, and polyphenols. Thus, as an average of the nine treatments, the 2012 wines were characterized by higher values of ethanol, ashes, and polyphenols (anthocyanins, A 420, A 520, A 620, color intensity, tannins, and total polyphenols index). On the other hand, the 2012 wines had lower concentration of tartaric and malic acids, consequently, lower titratable acidity.

The average of Merlot and Cabernet Sauvignon wines exhibited some important differences (Tables 1 and 2). The Merlot group had higher ethanol (11.0%), reducing sugars (15.4%), A 520 (46.7%), color intensity (32.1%), and total polyphenols index

Table 1. Wine composition of Merlot and Cabernet Sauvignon vine clones: classical variables. Three-year average.

| Clone | Density (g/mL) | Ethanol (% v/v) | Titrateable acidity (mEq/L) | Volatile acidity (mEq/L) | pH | Dry extract (g/L) | Reducing sugars (g/L) | Reduced dry extract (g/L) | Ethanol in weight/Reduced dry extract | Ashes (g/L) | Alkalinity of ashes (mEq/L) |
|---------------------|----------------|-----------------|-----------------------------|--------------------------|---------|-------------------|-----------------------|---------------------------|---------------------------------------|-------------|-----------------------------|
| M 181 | 0.9943 a | 12.8 a | 64.6 a | 6.8 a | 3.77 ab | 27.6 a | 3.79 a | 24.8 a | 4.21 a | 2.68 a | 24.3 a |
| M 346 | 0.9948 a | 12.1 ab | 66.0 a | 6.3 a | 3.70 b | 26.4 a | 3.50 a | 23.9 a | 4.09 a | 2.36 a | 23.9 a |
| M 347 | 0.9950 a | 11.5 abc | 63.6 a | 6.6 a | 3.71 b | 25.6 a | 3.56 a | 23.0 a | 4.04 a | 2.73 a | 26.3 a |
| M 348 | 0.9947 a | 11.9 abc | 62.7 a | 6.6 a | 3.72 ab | 26.2 a | 3.21 a | 24.0 a | 4.01 a | 2.80 a | 23.9 a |
| CS R5 | 0.9963 a | 10.5 bc | 59.8 a | 10.1 a | 4.04 a | 25.1 a | 3.07 a | 23.1 a | 3.63 a | 3.45 a | 32.7 a |
| CS 18A | 0.9921 a | 11.4 abc | 67.4 a | 7.8 a | 3.93 ab | 26.1 a | 3.34 a | 23.8 a | 3.82 a | 2.74 a | 29.2 a |
| CS 163 | 0.9953 a | 11.7 abc | 55.8 a | 9.9 a | 4.03 a | 26.4 a | 3.09 a | 24.3 a | 3.87 a | 3.36 a | 34.2 a |
| CS 338 | 0.9965 a | 10.3 c | 64.2 a | 8.8 a | 3.96 ab | 23.2 a | 2.87 a | 21.3 a | 4.11 a | 2.98 a | 31.4 a |
| CS 341 | 0.9964 a | 10.7 bc | 61.0 a | 8.6 a | 3.95 ab | 26.2 a | 2.90 a | 25.0 a | 3.53 a | 2.88 a | 27.8 a |
| <i>Significance</i> | | | | | | | | | | | |
| Clone | ns | ** | ns | ns | ** | ns | ns | ns | ns | ns | ns |
| Year | ns | *** | *** | ns | ns | ** | ** | ** | *** | ns | ns |
| <i>Mean</i> | | | | | | | | | | | |
| M | 0.9947 a | 12.1 a | 64.2 a | 6.59 b | 3.73 b | 26.5 a | 3.52 a | 23.9 a | 4.09 a | 2.64 b | 24.6 b |
| CS | 0.9953 a | 10.9 b | 61.0 a | 9.04 a | 3.98 a | 25.4 a | 3.05 b | 23.5 a | 3.79 a | 3.08 a | 31.0 a |

M= Merlot clones, CS= Cabernet Sauvignon clones, ns= not significant, ** = significant at 1%, *** = significant at 0.1%.

Table 2. Wine composition of Merlot and Cabernet Sauvignon vine clones: classical variables. Three-year average.

| Clone | Tartaric acid (g/L) | Malic acid (g/L) | Lactic acid (g/L) | Anthocyanins (mg/L) | A 420 | A 520 | A 620 | Color intensity | Hue | Tannins (g/L) | Total polyphenols index |
|---------------------|---------------------|------------------|-------------------|---------------------|---------|---------|---------|-----------------|----------|---------------|-------------------------|
| M 181 | 1.79 a | 0.17 a | 2.21 a | 359.0 a | 0.338 a | 0.522 a | 0.104 a | 0.964 a | 0.646 ab | 1.43 a | 47.4 a |
| M 346 | 1.49 a | 0.19 a | 1.75 a | 365.6 a | 0.312 a | 0.513 a | 0.095 a | 0.920 a | 0.611 b | 1.66 a | 48.2 a |
| M 347 | 2.15 a | 0.72 a | 1.95 a | 382.2 a | 0.333 a | 0.551 a | 0.100 a | 0.984 a | 0.636 b | 1.71 a | 49.3 a |
| M 348 | 1.67 a | 0.16 a | 2.34 a | 334.5 a | 0.279 a | 0.439 a | 0.082 a | 0.800 a | 0.647 ab | 1.67 a | 46.9 a |
| CS R5 | 1.41 a | 0.15 a | 2.85 a | 392.4 a | 0.261 a | 0.329 a | 0.087 a | 0.677 a | 0.810 a | 1.36 a | 43.3 a |
| CS 18A | 2.08 a | 0.16 a | 3.30 a | 346.1 a | 0.272 a | 0.365 a | 0.090 a | 0.727 a | 0.757 ab | 1.29 a | 41.1 a |
| CS 163 | 1.51 a | 0.16 a | 2.84 a | 408.6 a | 0.287 a | 0.384 a | 0.100 a | 0.771 a | 0.759 ab | 1.62 a | 42.6 a |
| CS 338 | 1.45 a | 0.16 a | 2.98 a | 343.6 a | 0.242 a | 0.322 a | 0.083 a | 0.647 a | 0.757 ab | 1.09 a | 33.7 a |
| CS 341 | 1.73 a | 0.14 a | 3.39 a | 286.5 a | 0.240 a | 0.327 a | 0.082 a | 0.649 a | 0.754 ab | 1.35 a | 39.6 a |
| <i>Significance</i> | | | | | | | | | | | |
| Clone | ns | ns | ns | ns | ns | ns | ns | ns | ** | ns | ns |
| Year | *** | ** | ns | ** | *** | ** | *** | ** | ns | *** | *** |
| <i>Mean</i> | | | | | | | | | | | |
| M | 1.77 a | 0.31 a | 2.06 b | 360.3 a | 0.316 a | 0.506 a | 0.095 a | 0.917 a | 0.635 b | 1.62 a | 47.9 a |
| CS | 1.64 a | 0.16 a | 3.07 a | 355.4 a | 0.260 a | 0.345 b | 0.088 a | 0.694 b | 0.767 a | 1.35 a | 40.1 b |

M= Merlot clones, CS= Cabernet Sauvignon clones, ns= not significant, ** = significant at 1%, *** = significant at 0.1%.

Table 3. Wine composition of Merlot and Cabernet Sauvignon vine clones: volatile compounds. Three-year average.

| Clone | Acetaldehyde | Ethyl acetate | Methanol | 1-Propanol | 2-Methyl-1-propanol | Amyl alcohols | Sum of higher alcohols |
|---------------------|--------------|---------------|----------|------------|---------------------|---------------|------------------------|
| | (mg/L) | | | | | | |
| M 181 | 5.72 a | 32.4 a | 234.4 ab | 26.6 ab | 51.2 ab | 343.2 a | 421.0 a |
| M 346 | 6.50 a | 29.7 a | 255.5 a | 23.0 b | 50.8 ab | 340.8 a | 414.6 a |
| M 347 | 4.99 a | 25.1 a | 233.3 ab | 23.0 b | 56.1 ab | 318.7 a | 397.8 a |
| M 348 | 6.27 a | 30.8 a | 237.0 ab | 26.8 ab | 48.7 b | 313.5 a | 387.1 a |
| CS R5 | 4.77 a | 32.8 a | 171.1 c | 32.0 ab | 54.3 ab | 288.0 a | 374.3 a |
| CS 18A | 5.11 a | 37.5 a | 179.8 c | 33.5 ab | 58.0 ab | 285.5 a | 377.0 a |
| CS 163 | 5.12 a | 37.1 a | 203.8 bc | 27.0 ab | 56.5 ab | 328.3 a | 411.9 a |
| CS 338 | 6.10 a | 31.1 a | 200.8 bc | 48.2 a | 56.8 ab | 253.6 a | 358.6 a |
| CS 341 | 3.72 a | 33.0 a | 194.1 bc | 31.6 ab | 59.1 a | 304.1 a | 394.7 a |
| <i>Significance</i> | | | | | | | |
| Clone | ns | ns | *** | * | * | ns | ns |
| Year | *** | *** | *** | *** | ns | ns | ns |
| <i>Mean</i> | | | | | | | |
| M | 5.87 a | 29.5 a | 240.1 a | 24.8 a | 51.7 b | 329.0 a | 405.6 a |
| CS | 4.96 a | 34.3 a | 190.7 b | 34.4 a | 56.9 a | 291.9 b | 383.3 a |

M= Merlot clones, CS= Cabernet Sauvignon clones, ns= not significant, * = significant at 5%, *** = significant at 0.1%.

Table 4. Wine composition of Merlot and Cabernet Sauvignon clones: minerals. Three-year average.

| Clone | P | K | Ca | Mg |
|---------------------|--------|----------|--------|--------|
| | (mg/L) | | | |
| M 181 | 121 ab | 1241 bc | 67.1 a | 90.9 a |
| M 346 | 155 ab | 1190 c | 64.3 a | 87.5 a |
| M 347 | 131 ab | 1238 bc | 63.9 a | 85.1 a |
| M 348 | 161 a | 1176 c | 60.2 a | 85.8 a |
| CS R5 | 150 ab | 1770 a | 76.4 a | 90.4 a |
| CS 18A | 100 b | 1604 abc | 67.8 a | 80.0 a |
| CS 163 | 153 ab | 1715 ab | 66.2 a | 79.8 a |
| CS 338 | 113 ab | 1633 abc | 73.4 a | 88.5 a |
| CS 341 | 129 ab | 1654 abc | 73.6 a | 81.8 a |
| <i>Significance</i> | | | | |
| Clone | * | ** | ns | ns |
| Year | *** | ns | ** | * |
| <i>Mean</i> | | | | |
| M | 142 a | 1211 b | 63.9 b | 87.3 a |
| CS | 129 a | 1675 a | 71.5 a | 84.1 a |

M= Merlot clones, CS= Cabernet Sauvignon clones, s= not significant, *= significant at 5%, **= significant at 1%, ***= significant at 0.1%.

(19.5%). Instead, those of Cabernet Sauvignon had higher pH (6.7%), ashes (16.7%), alkalinity of ashes (26.0%), hue (20.8%), lactic acid (49.0%), and volatile acidity (37.2%).

These results may be different according to a variety of factors, such as vine clones. In studies conducted in a high region, CS 169 was better correlated with individual phenolic compounds and CS 685 with anthocyanins (Burin et al., 2011). Another trial found that CS 169, CS 170, and CS R5 were the best for potential winemaking in that region (Brighenti et al., 2012).

The parameters of the classical variables (Tables 1 and 2) were in accordance – when specified – with Brazilian law (Brasil, 1998, 2018). All Cabernet Sauvignon and two Merlot wines had ethanol content below 12% v/v, which means that the grapes did not ripen sufficiently and sucrose should be added for must correction (chaptalization). The ethanol content of the Merlot group was higher than Cabernet Sauvignon (difference of 1.2% v/v), because the Merlot must had about 20 g/L more sugar (glucose and fructose). Ethanol was positively correlated with grape must total soluble solids ($r = 0.62$) and pH ($r = 0.59$), and negatively correlated with titratable acidity ($r = -0.39$). Among wine variables, ethanol correlated positively with total polyphenol index ($r = 0.84$) (A 420, A 520, A 620 nm, and color intensity) and negatively with density ($r = -0.51$). Ethanol is a very important compound for wine, as it acts in its preservation and improves its quality.

Tartaric and malic acids are the main organic acids in grapes, where malic acid becomes lactic acid during malolactic fermentation, especially in red wines. These acids as well as titratable acidity were not affected ($p > 0.05$) by any clone. However, pH was affected ($p < 0.01$) probably because the pH indicates the real concentration of H^+ ions that are ionized or dissociated in the solution, whereas titratable acidity estimates the amount of titratable acids. Organic acids play an important role in wine quality, especially in sensory attributes, influencing its balance. Thus, lactic acid is 'weaker' than malic acid, which makes wine less aggressive to the consumer's taste.

Volatile acidity, which shows the presence of acetic acid, was also unaffected ($p > 0.05$) in any wine, which ranged from 6.3 (M 346) to 10.1 (CS R5) mEq/L, demonstrating that the winemaking conditions were well controlled. These values are acceptable for consumers and are in accordance with Brazilian law, whose limit is 20 mEq/L. However, wines are difficult to consume with this value, which 'irritates' the throat. In reality, it should be as lower as possible.

The dry extract ranged from 23.2 (CS 338) to 27.6 (M 181) g/L (Table 1) and is an important tool for regulating the wine body (Boulton et al., 1998). The main components of the dry extract are glycerol and organic acids, as well as reducing sugars. All wines were considered dry because reducing sugars were below 4.0 g/L – average of 3.29 g/L –, which means that most of the sugar was turned into ethanol by yeasts. The ethanol for average weight/reduced dry extract ratio ($p > 0.05$) was 3.94, below 5.20, the maximum value allowed. The ashes are comprised of minerals present in the wine after calcination in the muffle, which ranged from 2.36 (M 346) to 3.45 (CS R5) g/L. However, ash content in Cabernet Sauvignon wine group averaged 16.7% higher than Merlot ($p < 0.05$). Thus, all wines showed ash parameters in accordance with the Brazilian law that establishes a minimum of 1.5 g/L (Brasil, 1998, 2018). Alkalinity of ashes was 26.0% higher ($p < 0.05$) in Cabernet Sauvignon wines, showing that it had less free organic acids than in Merlot.

Except for the hue (Table 2), no other polyphenolic compound was significantly affected by the clone, but the value of the Cabernet Sauvignon group for hue was 20.8% higher than Merlot ($p < 0.05$). However, Merlot wine group was higher ($p < 0.05$) in total polyphenols index (19.5%), A 520 (46.7%), and color intensity (32.1%). In general, the data of the present study are similar to those already recorded in previous studies conducted in the same region on Merlot (Miele et al., 2009b) and Cabernet Sauvignon (Miele & Rizzon, 2019) wines. Polyphenols are very complex, important compounds for red wines, with anthocyanins and tannins the main substances in this group that could influence the characteristics and quality of the wine.

The role of tannin polymers is on wine structure and its sensory characteristics. However, they may be responsible for wine astringency and bitterness when the grape is not ripe enough, which requires special attention from the winemaker. In addition, aged wines can have new molecules coming from oak wood, increasing their complexity. The phenolic composition of a wine may also be due to the winemaking practices, which can affect physical phenomena (diffusion of compounds from the grape solid phase to the must and the tannins extraction from

the wood during aging) and chemical and biochemical reactions (oxidation, degradation, and condensation) (Cheynier et al., 1998).

3.2 Volatile compounds

Wines were affected by methanol ($p < 0.001$), 1-propanol, and 2-methyl-1-propanol ($p < 0.05$) (Table 3); however, there was no effect ($p > 0.05$) on acetaldehyde, ethyl acetate, amyl alcohols, and sum of higher alcohols. Methanol did not differ ($p > 0.05$) among Merlot clones, and M 346 wine had more (34.5%) ($p < 0.001$) than the average of the five Cabernet Sauvignon wines, and as a group, Merlot was 25.9% higher ($p < 0.05$). The 1-propanol of CS 338 differed ($p < 0.05$) from M 346 and M 347, which was 2.1 times higher. The 2-methyl-1-propanol of CS 341 was 21.4% higher ($p < 0.05$) than M 348. The Cabernet Sauvignon group was 10.1% higher than Merlot group in 2-methyl-1-propanol and 16.7% in amyl alcohols. Four volatile compounds varied according to the vintage ($p < 0.001$), and exhibited the highest values in 2010, except methanol that was highest in 2011.

The average concentration of ethyl acetate was 31.9 mg/L, which is below the threshold of this compound, estimated at about 180 mg/L. Low values were mainly due to healthy grapes and the conditions under which alcoholic fermentation took place. On the other hand, higher concentrations give a vinegar note to the wine, which negatively affects its overall quality.

The methanol contents (Table 3) of all wines were lower (mean of 215.4 mg/L) than 300 mg/L specified by Brazilian law. Nevertheless, methanol was about 50% higher than found in other studies carried out in the same region (Miele & Rizzon, 2019). This alcohol is synthesized by the hydrolysis of pectin present in grape berries, mostly in the skin. High concentrations of methanol may be harmful to human health and wines of *V. labrusca* L. cultivars generally have more methanol than *V. vinifera* L. (Rizzon & Miele, 2006; Tecchio et al., 2007).

Higher alcohol content (Table 3) comes from the alcoholic fermentation. Its content in wines depends on the nitrogen present in the must, on yeasts and other actors involved in the fermentation process, such as temperature, oxygen, and sulfur dioxide. High concentrations of these substances are negative for the wine quality as they are responsible for undesirable aromas (Dirninger & Schaeffer, 1990). According to these authors, high levels of amyl alcohols (2-methyl-1-butanol and 3-methyl-1-butanol) (Table 3) may cause vegetative or herbaceous notes in wines. The 1-propanol is synthesized by bacteria, which depends on the healthy state of the grapes.

3.3 Minerals

Grapevine clones had a significant effect on two wine minerals (Table 4). Among them, P of M 348 was 61.0% higher than CS 18A ($p < 0.05$), and K of CS R5 was 46.1% higher ($p < 0.01$) than the average of the four Merlot wines. However, the minerals were affected by the vintage in most wines except K. Merlot and Cabernet Sauvignons groups effected ($p < 0.05$) only K and Ca, where K content of Cabernet Sauvignon wine was 38.3% higher than Merlot, and Ca 11.9%. Most minerals presented the higher values in 2010, but K was highest in 2011.

Minerals play a role in pH, stability, and limpidity of wines (Ribéreau-Gayon et al., 1998), along with its sensory attributes. Among them, K accounted for 83.3% of the macroelements, which is a characteristic of the Cabernet Sauvignon grown in Serra Gaúcha (Rizzon & Miele, 2002). The soils of this region are generally rich in this cation, which is taken up by the vine root system and transported through the xylem to the upper parts of the plant, including the fruit. Moreover, longer grape must maceration could have extracted more K, especially from the peel. The accumulation of K in different vine tissues has been shown (Kodur et al., 2010; Miele et al., 2009a; Rühl, 1989) as well in wine (Hale & Brien, 1978; Rizzon & Miele, 2017). Rootstocks with low K accumulation are an option for pH adjustment (Walker & Blackmore, 2012), because this cation can lead to problems in wine preservation when in high concentration. In fact, it acts on salification of tartaric acid, interfering with wine pH and, consequently, acidity (Ordoñez et al., 1983).

Ca and Mg are two other cations naturally present in relatively high concentration in wines (Rizzon et al., 2000) and can be mainly affected by the soil and the Bordeaux mixture to control vine diseases. They can also be influenced by winemaking practices, with Mg generally higher than Ca, which may be due to the higher solubility of its salts (Amerine & Ough, 1976). High Ca content can cause turbidity in wine.

Considering the set of variables evaluated, the Principal Component Analysis (PCA) discriminated the Merlot and Cabernet Sauvignon wine groups, where PC 1 (47.86%) and PC 2 (15.32%) explained 63.18% of the total variation. Merlot 181, 346, and 348 wines were better discriminated from Cabernet Sauvignon R5, 338, and 341. However, PCA also indicated that growers should prefer clones Merlot 181, 346, and 348 and Cabernet Sauvignon 18A and 163.

As the oenological practices in the production of wines were the same, the differences between wines were probably due to some combined factors, such as the genetic characteristics of the clones, their adaptation to the local soil and climate, and the vineyard management. The composition of wines from Merlot and Cabernet Sauvignon vine clones demonstrated their potential in the Serra Gaúcha viticultural region, as they were produced on a small scale, where winemaking practices are essential. However, additional oenological practices are generally used on a winery scale, which could change the wine composition and sensory attributes.

4 Conclusion

The evaluated Merlot and Cabernet Sauvignon vine clones are suitable for the production of quality wine in Serra Gaúcha; however, their parameters differ in some variables. As a group, Merlot wines present more ethanol, absorbance at 520 nm, color intensity, and total polyphenols index; on the other hand, Cabernet Sauvignon wines exhibit higher pH, ashes, alkalinity of ashes, hue, and potassium. Nevertheless, they need to be further chaptalized due to their lower ethanol content. Therefore, the Merlot is better adapted to the environmental conditions of that region, especially the clones 181, 346, and 348, while among Cabernet Sauvignon, 18A and 163 stand out.

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