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Phenolic Composition, Chromatic Parameters and Antioxidant Activity "in vitro" in Tropical Brazilian Red Wines

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Abstract Red wines are a rich source of several classes of polyphenols that have the ability to act as antioxidants chelating metals, inhibiting lipid peroxidation and sequestering free radicals scavenging. Our study aims to determine the phenolic composition**,** chromatic parameters and antioxidant activity *"in vitro"* in tropical Brazilian red wines from the Syrah and Cabernet Sauvignon varieties of the 2011, 2013 and 2014 vintages from São Francisco Valley. Total polyphenols, polyphenols index, total anthocyanins, condensed tannins, color intensity, tonality and the phenolic profile was determined. Consequently, color index ranged from 8.08 to 15.03; tonality between 0.72 and 1.0; total phenolics expressed as gallic acid equivalents ranged between 1,528.90 mg.L^{-1} and 4,003.96 mg.L^{-1}; anthocyanins ranged between 98.94 mg.L^{-1} and 501.2 mg.L^{-1} amd condensed tannins between 61.08 and 147.74 mg.L^{-1}. Resveratrol presented means ranging between 2.75 and 26.89 mg.L^{-1}, and the antioxidant activity ranged from 58.02% to 95.70%. We did not observe correlation between anthocyanins and color with antioxidant capacity. The results of this study showed better values of polyphenols and potent antioxidant activity when compared with other studies. These results can be associated with possible beneficial effects on health.

Keywords: *antioxidant activity, phenolic profile, polyphenols, red wines, tropical wines*

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1. Introduction

The Brazilian northeast is responsible for 26% of the national production of grapes, representing a total of 41 million tons. The grape production in the Northeast of Brazil is concentrated mainly in the region of the São Francisco Valley, located in the backwoods of Pernambuco and Bahia [1]. This region, situated between latitude 8° and 9° S -with a semiarid tropical climate, intra-annual variability, characterized by warm days and nights, produces grapes during different year seasons. Interactions between the vine and natural environmental factors mainly the solar radiation action about theirs photosynthetic and thermal mechanisms influencing significantly the chemistry composition and consequently the characteristics of grapes and wines [2,3].

It is the only region of the world that produces grapes year-round. Depending on the cultivar, the harvests can occur between two and three annually [4].

In the year 2014, the production of grapes destined to the processing of wine, juices and other derivatives was 673.422 million Kg of grapes, representing 46.89% of the national production [5]. In the state of Pernambuco, there was an increase of 3.52% among the varieties tested in the region of the São Francisco Valley whose climate is semi-arid tropical [5] and the São Francisco Valley stands out in production of table wines in Brazil [6].

The São Francisco Valley (SFV) is currently the second largest producer of fine wines in Brazil with six wineries, five of which are located in Pernambuco and one in Bahia [7]. In this region, the vines are cultivated under controlled irrigation conditions consequently the wines have been demonstrating a high concentration of phenolic compounds, bioactive with a beneficial effect on human health [8].

Among the cultivars of the VSF, the main varieties *Vitis vinifera L.* used in the elaboration of red wines in the São Francisco Valley, Syrah, Cabernet Sauvignon, Tempranillo, Ruby Cabernet and Alicante Bouschet grapes [9]. On the other hand, the Cabernet Sauvignon grape is considered one of the most prestigious grape varieties in the world [10]. It is one of the most successful grape varieties in the production of red wine, which is the result of the natural crossing between the varieties

Cabernet Franc and Sauvignon Blanc, also natural of the main wine producing region of the world [10]. Cabernet Sauvignon wine is characterized by its red color with sharp violet reflections, tannin richness and aroma complexity [10].

Previous studies have shown that wine polyphenols play an important role in oenology because of their influence on some important sensory properties of grapes and wines, such as color, stability, bitterness and astringency due to their antioxidant and anti-inflammatory properties. The phenolic compounds are also associated with several beneficial physiological effects derived from moderate wine consumption [11]. In the human body, the phenolic compounds act as non-enzymatic antioxidants suggesting a free radical scavenging role derived from reactive oxygen and/or nitrogen species [12].

Among the phenolic compounds of red wines, phenolic acids composed by hydroxycinnamic and hydroxybenzoic acids represent 30% of the phenolic compounds [12].

Stilbenes act as anti-fungal phytoalexins have great potential in biological and cellular processes applicable to human health by their ability to inhibit the cellular events associated with carcinogenesis, including initiation, promotion and tumor progression. The resveratrol is the best known example to Stilbenes [12]. Flavonoids are uncoloured phenolics more abundant in the shell of fruits. The anthocyanins (cyanidin, peonidin, delphinidin, petunidine, pelargonidin and malvidin) are the main red wine pigments responsible for the color of red wine [11]. Studies have shown beneficial effects of anthocyanins that act as antioxidants, anti-inflammatory and anticancer, anti-diabetes, cardiovascular and neurological diseases [15].

Thus, our study aims to contribute to the knowledge of the characteristics of Brazilian wines, particularly São Francisco Valley. The results obtained in this study can improve value to the local product and increase its commercialization. Considering the previously mentioned aspects, we propose the hypothesis that the red wines of the São Francisco Valley have a quality similar to the red wines of regions such as South America and the European Community. The objective of the study is to characterize the phenolic profile of the cultivars Cabernet Sauvignon and Syrah of the 2011, 2013 and 2014 vintages of the SFV and to analyze its correlation with the antioxidant capacity.

2. Material and Methods

Samples

Young, monovarietal and commercial tropical red wines were provided by the wineries of São Francisco Valley cultivars from Syrah and Cabernet Sauvignon, from the 2011, 2013 and 2014 harvests. The choice of samples was due to the fact that Syrah and Cabernet Sauvignon grapes are among the main varieties used in the elaboration of red wines in the São Francisco Valley and are pointed as important for winemaking in Brazil [16]. In addition, the demand and appreciation of the Syrah and Cabernet Sauvignon wines have been verified in the national and international markets [17,18,19,20].

2.1. Determination of the Phenolic Compounds and Color Parameters

Spectrophotometrics analysis

The Folin-Ciocalteu reagent, mixture of phosphomolibidenic and phosphotungstic acids, is used to determine the polyphenols total concentration. The method is based on initial reactions of reduction of the phenolic compounds to phenol ions, terminated by the alkalinization of the medium [12,21]. The total polyphenols compounds content of the wines was determined in triplicate using the Folin-Ciocalteau reagent [13]. The absorbance was measured using a spectrophotometer (Varian® UV-Vis), with quartz cuvettes, at the wavelength of 725nm. The total phenolic content was determined by a standard curve of gallic acid (0 to 8 mg.L^{-1}) and the results were expressed as mg of gallic acid equivalents per liter (mg GAE.L^{-1}).

Total polyphenols index (TPI), is based on the absorption capacity of ultraviolet (UV) radiation at 280 nm by the aromatic rings, whose concentration obeys the Lambert-Beer law [21]. The samples were diluted for 2% in distilled water and read in a spectrophotometer at 280nm in quartz cuvettes, and the results expressed through the absorbance, considering the dilution factor.

The determination of the total anthocyanins was performed by the spectrophotometric method of pH differential, through the transformation in the chromophore structure of the anthocyanins in acid medium [22]. The total anthocyanin content was determined in triplicate, using the pH differential method and a linearity factor of 388 [23]. The absorbance was measured using a spectrophotometer (Varian® UV-Vis) at the wavelength of 520nm.

Condensed tannins content of the wines were determined by the vanillin/HCl method as described by Price, [23] modified [28,29]. Catechin was used as the standard for the calibration curve with concentrations in mg.L^{-1}(0.18 at 1.80) and the results were expressed as mg of catechin equivalentes per liter (mg CE.L^{-1}).

The collor intensity was measured by sum of the absorbances at 420, 520 and 620 nm and the tonality by ratio between 420 and 520nm [21,24,25]. And the following colorimetric indices: % yellow, % red, and % blue at wavelengths of 420, 520, and 620 nm, respectively, in relation to the intensity of the color [26].

Chomatographic Analysis

For high performace liquid chromatograph (HPLC) coupled with UV-Vis detector Ultimate 3000 Dionex®, contening quaternary pump and a 20µL injection loop was used. The HPLC was controlled by a PC running Chromeleon® Software system. Stock solution of all standards was prepared in methanol, and the calibration curves were obtained from triplicate injections of five concentrations. For all standard curves correlation coefficients (r) were above 0.98. All the compounds were indentified by comparing their retention times with those pure standards (Sigma-Aldrich®).

Flavanols (+)-catechin), phenolic acids (gallic acid, siringic acid, ellagic acid, vanillic acid, caffeic acid, p-cumaric acid and ferulic acid), flavonols (rutin, myricetin, quercetin, and kaempferol) and of stilbens (trans-resveratrol) were measured in triplicate using an Acclaim® 120 DionexC-18 analytical column (250 mm x 4.6 mm, 5 µm particle size) at 36°C. The mobile phase was consisted of A (methanol: phosphoric acid 0.5% in water, 10:90 v/v) and B (methanol: phosphoric acid 0.5% in water, 90:10 v/v). The gradient elution conditions were as follow: 0-25min (100-15% A); 25-50min (15-5% A) and 50-52 min (5-100% A). The flow rate was 0,6 ml.min^{-1}.Before analysis the samples were filterd with 0,45µm filter with PTFE membrane (Millipore®). The wavelengths were used as follow: 220nm (gallic acid, catequin, vanillic acid, siringic acid and caffeic acid), 260nm (rutin and ellagic acid), 306nm (ferulic acid, p-cumaric acid and trans-resveratrol) and 368nm (myricetin, quercetin and kaempferol) [2,30].

2.2. Determination of Antioxidant Activity *"in vitro"*

According to methodology described by Porgali and Büyüktuncel [33], solutions at different concentrations of DPPH* (1,1-diphenyl-2-picrythydrasyl radical) have had their absorbance measured at 517nm in a spectrophotometer (Varian® 50 Bio UV/Vis). The free radical-scavenging activity towards the DPPH* was determined in triplicate [32]. Following this method of each one wines dilutions 0,1mL was mixed with 2,9mL of metanolic solution (60µM of DPPH*). After 30 minutes, the absorbance was measured at 517nm. The free radical-scavenging activity was expressed as the percentage of sequestering activity (%SA), calculated by the equation (1):

$$\%SA = 100x\frac{(Acontrol - Asample)}{Acontrol} \quad (1)$$

Where, $A_{control}$ is the absorbance of the solution containing radical DPPH* and methanol and A_{sample} is the absorbance of the sample.

2.3. Statistical Analysis of Data

In vitro analyzes were performed in triplicate and the results were presented as mean and standard deviation. To compare the results, we used variance analysis (ANOVA) with Bonferonni's post-test (p <0.05) to identify possible differences between the means. The Graph prism for Windows 6.0 program was used at the 5% level of significance.

3. Results

3.1. Phenolic Composition of the Wines and Its Antioxidant Activity "in vitro"

The characterization of the cultivars and vintages of the wines of the São Francisco Valley show great diversity in the indices evaluated as intensity of color, phenolics, anthocyanins, condensed tannins and the phenolic profile. However, the evaluation of the antioxidant activity *in vitro* shows great homogeneity for Cabernet Sauvignon wine independent of the crop and presents more scientific evidence in studies when compared to the Syrah wine.

The Table 1 shows the variation of the chromatic parameters of the red wines of the cultivars Syrah and Cabernet Sauvignon found in the study.

According to the data presented in Table 1, the color intensity did not show significant differences between the wines Cabernet Sauvignon 2011 (CSI 11) and Cabernet Sauvignon 2014 (CSIII14) despite the color tone, the percentage of yellow, the percentage of red presented significant differences for the same wines. On the other hand, the color index showed an average variation of 8.08 to 14.03 in the Syrah wines and 10.64 a 15.03 in the Cabernet Sauvignon wines.

The values for color tonality of the wines inour study vary from 0.72 to 1.01. While the percentage of shades of the present study shows a variation of yellow from 36.6% to 43.5%, red from 43,7 to 50.9% and blue from 12 to 13% in the different cultivars and harvests analyzed. On the other hand, our results indicate that the wines Syrah and Cabernet Sauvignon of the São Francisco Valley of the studied crops, present a maximum absorbance at 520nm. This finding runs counter to the hypothesis that the spectrum of young red wines exhibits a more or less narrow absorbance maximum at 520 nm.

The Figure 1, shows the variation of the total polyphenols index (TPI), total polyphenols and total anthocyanins of wines studied.

Regarding to the total polyphenols index (Figure 1A) the results showed averages ranging from 103.6 in the Syrah of 2013; 64.06 in Cabernet Sauvignon of 2013; 97.83 in Cabernet Sauvignon, of 2014; 75.87 in Cabernet Sauvignon of 2011 and 73.48 in Syrah of 2014. However, these wines did not show significant differences (p<0.05) for the total polyphenol content between the 2011 Cabernet Sauvignon and the 2014 Syrah wines.

Table 1. Chromatic parameters of red tropical wines of cultivars Syrah (SY) and Cabernet Sauvignon (CS). Studies as color intensity (CI), color tonality (TC), percentage of yellow (%yellow), percentage of red (% red) and percentage of blue (% blue).

Sample	CI	TC	% yellow	% red	% blue
CS I 11	11.13±0.26^{c}	1.02±0.018^{a}	43.58±0.06^{a}	43.73±0.07^{c}	12.69±0.04^{c,a}
CS II 13	15.03±0.43^{a}	0.74±0.01^{c}	37.03±0.02^{c}	50.65±0.03^{a}	12.32±0.05^{a,b}
SY I 13	14.03±0.49^{b}	0.72±0.01^{c}	36.71±0.03^{c}	50.64±0.07^{a}	12.65±0.05^{a}
CS III 14	10.64±0.16^{c}	0.92±0.01^{b}	41.91±0.16^{b}	45.96±0.19^{b}	12.13±0.04^{a}
SY II 14	8.08±0.10^{d}	0.72±0.01^{c}	36.66±0.02^{c}	50.98±002^{a}	12.35±0.01^{a}

Color intensity (CI), tonality (T), percentage of yellow (% yellow), percentage of red (% red) and percentage of blue (%blue); CS I 11 (Cabernet Sauvignon, winery I, harvest 2011); CS II 13 (Cabernet Sauvignon, winery II, harvest 2013); SY I 13 (Syrah, winery I, harvest 2013); CS III 14 (Cabernet Sauvignon, winery III, harvest 2014); SY II 14 (Syrah, winery II, harvest 2014). Analysis of variance (ANOVA) one way followed by Bonferonni's post-test. Differents letters, in the column, indicate significance variation (p<0.05).

The mean of total phenolic contentequivalent to gallic acid (Figure 1B) varied in the samples at 2,273.52 mg.L^{-1} in the Syrah wine of 2013; 2,533.18 mg.L^{-1} in Cabernet Sauvignon 2013; 2,233.21 mg.L^{-1} in Cabernet Sauvignon, 2014; 1,528.9 mg.L^{-1} in Cabernet Sauvignon of 2011 and 4,003,96 mg.L^{-1} in Syrah of 2014. We have noted that there are no significant differences between the wines Syrah of 2013, Cabernet Sauvignon of 2013 and Cabernet Sauvignon of 2014 for $p<0.05$.However there is significance between Syrah of 2013 wines and Cabernet Sauvignon of 2011 and 2014 wines.

The content of totoal anthocyanins (Figure 1C) varied in average of 384.3 mg.L^{-1} in Syrah wine of 2013; 359.7 mg.L^{-1} in Cabernet Sauvignon 2013; 98.94 mg.L^{-1} in Cabernet Sauvignon, 2014; 101.3 mg.L^{-1} in Cabernet Sauvignon 2011; 501.2 mg.L^{-1} in Syrah of 2014.In previous study by BAJČAN et al. (2016) with wines of Cabernet Sauvignon cultivar from different areas of Slovakia, anthocyanin levels ranged from 68.6 mg.L^{-1} to 430.7 mg.L^{-1}.

The content of condensed tannins in our study (Figure 1D) showed significant differences in the wines - CS I 11, 61.08 mg.mL^{-1}; CSIII 14, 80.83mg.mL^{-1}, and SYII 14, 121.27 mg.mL^{-1}, whereas the SY I 13 - 147.74 mg.mL^{-1} and CS II 13 - 146.89 mg.mL^{-1}, did not present any significant differences among themselves.

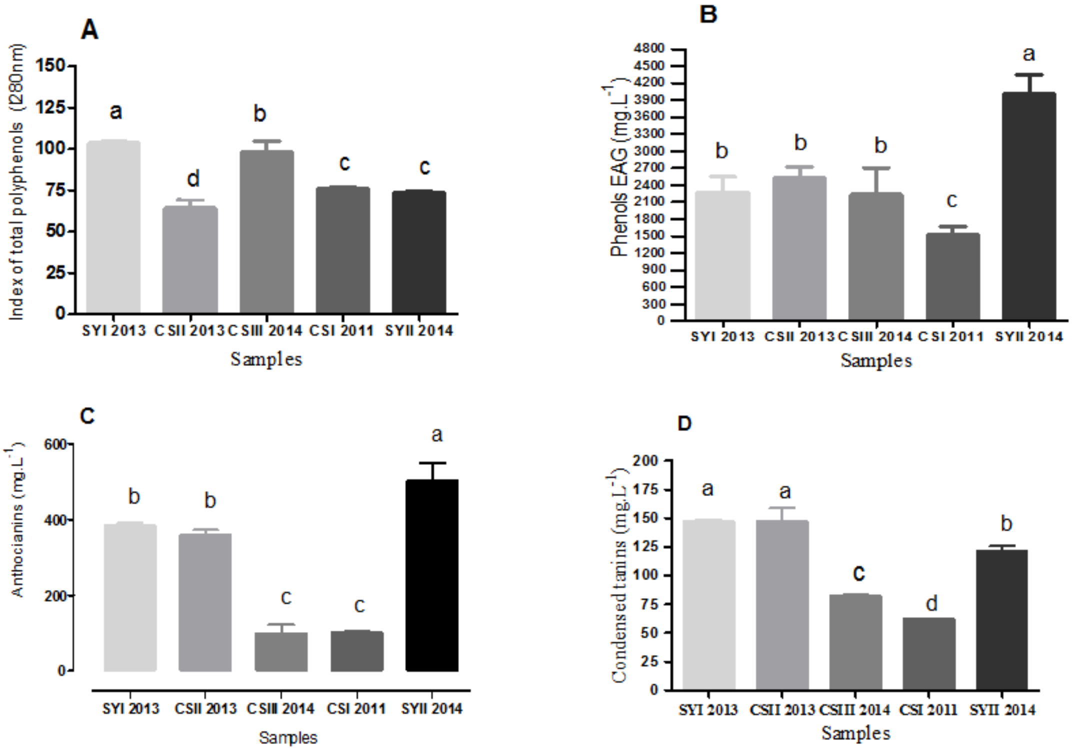

Figure 1. Total polyphenols index (A),concentration total phenolics expressed as gallic acid equivalents (B), total anthocyanins expressed in mg.L^{-1} of 3-glucose malvidin, (C) condensed tannins in mg.L^{-1} (D) of Cabernet Sauvignon and Syrah wines. Cabernet Sauviginon/winery I/2011 (CS I 11); Cabernet Sauvignon/ winery III, 2014 (CS III 14); Cabernet Sauvignon/winery II/2013 (CS II13); Syrah/winery I/2013 (SY I 13); and Syrah/wirery II/2014 (SY II 14). ANOVA one way followed by Bonferonni's post-test. Differents letters indicate significance variation ($p<0.05$)

Table 2. Phenolic profile of Cabernet Sauvignon and Syrah wines, 2011, 2013 and 2014 vintages of the São Francisco Valley

Compounds	Concentration in wines (mg.L^{-1})				
	SY I 13	CS II 13	CS III 14	CS I 11	SY II 14
Gallic acid	58.26 ± 0.26^{a}	29.78 ± 0.13^{b}	38.05 ± 0.82^{a}	32.73 ± 0.00^{b}	69.05 ± 000^{a}
Vanillic acid	4.80 ± 0.05^{c}	4.43 ± 0.12^{c}	44.36 ± 0.75^{a}	3.12 ± 0.00^{d}	6.13 ± 0.00^{b}
Syringic acid	5.38 ± 0.22^{a}	$1.42\pm0.01^{b,a,c}$	$0.56\pm0.00^{c,d,b}$	ND	$0.34\pm0.00^{d,c}$
Caffeic acid	38.10 ± 0.23^{a}	7.81 ± 0.35^{d}	15.16 ± 0.30^{c}	ND	33.02 ± 0.00^{b}
Ferulic acid	3.11 ± 0.15^{a}	ND	3.94± 0.00a	ND	2.06±0.00b
Cumaric acid	ND	1.09 ± 1.00^{b}	$1.68\pm0,00^{a}$	ND	ND
Elagic acid	ND	ND	ND	ND	ND
Catechin	45.73 ± 0.08^{b}	32.99 ± 2.11^{c}	57.27 ± 0.04^{b}	81.00 ± 0.00^{a}	29.05 ± 0.00^{d}
Resveratrol	10.66 ± 0.05^{b}	2.75 ± 0.05^{c}	2.67 ± 0.52^{a}	2.89 ± 0.00^{a}	10.48 ± 0.00^{b}
Myricetine	3.07 ± 0.14^{b}	1.79 ± 0.03^{d}	$2.75\pm0.13^{c,b}$	1476 ± 0.00^{a}	$0.62\pm0.00^{c,d}$
Quercetin	13.66 ± 0.30^{b}	25.84 ± 0.09^{a}	12.52 ± 0.19^{b}	ND	9.26 ± 0.00^{c}
Kaempferol	ND	0.22±0.02	0.75±0.00	ND	ND
Rutin	5.29 ± 0.03^{a}	0.56 ± 0.00^{d}	4.77 ± 0.00^{c}	ND	5.02 ± 0.00^{b}

Mean and standard deviations with horizontal letters do not differ significantly from one another by ANOVA followed by Benferoni tests ($p<0.05$). ND - not detectable; Cabernet Sauviginon/winery I/2011 (CS I 11); Cabernet Sauvignon/ winery III, 2014 (CS III 14); Cabernet Sauvignon/winery II/2013 (CS II 13); Syrah/winery I/2013 (SY I 13); and Syrah/wirery II/2014 (SY II 14). ANOVA one way followed by Bonferonni's post-test. Differents letters in the lines indicate significance variation ($p<0.05$).

The phenolic profile of the Cabernet Sauvignon and Syrah red wine samples analyzed in our study (Table 2).

The phenolic profile of the Cabernet Sauvignon and Syrah red wine samples analyzed in our study (Table 2) presented mean values of Gallic Acid ranging from 29.78 to 38.05 mg.L^{-1} in Cabernet Sauvignon wines and 58.26 to 69.05 mg.L^{-1} in Syrah wines. Catechin ranged from 32.99 to 81.00 mg.L^{-1} in Cabernet Sauvignon wines and 29.05 to 45.73 mg.L^{-1}, mean values of Vanillic Acid ranged from 4.43 to 44.36 mg.L^{-1}.

On the other hand, Resveratrol presented mean values ranging from 2.75 to 26.89 mg.L^{-1} in Cabernet Sauvignon wines and 10.66 to 10.48 mg.L^{-1} in Syrah wines, Syringe Acid between 1.42 To 0.56 mg.L^{-1} in Cabernet Sauvignon wines and 0.34 to 5.38 mg.L^{-1} in Syrah wines. Caffeic acid varied in average from 7.81 to 15.16 mg.L^{-1} in Cabernet Sauvignon wines and 33.02 and 38.10 mg.L^{-1} in Syrah wines.

For Ferulic Acid, we observed average variations of 3.94 mg.L^{-1} in Cabernet Sauvignon wines and 2.06 to 3.11 mg.L^{-1} in Syrah wines. Mice with mean values of 1.79 to 14.76 mg.L^{-1} in Cabernet Sauvignon wines and 0.62 to 3.07 mg.L^{-1} in Syrah wines, Quercetin ranged from 12.52 to 25 , 84 mg.L^{-1} in Cabernet Sauvignon wines and 9.26 to 13.66 mg.L^{-1} in Syrah wines, Campferol with 0.22 to 0.75 mg.L^{-1} in Cabernet Sauvignon wines, Rutina With mean values varying from 0.56 to 4.77 mg.L^{-1} in Cabernet Sauvignon wines, 5.02 to 5.29 mg.L^{-1} in Syrah wines and Cumaric Acid had mean values varying from 1.09 to 1.09 1.68 mg.L^{-1} in Cabernet Sauvignon wines.

Results of our study on antioxidant activity (Figure 2), determined by percentage of free radical sequestration activity (% SA) of DPPH*, showed mean values varying 58.02 at 95.70% in the Syrah wine and 82.32 at 85.08% in Cabernet Sauvignon ones. Significant differences were found in Syrah wines and absence of significance were observed among Cabernet sauvignon wines.Therefore, the results of these studies allow to consider that the wines analyzed in this study have good antioxidant activity or free radical sequestration.

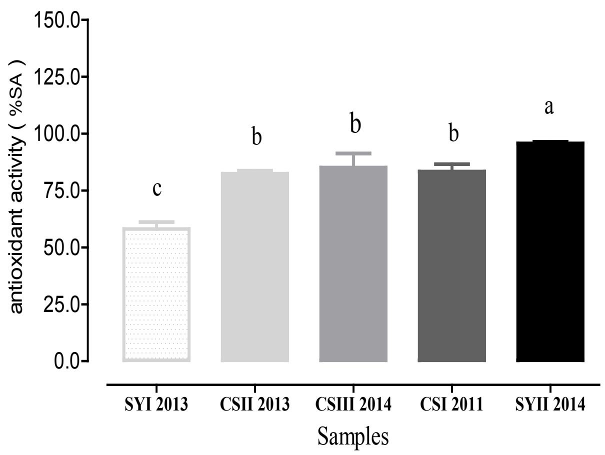

Figure 2. Antioxidant activity, percentage of free radical sequestration activity (% SA) of DPPH* in wines of Cabernet Sauvignon/winery I/2011 (CS I 11); Cabernet Sauvignon/ winery III, 2014 (CS III 14); Cabernet Sauvignon/winery II/2013 (CS II 13); Syrah/winery I/2013 (SY I 13); and Syrah/wirery II/2014 (SY II 14). ANOVA one way followed by Bonferonni's post-test. Different letters indicate significance variation (p <0.05)

The Table 3 shows the correlations between the different parameters of the Cabernet Sauvignon wines of 2011, 2013, 2014 and Syrah wines of 2013 and 2014.

Table 3. Correlations between the antioxidant activity (%SA) and the different parameters of wines from Cabernet Sauvignon of 2011, 2013, 2014 and Syrah 2014 seasons

%SA of the samples	Correlation coeficiente (r^2)					
	TPI	CI	T	ANT	TP	TN
CS II13	0.543*	0.503*	0.114	0.588*	0.500*	0.555**
CS III 14	0.940*	-0.083	0.250	0.085	0.283	0.269
CS I 11	-0.144	0.361	0.139	-0.877**	-0.144	-0.565
SY II 14	-0.116	-0.003	-0.318	0.142	-0.116	0.865**
SY I13	-0.354	-0.177	-0.038	0.230	-0.227	0.423

Correlation of Person is significant for (p<0.05*) and (p<0.01**), 2-tailed and the confidence interval is 95%. The values indicate the correlation coefficient of Person - r^2 of the free radical scavenging activity (% SA). Cabernet Sauviginon/winery I/2011 (CS I 11); Cabernet Sauvignon/ winery III, 2014 (CS I 14); Cabernet Sauvignon/winery II/2013 (CS II 13); Syrah/winery I/2013 (SY I 13); and Syrah/wirery II/2014 (SY II 14); total polyphenols index (PTI); color intensity (CI); tonality (T); total anthocuanins (ANT); total polyphenols (TP); tannins (TN).

The Cabernet Sauvignon wine, harvest 2013, obtained a moderate positive correlation between total polyphenol index, color intensity, total anthocyanins and total polyphenol with antioxidant activity, (r^2>0.5). Cabernet Sauvignon, harvest 2014, had a strong positive correlation between total polyphenol index and antioxidant activity (r^2> 0.9), while the same cultivar harvest 2011 had a strong inverse correlation between total anthocyanins (r^2<-0.8). However, we did not observe relationships between the parameters analyzed with the antioxidant activity in the Syrah wines of 2013 and 2014 harvests.

4. Discussion

4.1. Phenolic Composition of the Wines and Its Antioxidant Activity “in vitro”

The characterization of the cultivars and vintages of the wines of the SãoFrancisco Valley show great diversity in the indices evaluated as intensity of color, phenolics, anthocyanins, condensed tannins and the phenolic profile.

The color index average in the Syrah and Cabernet Sauvignon (8.08 to 15.03) wines in our study are superior to those found in wines from Serra Gaucha [31] witch found color index varying around 10.4.On the other hand, some studies [34] with red and dry table wines produced in the central region of Rio Grande do Sul did not find any difference in color intensity among the wines analyzed.

The values for tonality of the wines of the present study vary from 0.72 to 1.01, being very similar to the European wines from of Cabernet Sauvignon of the region of Slovakia [35]

The diversity of results between the studies may be due to the great variation among the samples, since they are quite heterogeneous in relation to the type of grape, cultivar and crop [34]. However, color is one of the main sensory qualities of red wine, with great importance, since it is the first element of appreciation observed by the consumer, being a characteristic usually associated with the beneficial properties for health. In addition, the intensity of the color can provide information about possible defects or qualities of a wine [34].

The variation of yellow and blue colors in the different cultivars and harvests analyzed in our study are similar to those found in the studies with wines from Serra Gaucha [31] who found the percentage of yellow varying around 41.3% and the red in 48.6%, the percentage of blue of showed to be inferior to the present study, around 10.6%.

The results in our study indicate that the wines Syrah and Cabernet Sauvignon of the São Francisco Valley of the studied crops, present a maximum absorbance at 520nm. This finding runs counter to the hypothesis that the spectrum of young red wines exhibits a more or less narrow absorbance maximum at 520 nm due to anthocyanins and their combinations in the form of flavilium ion, which decreases with aging and Increases its absorbance at 420nm, in the region of yellow-brown where the absorbance is minimal [36].

However, the color varies in consonance with the chemical structures and the physical-chemical conditions of the wine, being able to vary from pink to blue with the increase of hydroxyl groups. The inverse effect is observed when hydroxyl groups are replaced by methoxy groups [36]. In wines, the color is also related to the techniques of vinification and the numerous reactions that take place during its storage. In the particular case of red wines, the color varies constantly during vinification and storage, with consequent organoleptic changes. These modifications occur due to the reactivity of the wine's phenolic compounds [34].

In relation to total polyphenols content (Figure 1A), we have noted that there are no significant differences between the wines Syrah of 2013, Cabernet Sauvignon of 2013 and Cabernet Sauvignon of 2014 for $p<0.05$. However, phenolic compounds play a key role in determining wine quality [37]. The differences are influenced by grape type, growing conditions and various factors related to processing [38].

In relation to total phenolic equivalent to gallic acid (Figure 1B), the significance between Syrah of 2013 wines and Cabernet Sauvignon of 2011 and 2014 wines corroborates with studiesin red wines from several countries of the Southern Hemisphere (Brazil-São Francisco Valley and Rio Grande do sul, Chile, Australia and South Africa) [22]. These authors found some significant differences in the polyphenol contents in Cabernet Sauvignon and Syrah wines from the São Francisco Valley. Our results are also similar to the findings of that observed significant differences ($p <0.001$) among different cultivars [37]. On the other hand, the values of phenolic equivalent to gallic acid found in our study presented higher valuesthan those found in the study with samples of Italian red wine from the 2015 harvest [39]which presented values ranging from $114mg/L^{-1}$ to $330mg/L^{-1}$. However, our results are similar to the findings that observed significant differences ($p <0.001$) among different cultivarsof wines from 13 clones of Autochthon caste Prokupacwhich had polyphenols content equivalent to gallic acid ranging from $114mg.L^{-1}$ to $330mg.L^{-1}$.

The proportion of different polyphenols in wines may vary according to the type of total phenolic content and vinification processes. These factors when combined with the total anthocyanins proanthocyanidin and tannin content determine the quality of the wine. The amount and composition of polyphenols also depends on genetic, environmental and cultural practices, as well as grape morphology [37]. On the other hand, phenolic compounds can be influenced by the alcoholic content of the wine, since the increase of ethanol during alcoholic fermentation results in the progressive denaturation of pigments due to the rupture of hydrogen bridges between the phenolic compounds, transforming them into colorless substances [40].

The content of totoal anthocyanins found in our study (Figure 1C), agree with previous study [35] with wines of Cabernet Sauvignon cultivar from different areas of Slovakia, anthocyanin levels ranged from $68.6\ mg.L^{-1}$ to $430.7\ mg.L^{-1}$. However, another studies found average anthocyanin levels of $299.4\ mg.L^{-1}$ [34]. A study conducted in Italian wines of nine cultivars, anthocyanin values ranged from 18 to $687mg.L^{-1}$ [41] as found in wines from different countries in the southern hemisphere anthocyanins ranging from 101.96 to $230.51\ mg.L^{-1}$ for the Syrah cultivar and 108.48 to $279.58\ mg.L^{-1}$ for the Cabernet Sauvignon cultivar, which are lower than the findings in this study for the same cultivars [22].

Anthocyanins constitute the highest percentage of phenolic compounds, representing important constituent red wines because they contribute to the sensorial attributes and, mainly, to the coloration of the wine [42]. It is probable that the quantities of monomeric anthocyanins were not responsible for the high phenolic content of the SãoFrancisco Valley samples [43]. Several beneficial properties have been attributed to anthocyanins (dietary flavonoids), including antioxidats effects.

The content of condensed tannins ($0.5g.L^{-1}$ at $1.5g.L^{-1}$) are the main phenolic compounds of red wine. Thus tannins play an important role in astringency and also contribute to the sensation of bitterness [44]. However, its quantity in the wines is related to the extraction form in the vinification process [34]. On the other hand, tannins are characterized as high molecular weight phenolic compounds that precipitate proteins, including salivary proteins from the oral cavity. These properties are fundamental to explain the role of tannins in protecting the body against diseases [47]. The tannins are co-pigments formed by condensation of anthocyanins and tannins that can occur by several mechanisms depending on the compounds involved and can form compounds of different characteristics [44]. Tannins as well as other phenolic compounds are important for wine quality, quantities and extractable qualities, they depend on a number of factors that interfere positively or negatively (climatic conditions, soil composition, genetic factors inherent in the grape, cultural treatment and stage of maturation) [34]. Acording to Vilela et al., [44], the tannins are extracted at the beginning of the maceration and during the alcoholic fermentation when there is formation of ethanol that solubilizes them.

In relation to the phenolic profile of the wines analyzed in our study, gallic acid had lower mean values than the wines from Turkey studied by Anli and Vural [52], ranging from 40.8 to 70 mg.L^{-1} and higher than the mean values of catechin ranging from 19.3 to 3.9 mg.L^{-1}. However, gallic acid has many healthy properties, including antioxidant, neuroprotective and antimicrobial effects [44] and catechin is the most important flavanol that can be found in bark and grape seeds, representing 60% of the phenolics responsible for the astringency and structure of wines [46].

The mean values of resveratrol found in our study are higher than those found in red wines from several countries of the Southern Hemisphere (Brazil-São Francisco Valley and Rio Grande do sul, Chile, Australia and South Africa) [22], which ranged from 0.00 to 0.32 mg.L^{-1} in Cabernet Sauvignon wines and 0.00 to 0.29 in Syrah wines. However, resveratrol by enzymatic hydrolysis of its glycosides can lead to free *trans-* and *cis*-resveratrol structures, whose concentration depends on grape variety, possible fungal contamination and climatic conditions, which conditions its variation [19]. On the other hand, studies have demonstrated that the vinification process is the factor responsible for the high levels of resveratrol in red wines, when compared to white wines [48]. Although resveratrol is the major functional component in red wines, its concentration is low relative to other phenolic compounds. But in our samples, the Cabernet Sauvignon cultivar of 2011 and Syrah of 2014 showed the best values.

The mean values of vanillic and sirigic acids found in our study were higher than those found by Silva et al. [22] of 5.89 mg.L^{-1}, 3.89 mg.L^{-1} and 2.42 mg.L^{-1} in African wines, Rio Grande do Sul and Australians, respectively. Hydroxybenzoic acids comprise *p*-hydroxybenzoic acid, syringic acid, vanillic acid and gallic acid.Gallic acidcould be also originated from the hydrolysisof gallate esters of hydrolyzable tannins and condensed tannin [44].

The significant differences ($p<0.05$) in the antioxidant activity in the Syrah wines of the 2013 and 2014 harvests in this study, contradict the findings in Slovak cabernet sauvignonred wine analysis for the determination of antioxidant activity that did not present significant differences ($p=0.05$) [35]. However, studies from South American red wines emphasized that the effectiveness of antioxidants is dependent on the energy required to provide dissociations between oxygen and phenolic hydrogen, pH, reduction potential, solubility, structure and antioxidant radical location (group - OH) [49]. On the other hand, solvents, preservatives and excessive alcoholic additives can influence the quantification of phenolic compounds and antioxidant activity as demonstrated by [11,50].

In the study from the analysis of red wines of the cultivar Cabernet Sauvignon and Syrah, produced in different countries of the Southern Hemisphere (Brazil - São Francisco Valley) and Rio Grande do Sul, Chile, Australia and South Africa) harvest of 2012 verified by the DPPH* method variations between 96.8% and 97.47% [22]. These values are higher than the mean values found in our study. However, our results are superior to those found in samples of Cabernet Sauvignon wines from several areas of Slovakia that had free radical sequestering activity ranging from 69.0% to 84.2% [35]. The antioxidant capacity of Turkish red wines when compared to wines from Spain, Portugal and California showed better antioxidant activity between 18.1% to 22.6% [52]. Studies carried out in Brazil, Argentina and Chile showed respectively antioxidant activity of 66.44%, 67.71% and 55.25% [49], showing a very similarity with the results found in our study. Other regions of the world showed antioxidant activity around 71.30 to 83.53% for wines from the Balkan region [50] and 54.6 to 82.6% for red wines from Croatia [53]. Therefore, the results of these studies allow considering that the wines analyzed in this study have good antioxidant activity or free radical sequestration.

The correlations evaluated in our study reveal that similarities between color intensity (CI), total polyphenolindex (TPI) and total polyphenol contente (TP) are in agreement with results obtained by [22]. However positive correlation between antioxidant capacity and total phenol content ($r^2> 0.5$) was found in dry red table wines produced in the region of Rio Grande do Sul [34]. Similarly, another study demonstrated the existence of a strong correlation ($r^2=0.99$) between antioxidant activity and total polyphenols in red wine samples from Curitiba, Garibaldi and Campo Largo [54].

However, among the external factors that can intervene in the low extractability of the compounds are the anthocyanins present in the cells of the grape bark, in the free form inside the vacuoles, that can be diluted by the sap accidentally released in the berry causing its content to be detected on a small scale during the analysis [37]. This may explain in part the low correlation found in the results of this study between antioxidant capacity and anthocyanin and color content as well [37].

5. Conclusion

The wines of the Cabernet Sauvingnon cultivar of 2011, 2013 and 2014 harvests analyzed in our study showed best values of total polyphenols and potent antioxidant capacity when compared with other studies.

Although we did not find correlations between the parameters analyzed in our study with the antioxidant activity in wines of the Syrah cultivars the correlations of Cabernet sauvignon wines are in agreement with previous studies.

The results of this study point to the influence of the phenolic type present in the wines on its antioxidant capacity.

These results can be associated with possible beneficial effects on health.

Potential Conflict of Interest

We declare that there is no relevant conflict of interest.

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