Particularities of Syrah wines from different growing regions of Southern Brazil: grapevine phenology and bioactive compounds

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Abstract The aim of this study was to monitor the phenological parameters of grapevine (*Vitis vinifera*) of Syrah variety recently introduced in the region of Marari, Água Doce, Campos Novos and São Joaquim, Santa Catarina State (SC), Brazil, and to characterize the phenolic composition and antioxidant activity of wines produced from this variety of the vintages 2010 and 2011. The adaptation of the grapevine to climate conditions of these grape growing regions of Southern Brazil for this variety has also been assessed. The climate variations occurring between the phenological cycles of grapevine of Syrah for each growing region influenced the phenological extension and heat accumulation of the grapevine. The wines showed significant levels of phenolic compounds and high antioxidant activity, while catechin, a potent antioxidant, was the main phenolic compound quantified in wines. Positive

correlations between the phenolic compounds and antioxidant activity were observed. The principal component analysis confirmed the influence of the growing region and vintages on the phenolic composition of wines, indicating the importance of climate conditions. This study identified possible phenolic markers indicative of climatic influence.

Keywords *Vitis vinifera* · Climate · Wine · Bioactive compounds · Antioxidant activity · Food quality

Introduction

Phenolic compounds constitute one of the most important wine quality parameters since they contribute to the sensory characteristics, in particular the color, flavor and astringency. Polyphenols have been associated with the bioactive potential of wine due to their antioxidant properties, with cardioprotective effects and other health benefits (Gómez Gallego et al. 2012; Gris et al. 2013).

All polyphenols, both class of flavonoids and non-flavonoid, contribute to the characteristics of wine. Factors such as the stage of grape ripeness at harvest, winemaking technology and specific climatic conditions of the growing regions affect the composition of wine (Jones and Davis 2000; Orduña 2010). The chemical characterization of wine phenolics is carried out in order to identify the characteristics of the production region (Stockham et al. 2013) and thus find the determinant factors of expression of a *terroir*.

In viticulture the phenological stages of the grapevine are important in relation to characterizing the grape varieties, as well as the different growing regions (Orduña 2010). Phenological phases vary with genotype, climatic conditions and geographical location and these factors have been recognized as influencing the quality of the grapevine

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(Jackson and Lombard 1993). Grapevines are cultivated in different climatic regimes around the world and there is an optimum seasonal climate regime that greatly contributes to their quality (Jones and Davis 2000).

The climatic conditions in some regions of Santa Catarina State (SC) in southern Brazil are promising for the development of viticulture. The wine growing tradition of this state was established with the production of American and hybrid grapes. However, a new viticulture has begun to be implanted in the state based on vineyards located in regions considered of altitudes (900 m above sea level), with the purpose of producing grapes *Vitis vinifera* for the production of quality wines and increasing the competitiveness of Brazilian wines (Protas and Camargo 2011).

The aim of this study was to monitor the phenological parameters of grapevine (*Vitis vinifera*) of the Syrah variety recently introduced in the regions of Marari, Água Doce, Campos Novos and São Joaquim, Santa Catarina State (SC), Brazil, and to characterize the phenolic composition and antioxidant activity of the wines produced with this variety of the vintages 2010 and 2011. The study sought to identify a relationship between the adaptation of this variety to the climatic conditions of these growing regions of the South of Brazil, which so far have not been studied, as well as the quality and phenolic characteristics of the wines produced.

Materials and methods

Chemicals and reagents

The phenolic compounds standards, DPPH (1,1-diphenyl-2-picrylhydrazyl), ABTS [2,2-azino-bis (3-ethylbenzothiazoline-6-sulphonic acid)], Trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid), Folin-Ciocalteu, TPTZ [2,4,6-tri (2-pyridyl)-s-triazine acid] were obtained from Sigma-Aldrich (St. Louis, Missouri, USA). The DMACA (p-dimethylaminocinnamaldehyde) reagent was purchased from the Fluka Company (Steinheim, Germany). All chromatographic solvents were HPLC grade and were purchased from Merck (Darmstadt, Germany). Milli-Q water was obtained from a Milli-Q Plus water system (Millipore, Bedford, MA, USA).

Stock solutions of individual phenolic compounds (1 g L^{-1}) were prepared in methanol and kept in the dark under refrigeration (4°C). The working standard solutions were prepared in a synthetic wine system (alcohol solution 12% v/v ethanol added to 5 g L^{-1} of tartaric acid with a final pH of 3.2).

Samples and location

The study was conducted on red wines produced from grapes of the Syrah variety from crops grown in four

different regions of altitude (around 900 m above sea level) in Santa Catarina State (SC) in southern Brazil, during the phenological cycles 2010/2011 (vintage 2011) and 2011/2012 (vintage 2012). The vineyards are located in the following experimental areas: I) São Joaquim Unit, located in São Joaquim, with 1415 m of altitude, $28^\circ16'50''\text{S}$ latitude and $49^\circ57'00''\text{W}$ longitude; II) Campos Novos Unit, located in the municipality of Campos Novos, with 965 m of altitude, $27^\circ19'83''\text{S}$ latitude and $50^\circ49'18''\text{W}$ longitude; III) Tangará Unit—located in Saw do Marari, with 1059 m of altitude, $27^\circ12'24''\text{S}$ latitude and $51^\circ06'96''\text{W}$ longitude; and IV) Água Doce Unit, located in Água Doce, with 1300 m of altitude, $26^\circ43'53''\text{S}$ latitude and $51^\circ30'26''\text{W}$ longitude (Supplementary Material). The vineyards were planted in 2006, in a vertical trellis system, with a planting spacing of 3.00 m between rows and 1.50 m between plants. The seedlings of the Syrah variety grapevines, clone Italian ENTAV 470, were of the grafted rootstock Paulsen 1103 113F.

Microvinification

The grapes at harvest showed good technical maturity with means values of 19 °Brix, pH of 3.6 and total acidity of 7.5 g L^{-1} of tartaric acid, both vintages. The wines were produced by microvinification under the same conditions at Epagri (Empresa de Pesquisa Agropecuária e Extensão Rural de Santa Catarina) in Videira, SC. The grapes were separated from the bunches and kept in a stainless steel tank (20 L). The maceration period was 10 days, with twice daily pumping. The must was separated from the solid matter and transferred to a stainless steel tank. Before starting the alcoholic fermentation, a commercial sulfiting agent was added to the must ($20 \text{ g}/100 \text{ kg}$ of must, corresponding to 10 mg L^{-1} free SO_2) (Noxitan, Pascal Biotech, Paris), and at the beginning of alcoholic fermentation *Saccharomyces cerevisiae* was added ($20 \text{ g}/100 \text{ kg}$) (Fermol Rouge, Pascal Biotech). After fermentation the wine was stabilized in cold storage for 20 days, free SO_2 was added (40 mg L^{-1}) (Noxitan Pascal Biotech, Paris) and the samples were then bottled.

The wines of vintage 2011 were analyzed after 2 years of storage and the wines of vintage 2012 after 1 year of storage. The wines showed suitable enological parameters with means values of pH of 3.5, total acidity of 5.6 g L^{-1} of tartaric acid, volatile acidity of 0.45 g L^{-1} of acetic acid and alcohol content of 10.7% vol., vintages 2011 and 2012. For the purposes of this study the wines were coded as Mr, AD, CN and SJ wines, corresponding to wines made from grapes grown in the regions of Marari, Água Doce, Campos Novos and São Joaquim, respectively.

Climatic characterization and phenology

The monitoring of the climatic conditions was conducted by collecting data from automatic weather stations located at each experimental unit belonging to Epagri/Ciram (Centro de Informações de Recursos Ambientais e Hidrometeorologia de Santa Catarina)—Florianópolis, SC. The climatic parameters on which data was collected were the maximum and minimum air temperatures (°C), thermal amplitudes (°C), rainfall (mm), relative humidity (%) and global solar radiation (MJ m^{-2}). The climatic characterization of each unit was carried out considering the bioclimatic index for viticultural zonation, corresponding to the heat accumulation as growing degree days (GDD). To calculate the GDD were used the data on the air temperature, using the following formula: $\text{GDD} = \sum_{\text{maximum}} \{[(T_{\text{maximum}} + T_{\text{minimum}})/2] - 10.0\}$, 10 °C being the base temperature of the grapevine, according Hall and Jones (2010). For the calculation, were considered the average temperatures recorded between the subperiods budburst and harvest of the grapes for each experimental area. The regions were rated according to Winkler et al. (1974) and classified according to the phenological development of the Syrah variety.

For the definition of phenological stages of the grapevines the BBCH scale (Lorenz et al. 1995) was used. The main stages of development considered were: budburst (BBCH07); blooming (BBCH65); véraison (BBCH85) and full véraison (harvest)—established based on the evaluation of the chemical composition of the berries and health of plants. Thus, the number of days between each phenological subperiod for the Syrah variety was determined and the average values were identified for each experimental unit (Bock et al. 2011).

Wine characterization

Spectrophotometric analysis

The spectrophotometric analysis of the wines was carried out using a UV–Vis spectrophotometer (Hitachi U-2010, CA, USA). The total monomeric anthocyanins (mg L^{-1} malvidin-3-glucoside) were quantified using the method of differential pH (Giusti and Wrolstad 2001). The content of total polyphenols (mg L^{-1} gallic acid) was determined through the Folin-Cicalteu reaction (Singleton and Rossi 1965). The *ortho*-diphenols (mg L^{-1} catechin) were determined using Arnow's reagent (Flanzy and Aubert 1969), and the determination of total flavanols (mg L^{-1} catechin) was performed using *p*-dimethylaminocinnamaldehyde (DMACA) (Arnous et al. 2002). The in vitro antioxidant activity of wines was assessed using the

methods FRAP (Benzie and Strain 1996), DPPH (Kim et al. 2002) and ABTS (Re et al. 1999), the results expressed in Trolox equivalent (mmol TEAC L^{-1}).

HPLC analysis

Chromatographic analysis was performed using a high performance liquid chromatograph (Shimadzu, Kyoto, Japan). The separations were performed using C18 reverse-phase column (4.6×250 mm, 5 μm in particle size) and C18 guard column (4.6×12.5 mm) (Shimadzu L-ODS, Kyoto, Japan). Detection of the compounds was performed using a photodiode array detector (DAD). The wine samples were filtered through a 0.45 μm PTFE membrane filter (Millipore, Massachusetts, USA) and injected into the chromatography system.

The individual phenolic compounds of the groups flavonols (myricetin, quercetin, kaempferol), flavanols (catechin and epicatechin) cinnamic derivatives (*p*-coumaric, caffeic, ferulic and *trans*-caftaric), tyrosol and *trans*-resveratrol were determined according to the method proposed by Ferreira-Lima et al. (2013). Mobile phase A was $\text{H}_2\text{O}:\text{CH}_3\text{COOH}$ (98:2 v/v) and mobile phase B was $\text{H}_2\text{O}:\text{CH}_3\text{COOH}:\text{CH}_3\text{CN}$ (58:2:40 v/v/v). The gradient elution conditions were: 0–80% solvent B for 55 min, 80–90% B for 15 min, 90–100% B for 20 min, and finally 0% B for 10 min (conditioning step). The flow rate was 1.0 mL min^{-1} . The detection of tyrosol, catechin, and epicatechin was carried out at 280 nm, the hydroxycinnamic acids detection at 320 nm, flavonols detection at 360 nm and *trans*-resveratrol detection at 306 nm.

The hydroxybenzoic acids (gallic, protocatechuic, vanillic, syringic and ellagic acids) were determined according to Burin et al. (2011a). Mobile phase A was $\text{H}_2\text{O}:\text{CH}_3\text{COOH}$ (98:2 v/v) and mobile phase B was 20% of mobile phase A with 80% of CH_3CN . The elution was carried out applying a linear gradient: 0–30% solvent B for 35 min, 30–50% B for 5 min, 50–100% B for 5 min, and finally 0% B for 15 min to recondition the column in preparation for a new chromatographic run. The flow rate was 1.2 mL min^{-1} with detection at 280 nm for all phenolic compounds, with the exception of ellagic acid which was detected at 254 nm.

The contents of anthocyanin monoglucosides (malvidin, cyanidin, delphinidin and peonidin) were determined according to Revilla et al. (1999). Mobile phase A was $\text{H}_2\text{O}:\text{CH}_2\text{O}_2$ (90:10 v/v) and mobile phase B was $\text{H}_2\text{O}:\text{CH}_4\text{O}:\text{CH}_2\text{O}_2$ (45:45:10 v/v/v). The elution gradient was obtained with a concentration of 35–95% solvent B for 20 min, 95–100% B for 5 min and 100% B for 5 min. The flow rate was 0.8 mL min^{-1} , with detection of the compounds at 520 nm. The determination and quantification of all compounds was carried by constructing a calibration

curve prepared by overlaying the array with a synthetic wine system.

Statistical analysis

All analysis was carried out in triplicate. The STATISTICA v. 8.0 (2007) (StatSoft Inc., Tulsa, OK, USA) software program was used for the analysis of variance (ANOVA), Tukey HSD test ($p < 0.05$), correlation analysis and principal component analysis (PCA).

Results and discussion

Climatic characterization and phenology

The main climatic parameters monitored during the phenological phases from the budburst to harvest for the grapes of the Syrah variety cultivated in the regions of Marari, Água Doce, Campos Novos and São Joaquim, SC, are shown in Fig. 1. The mean maximum temperatures recorded during the period from budburst to harvest of the grapes in the different growing regions ranged from 17.9 to 27.1 °C during 2010/2011 and from 19.0 to 28.2 °C during 2011/2012 (Fig. 1a, b). During the same period, the average minimum temperatures were 8.4–17.1 °C for 2010/2011 and 9.3–17.4 °C for 2011/2012 cycle (Fig. 1c, d). The highest air temperatures (maximum and minimum) were recorded in the wine growing region of Campos Novos (lowest region) while the region of São Joaquim (highest region) had the lowest temperatures. According to Jackson (2008), the annual temperature tends to decrease by around 0.5 °C for each 100 m of altitude, so altitude can significantly affect the maturation of the grapes.

The values for the total volume of rainfall registered during the phenological period of budding to harvest of the grapes in 2010/2011 cycle were approximately 900 mm for Marari, 1100 mm for Água Doce and Campos Novos, and 1500 mm for São Joaquim (Fig. 1e). With regard to 2011/2012 cycle the corresponding values were, in general, lower (900 mm for Marari, Campos Novos and São Joaquim, and 700 mm for Água Doce), demonstrating that this cycle was drier than the previous one (Fig. 1f). These values can be considered high for grapevines, since the ideal amount of rainfall during the entire phenological cycle is around 700–800 mm (Jackson and Lombard 1993). The climate database of the studied regions demonstrate that these conditions were reported in their historical series, being that the mean rainfall in these regions was 1180 mm for Marari, 1196 mm for São Joaquim, 1094 mm for Campos Novos and 998 mm for Água Doce. Excessive rainfall favors the occurrence of fungal diseases and increases the incidence of rot, hence the process of

maturation is delayed or not completed due to low solar radiation and high availability of soil water (Jackson and Lombard 1993). The relative humidity of the wine growing regions studied ranged from around 70 to 80% and the thermal amplitudes obtained during the cycles studied were very similar for all regions, with values close to 10 °C (data not shown).

The accumulated global solar radiation during the phenological cycle was higher in São Joaquim (4589 MJ m⁻²), followed by Água Doce (4263 MJ m⁻²), Campos Novos (3961 MJ m⁻²) and Marari (3579 MJ m⁻²). The difference between the growing regions is the result of times of occurrence of the onset of budburst and the end véraison, as well as the duration of these phenological phases. The monitoring of this parameter is important, since radiation influences the photosynthetic activity, and consequently, the satisfactory development of the fruit (Jackson and Lombard 1993).

The results for the heat accumulation in growing degree-days (GDD) for the Syrah variety are shown in Fig. 2. In both cycles evaluated, the precocious occurrence of the phenological cycle was observed in the vineyard of Campos Novos, with a heat accumulation of up 1700 GDD. A later cycle was observed for the São Joaquim vineyard, with a heat accumulation of close to 1300 GDD. For the vineyards of Marari and Água Doce the heat accumulation was around 1500 GDD. The heat accumulation during the main phenological events of the grapevine, according to the Winkler index, classified São Joaquim as “Region I” which features a cold climate (<1.389 GDD); the regions of Marari and Água Doce as “Region II” with moderately cold climates (1.390–1.667 GDD); and Campos Novos as “Region III”, rated as a mild climate region (1.668–1.944 GDD), according to the Winkler et al. (1974), as modified by Hall and Jones (2010). These results were also observed in other studies with the regions of São Joaquim (Falcão et al. 2010; Gris et al. 2010; Borghezani et al. 2011; Burin et al. 2011b), and Água Doce (Falcão et al. 2010). However, research related to the classification of the regions of Marari and Campos Novos in Santa Catarina State were scarce and the study reported herein represents the first classification of these wine producing regions according to the Winkler scale.

The durations of the main phenological stages of the grapevines of the Syrah variety are shown in Table 1. For both cycles, it was found that budburst occurred between September and early October. Precocious budding occurred in the growing region of São Joaquim. For the same period, late budburst was recorded for the region of Água Doce. Véraison of the grapes took place in February and March. The grape harvest took place between the months of March and April, and the earliest harvest occurred in Campos Novos, while the latest harvest was recorded for São Joaquim.

Fig. 1 Climatic parameters obtained for the phenological phases of budburst to harvest for grapes grown in the regions of Marari (Mr), Água Doce (AD), Campos Novos (CN) and São Joaquim (SJ), SC, cycles 2010/2011 and 2011/2012

It was observed that the longest phenological cycles occurred in the São Joaquim region, this region showed a precocious budburst and late harvest, and a longer period for the maturation of the grapes. The shortest duration of

the phenological cycles was recorded for the region of Campos Novos. According to Jackson (2008), plant growth is related to climate changes, mainly during the maturation phase. In warm environments, the grapevine passes through

Fig. 2 Heat accumulation (GDD) for the main phenological stages for the Syrah variety evaluated in the regions of Marari (Mr), Água Doce (AD), Campos Novos (CN) and São Joaquim (SJ), SC, cycles 2010/2011 and 2011/2012

Table 1 Dates for onset of the main phenological stages of the Syrah variety grown in the regions of Marari (Mr), Água Doce (AD), Campos Novos (CN) and São Joaquim (SJ), SC, cycles 2010/2011 and 2011/2012

Location	Cycle	Phenological phases				
		Budburst	Blooming	Véraison	Harvest	Duration/days
Mr	2010/2011	22/Sept	22/Nov	29/Jan	04/Apr	194
	2011/2012	29/Sept	18/Nov	16/Feb	03/Apr	187
	mean $\pm$ SD ^a	25/Sept $\pm$ 4.95	20/Nov $\pm$ 2.83	07/Feb $\pm$ 12.73	03/Apr $\pm$ 0.71	190.5 $\pm$ 4.95
AD	2010/2011	10/Oct	20/Nov	07/Feb	30/Mar	171
	2011/2012	27/Sept	27/Nov	13/Feb	03/Apr	189
	mean $\pm$ SD ^a	03/Oct $\pm$ 9.19	23/Nov $\pm$ 4.95	10/Feb $\pm$ 4.24	01/Apr $\pm$ 2.83	180 $\pm$ 12.73
CN	2010/2011	01/Oct	18/Nov	08/Feb	29/Mar	179
	2011/2012	28/Sept	15/Nov	05/Feb	13/Mar	167
	mean $\pm$ SD ^a	29/Sept $\pm$ 2.12	16/Nov $\pm$ 2.12	06/Feb $\pm$ 2.12	21/Mar $\pm$ 11.31	173 $\pm$ 8.49
SJ	2010/2011	09/Sept	07/Dec	20/Feb	25/Apr	228
	2011/2012	26/Sept	11/Dec	10/Mar	02/May	219
	mean $\pm$ SD ^a	17/Sept $\pm$ 12.02	09/Dec $\pm$ 2.83	01/Mar $\pm$ 12.73	28/Abr $\pm$ 4.95	223.5 $\pm$ 6.36

^a Results are expressed as mean values $\pm$ standard deviation in days

the phenological cycles faster. The variety Syrah originated from the South of France is typical of cultivation in warmer climates, requiring a shorter phenological cycle for the full

maturity. According to Jones and Davis (2000), the period between the phenological stages varies greatly according to the grapevine variety, climate and geographical location.

Wine characterization

Total phenolic compounds

The results for the total phenolic compounds determined by spectrophotometric methods in wine samples are shown in Table 2. The AD wines of the 2011 vintage had the highest concentrations the total phenolic, differing significantly ($p < 0.05$) from other wines of this vintage. The lowest values for the total polyphenols were obtained for the Mr wines, and for total monomeric anthocyanins the SJ wines were those with the lowest values, this wine also had a higher percentage of yellow color, resulting in an increased color tone of the wine due to the formation of pigmented polymers (data not shown).

During wine aging several chemical reactions occur, such as condensation mediated by acetaldehyde, copigmentation and self-association. These reactions of anthocyanins with other compounds may lead to changes in the color of red wines due to partial loss of the flavylum cations. According to Stockham et al. (2013), the total polyphenol content is directly related to the annual precipitation. This indicates that in the region of São Joaquim, high rainfall in the case of the 2011 vintage (total 1500 mm) may have compromised the maturation of the Syrah grapes, especially the development of pigments such as anthocyanins.

For samples of the 2012 vintage, the highest values for total polyphenols and total monomeric anthocyanins were obtained for the CN wines. The AD wines did not differ significantly ($p < 0.05$) from the CN wines in terms of the polyphenol content. Samples of the SJ wines presented the lowest concentrations of phenolic compounds and total monomeric anthocyanins compared with the other wines. The lowest values regarding the phenolic composition, mainly related to anthocyanins, of Syrah wines from São Joaquim can be justified by the fact that this variety is generally cultivated in warmer climate regions. In fact, according to Brighenti et al. (2014), the low temperatures during budbreak and the volume of rainfall are the most limiting climatic aspects for cultivating the varieties *Vitis vinifera* in São Joaquim.

Individual phenolic compounds and antioxidant activity

The results for the concentrations of individual phenolic compounds in samples quantified by HPLC are shown in Table 2. The hydroxybenzoic acids were detected in higher concentrations in AD wine samples, with a total of 38.55 mg L⁻¹ for the 2011 vintage and 43.58 mg L⁻¹ for the 2012 vintage. Among the hydroxycinnamic acids evaluated, the major compound in the wines was caftaric acid, except for the SJ wine (2011), which had higher

concentrations of *p*-coumaric. Other studies have also indicated that caftaric acid is the predominant hydroxycinnamic acid in red wine (Gómez-Alonso et al. 2007; Gómez Gallego et al. 2012).

Among the flavonol compounds investigated, the highest concentrations in the wine samples were observed for quercetin and myricetin. The AD wines (2011) and CN wines (2012) showed higher levels of total flavonols (53.62 and 53.67 mg L⁻¹, respectively). According to Gómez Gallego et al. (2012) flavonols play an important role in the stabilization of wine color, due to the reactions involved in the copigmentation of anthocyanins.

The compounds found in the highest concentrations in wines were the flavanols, in particular (+)-catechin, a potent antioxidant, which was identified as the major compound in the analyzed wines. Other authors have also reported that catechin was the main flavan-3-ol found in red wines (Gómez-Alonso et al. 2007; Kelebek et al. 2010). The highest concentrations the catechin were in the Mr wines (74.78 mg L⁻¹) and SJ wines (117.08 mg L⁻¹), of the 2011 and 2012 vintages, respectively. The epicatechin concentrations ranged from 5.58 to 52.32 mg L⁻¹, the highest concentrations being obtained for the Mr wines, regardless of the vintage.

Trans-resveratrol was found at variable concentrations in the wine samples. Studies by Gris et al. (2011) found levels similar ranging from 2.70 to 7.44 mg L⁻¹ in different wines grown in the São Joaquim region, SC. According to these authors, the levels of stilbene, as *trans*-resveratrol found in wines made from grapes grown in the southern regions of Brazil are related to climatic and orographic conditions, which stimulate its production by the grapevines.

Among the anthocyanin monoglucosides determined in this study, malvidin-3-monoglucoside was the main anthocyanin found in the wines analyzed. The 2011 vintage wines showed lower levels of monomeric anthocyanins compared to the 2012 vintage wines, which may indicate degradation, copigmentation or polymerization of these compounds. The anthocyanin content varies as a result of many factors, such as climate, vintage and growing region, what can be observed in this study. In addition, an important factor that influenced the phenolic compounds in this study is its evolution during storage that was evident for the 2011 vintage, in which wines had longer aging time. The storage of these wines allowed observe the evolution of phenolic constituents in Syrah wines from these regions, indicating the potential of these growing locations in producing wines with typical quality.

The values for the in vitro antioxidant activity were higher employing the ABTS method for all samples and the two vintages evaluated (Table 2), corroborating other studies (Burin et al. 2011a). The correlation analysis

Table 2 Individual phenolic compounds (mg L⁻¹), total polyphenol compounds and antioxidant activity for Syrah wines produced from grapes grown in the regions of Marari (Mr), Água Doce (AD), Campos Novos (CN) and São Joaquim (SJ), SC, vintage 2011 and 2012

	Vintage 2011				Vintage 2012			
	Mr	AD	CN	SJ	Mr	AD	CN	SJ
<i>Hydroxybenzoic acids</i>								
Galic	8.07 ± 0.05 ^b	14.09 ± 0.04 ^d	2.07 ± 0.01 ^a	11.76 ± 0.10 ^c	12.07 ± 0.11 ^b	18.39 ± 0.01 ^c	9.76 ± 0.06 ^a	9.82 ± 0.14 ^a
Protocatechuic	9.43 ± 0.05 ^a	9.17 ± 0.02 ^a	9.21 ± 0.13 ^a	6.42 ± 0.16 ^b	7.13 ± 0.01 ^b	12.15 ± 0.05 ^c	4.85 ± 0.03 ^a	12.65 ± 0.01 ^d
Vanillic	3.52 ± 0.04 ^a	8.58 ± 0.03 ^b	9.73 ± 0.27 ^c	11.28 ± 0.02 ^d	2.31 ± 0.01 ^b	5.66 ± 0.01 ^a	5.67 ± 0.03 ^a	12.14 ± 0.18 ^c
Syringic	4.14 ± 0.06 ^c	3.76 ± 0.02 ^b	2.81 ± 0.05 ^a	5.21 ± 0.05 ^d	0.95 ± 0.01 ^c	0.86 ± 0.01 ^a	0.92 ± 0.01 ^b	1.18 ± 0.02 ^d
Ellagic	1.21 ± 0.03 ^c	2.95 ± 0.02 ^d	0.70 ± 0.01 ^b	0.49 ± 0.01 ^a	5.29 ± 0.02 ^b	6.52 ± 0.09 ^c	6.97 ± 0.04 ^d	3.10 ± 0.08 ^a
<i>Hydroxycinnamic acids</i>								
Caffeic	0.64 ± 0.01 ^a	5.66 ± 0.16 ^c	0.17 ± 0.01 ^b	0.68 ± 0.01 ^a	3.34 ± 0.01 ^b	15.98 ± 0.57 ^d	9.89 ± 0.01 ^c	0.27 ± 0.01 ^a
trans-caftaric	3.72 ± 0.12 ^c	14.58 ± 0.11 ^d	1.70 ± 0.06 ^b	0.46 ± 0.01 ^a	6.74 ± 0.08 ^b	17.77 ± 0.37 ^c	22.20 ± 0.28 ^d	2.19 ± 0.02 ^a
p-coumaric	0.79 ± 0.01 ^a	1.02 ± 0.01 ^b	1.08 ± 0.02 ^c	0.78 ± 0.01 ^a	0.81 ± 0.01 ^a	4.62 ± 0.02 ^d	3.97 ± 0.01 ^c	0.87 ± 0.01 ^b
Ferulic	0.10 ± 0.01 ^a	5.08 ± 0.06 ^c	0.29 ± 0.07 ^b	0.15 ± 0.01 ^a	3.68 ± 0.08 ^c	0.19 ± 0.01 ^{a,b}	0.12 ± 0.01 ^a	0.28 ± 0.01 ^b
<i>Flavonols</i>								
Kaempferol	4.69 ± 0.03 ^d	3.88 ± 0.20 ^c	2.99 ± 0.03 ^b	1.13 ± 0.04 ^a	3.86 ± 0.03 ^c	2.65 ± 0.06 ^b	7.04 ± 0.01 ^d	0.69 ± 0.01 ^a
Quercetin	23.84 ± 1.64 ^b	35.31 ± 1.64 ^c	4.71 ± 0.04 ^a	3.30 ± 0.08 ^a	31.23 ± 0.01 ^b	33.07 ± 0.59 ^c	36.31 ± 0.12 ^d	8.04 ± 0.02 ^a
Myricetin	10.04 ± 0.61 ^c	14.43 ± 0.42 ^d	7.57 ± 1.26 ^b	1.64 ± 0.01 ^a	14.05 ± 0.08 ^a	13.91 ± 0.08 ^a	10.32 ± 0.01 ^c	9.82 ± 0.14 ^b
<i>Flavanols</i>								
(+)-catechin	74.78 ± 0.37 ^c	49.85 ± 2.85 ^a	51.91 ± 1.73 ^a	5.97 ± 0.04 ^b	96.49 ± 0.02 ^c	81.01 ± 0.80 ^a	93.46 ± 0.03 ^b	117.08 ± 0.19 ^d
(-)-epicatechin	39.43 ± 0.62 ^c	36.21 ± 0.15 ^b	7.28 ± 0.05 ^a	5.58 ± 1.37 ^a	52.32 ± 0.04 ^c	16.51 ± 0.53 ^a	16.02 ± 0.11 ^a	23.01 ± 0.03 ^b
<i>Others</i>								
trans-resveratrol	0.95 ± 0.01 ^d	0.55 ± 0.01 ^c	0.52 ± 0.02 ^b	0.49 ± 0.01 ^a	0.68 ± 0.01 ^a	2.85 ± 0.05 ^b	6.57 ± 0.05 ^c	0.60 ± 0.01 ^a
Tyrosol	9.04 ± 0.03 ^a	23.49 ± 1.64 ^b	28.57 ± 0.72 ^c	9.21 ± 0.07 ^a	26.03 ± 0.24 ^b	46.86 ± 0.89 ^d	33.61 ± 0.46 ^c	19.72 ± 0.52 ^a
<i>Anthocyanins 3-monoglucosides</i>								
Delphinidin	1.31 ± 0.01 ^a	2.19 ± 0.01 ^c	1.46 ± 0.01 ^b	1.30 ± 0.03 ^a	2.79 ± 0.03 ^b	3.30 ± 0.02 ^c	3.53 ± 0.06 ^d	2.06 ± 0.01 ^a
Cyanidin	0.20 ± 0.01 ^a	1.11 ± 0.03 ^c	0.30 ± 0.01 ^b	nd	2.22 ± 0.02 ^a	2.25 ± 0.05 ^a	2.95 ± 0.03 ^c	1.03 ± 0.03 ^b
Peonidin	0.81 ± 0.01 ^b	2.06 ± 0.04 ^c	0.50 ± 0.02 ^a	0.51 ± 0.02 ^a	2.25 ± 0.01 ^b	4.41 ± 0.08 ^d	3.29 ± 0.09 ^c	1.38 ± 0.03 ^a
Malvidin	14.17 ± 0.07 ^c	16.96 ± 0.15 ^d	11.81 ± 0.09 ^b	4.92 ± 0.49 ^a	33.28 ± 0.12 ^c	28.84 ± 0.56 ^a	29.56 ± 0.44 ^a	15.32 ± 0.30 ^b
ABTS ¹	5.78 ± 0.13 ^a	7.67 ± 0.14 ^c	6.08 ± 0.27 ^{a,b}	6.27 ± 0.14 ^b	5.12 ± 0.04 ^a	5.29 ± 0.01 ^a	5.16 ± 0.13 ^a	4.33 ± 0.13 ^b
DPPH ¹	4.06 ± 0.17 ^b	6.31 ± 0.12 ^c	5.03 ± 0.11 ^a	5.21 ± 0.12 ^a	5.07 ± 0.09 ^a	5.24 ± 0.07 ^a	5.01 ± 0.18 ^a	4.24 ± 0.24 ^b
FRAP ¹	1.93 ± 0.06 ^b	2.54 ± 0.03 ^a	2.19 ± 0.05 ^c	2.52 ± 0.07 ^a	3.78 ± 0.07 ^a	3.86 ± 0.03 ^a	4.03 ± 0.06 ^b	3.81 ± 0.06 ^a
TP ²	1176.23 ± 16.39 ^b	1569.67 ± 10.84 ^c	1233.61 ± 21.69 ^a	1270.49 ± 24.93 ^a	2245.90 ± 8.20 ^c	2413.93 ± 28.93 ^a	2434.43 ± 0.01 ^a	2118.85 ± 4.10 ^b
TMA ²	39.58 ± 0.74 ^a	55.02 ± 3.45 ^c	43.76 ± 1.19 ^a	27.31 ± 1.53 ^b	122.62 ± 1.91 ^c	114.40 ± 0.47 ^b	133.76 ± 0.76 ^d	81.46 ± 0.22 ^a
OD ²	247.12 ± 19.95 ^a	395.17 ± 5.66 ^c	249.29 ± 13.60 ^a	312.43 ± 9.98 ^b	432.18 ± 6.80 ^a	573.15 ± 4.90 ^c	507.84 ± 4.90 ^b	440.89 ± 0.01 ^a

Table 2 continued

	Vintage 2011				Vintage 2012			
	Mr	AD	CN	SJ	Mr	AD	CN	SJ

TFA² 321.42 ± 3.10^c 209.76 ± 5.69^b 299.73 ± 6.68^a 293.83 ± 3.35^a 535.84 ± 3.32^d 479.42 ± 6.64^b 493.81 ± 1.11^c 451.77 ± 1.11^a

Results are expressed as mean values ± standard deviation (n = 3). Different letters in the same line indicate significant difference ($p < 0.05$) between regions. Tukey test performed separately for each vintage. nd: not detected

¹ Antioxidant activity expressed as Trolox equivalents (mmol TEAC L⁻¹)

² TP, total polyphenols (mg L⁻¹ gallic acid); TMA, total monomeric anthocyanins (mg L⁻¹ malvidin-3-glucoside); OD, *ortho*-diphenols (mg L⁻¹ catechin); TFA, total flavanols (mg L⁻¹ catechin)

showed a significant correlation between the antioxidant activity and individual phenolic compounds in this study. In the 2011 vintage, both the method ABTS as DPPH they were strongly correlated with the ferulic acid ($R = 0.95$ and 0.84), caffeic acid ($R = 0.95$ and 0.81) and total polyphenols ($R = 0.98$ and 0.92). However, the anthocyanin monoglucosides (delphinidin, peonidin and cyanidin), were positively correlated ($R > 0.90$) in ABTS method. For the wines of the 2012 vintage, the individual phenolic compounds such as quercetin ($R > 0.90$), ellagic acid ($R = 0.92$ and 0.85), caffeic acid ($R = 0.81$ and 0.74) and all anthocyanins monoglucosides ($R > 0.90$) showed a positive correlation using the ABTS and DPPH methods respectively. Among polyphenols, positive correlations were found between total monomeric anthocyanins and antioxidant activity determined by the ABTS and DPPH methods ($R = 0.83$ and 0.80), which is indicative of wines of younger vintages.

Considering the climatic variations of growing regions and its relationship with the phenolic profile of wines (Table 2), it was observed that total monomeric anthocyanins and anthocyanin monoglucosides were significantly lower in SJ wines, whilst this region had the lowest temperatures. In contrast, this region had the highest global solar radiation, and the concentrations of vanillic acid in these wines were significantly higher when compared with the other wines. These findings suggest that these phenolic compounds were influenced by those specific climatic factors and could be further investigated as phenolic markers of climate influence. Another study has indicated individual phenolic compounds in wines as markers of climate change. As reported by Stockham et al. (2013), polyphenols such as rutin, protocatechuic acid, vanillic acid, chlorogenic and *p*-coumaric acids are potential phenolic markers for climate change due to their most variation in wines from different growing regions of Australia. Apart from climate factor, the soil composition is considered an important factor to investigate polyphenolic profile of wine growing regions. Nevertheless, further studies with longer monitoring of climatic factors (historical series) are needed in order to correlate the effect of climate on the phenolic compounds of wines.

Principal component analysis (PCA) was performed to verify the influence of the growing region and vintages on the phenolic composition of the wines (Fig. 3). Factor 1 accounted for 59.16% of the total dispersion, and explained the largest variance of the data. The 2011 vintage wines were positioned to the left side negative to Factor 1, and the 2012 vintage wines on right side positive, being associated with most quantitative analyzes. The CN, AD and Mr wines of the 2012 vintage were associated with most individual phenolic compounds (catechin, *trans*-resveratrol, tyrosol, kaempferol, quercetin and myricetin, and the

Fig. 3 Principal Components Analysis (PCA) using the results for individual phenolic compounds, total polyphenols, total monomeric anthocyanins and antioxidant activity obtained with ABTS, DPPH and FRAP methods for Syrah wines produced from grapes grown in the regions of Marari (Mr), Água Doce (AD), Campos Novos (CN) and São Joaquim (SJ), SC, vintages 2011 and 2012. 1. Gallic acid, 2. Vanillic acid, 3. Syringic acid, 4. Ellagic acid, 5. *trans*-caftaric acid, 6. Tyrosol, 7. Catechin, 8. Caffeic acid, 9. *p*-coumaric acid, 10. Ferulic acid, 11. Myricetin, 12. *trans*-resveratrol, 13. Quercetin, 14. Kaempferol, 15. Delphinidin, 16. Cyanidin, 17. Peonidin, 18. Malvidin, 19. Total polyphenols, 20. Total monomeric anthocyanin, 21. ABTS, 22. DPPH, 23. FRAP

ellagic, coumaric, caffeic, caftaric and gallic acids), total polyphenols, total monomeric anthocyanin and anthocyanin monoglucosides (malvidin, delphinidin, peonidin and cyanidin). The SJ wines of the 2012 vintage was positioned in the upper quadrant and separated from the other wines of the same vintage, getting along with the 2011 vintage wines, probably due to its lower content of anthocyanins when compared to other wines. The CN and

Mr wines of the 2011 vintage had a strong association with vanillic acid, and AD wines of the 2011 vintage with antioxidant activity by ABTS method. The results indicate that the PCA analysis established a differentiation at the wines samples in relation the variables studied.

Conclusion

The results showed that the climate conditions in the wine growing regions influence the duration of the phenological cycle and heat accumulation in the grapevine. The regions of Marari, Água Doce and Campos Novos showed better conditions for phenological adaptation of Syrah variety. Syrah wines showed particular chemical characteristics according to the growing regions and vintage. The volume of rainfall and the low temperatures registered for the São Joaquim region were suggested as a limiting factor for the cultivation of this variety. The climate of these growing regions influenced the polyphenolic profile of the wines, suggesting possible phenolic markers indicative of climatic influence given their variations in wines from regions with distinct climatic conditions. The AD wines of vintage 2011 and the CN and AD wines of vintage 2012 showed higher concentrations of phenolic compounds and higher antioxidant activity, indicating the potential of these Brazilian regions for the production of quality Syrah wines as an attractive source of bioactive compounds. Notwithstanding, further long term studies are required in order to find specific phenolic compounds that are influenced by climatic factors as well as the effect of climate change on polyphenols and their effect on quality wines.

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References

- Arnous A, Makris DP, Kefalas P (2002) Correlation of pigment and flavanol content wine antioxidant properties in selected aged regional wines from Greece. *J Food Compos Anal* 15:655–665
- Benzie IFF, Strain JJ (1996) The ferric reducing ability of plasma (FRAP) as a measure of “antioxidant power”: the FRAP assay. *Anal Biochem* 239:70–76
- Bock A, Sparks T, Estrella N, Menzel A (2011) Changes in the phenology and composition of wine from Franconia, Germany. *Clim Res* 50:69–81
- Borghesan M, Gavioli O, Pit FA, Silva AL (2011) Comportamento vegetativo e produtivo da videira e composição da uva em São Joaquim, Santa Catarina. *Pesq Agropec Bras* 46:398–405

- Brighenti AF, de Silva AL, Brighenti E, Porro D, Stefanini M (2014) Desempenho vitícola de variedades autóctones italianas em condição de elevada altitude no Sul do Brasil. *Pesqui Agropec Bras* 49:465–474
- Burin VM, Costa LLF, Rosier JP, Bordignon-Luiz MT (2011a) Cabernet Sauvignon wines from two different clones, characterization and evolution during bottle ageing. *LTW Food Sci Technol* 44:1931–1938
- Burin VM, Silva AL, Malinowski LI, Rosier JP, Falcão LD, Bordignon-Luiz MT (2011b) Characterization and multivariate classification of grapes and wines of two Cabernet Sauvignon clones. *Pesq Agropec Bras* 46:474–481
- de Orduña RM (2010) Climate change associated effects on grape and wine quality and production. *Food Res Int* 4:1844–1855
- Falcão LD, Burin VM, Chaves ES, Vieira HJ, Brighenti E, Rosier JP, Bordignon-Luiz MT (2010) Vineyard altitude and mesoclimate influences on the phenology and maturation of Cabernet Sauvignon grapes from Santa Catarina State. *J Int Sci Vigne Vin* 44:135–150
- Ferreira-Lima NE, Burin VM, Bordignon-Luiz MT (2013) Characterization of Goethe white wines: influence of different storage conditions on the wine evolution during bottle aging. *Eur Food Res Technol* 237:509–520
- Flanzly M, Aubert S (1969) Évaluation des composés phénoliques des vins blancs. *Ann Technol Agric* 18:27–44
- Giusti MM, Wrolstad RE (2001) Anthocyanins: characterization and measurement with UV-visible spectroscopy. In: Wrolstad RE (ed) *Current protocols in food analytical chemistry*. Wiley, New York
- Gómez Gallego MA, Gómez García-Carpintero E, Sánchez-Palomo E, González Viñas MA, Hermosín-Gutiérrez I (2012) Oenological potential, phenolic composition, chromatic characteristics and antioxidant activity of red single-variety wines from Castilla-La Mancha. *Food Res Int* 48:7–15
- Gómez-Alonso S, García-Romero E, Hermosín-Gutiérrez I (2007) HPLC analysis of diverse grape and wine phenolics using direct injection and multidetection by DAD and fluorescence. *J Food Compos Anal* 20:618–626
- Gris EF, Burin VM, Brighenti E, Vieira H, Bordignon-Luiz MT (2010) Phenology and ripening of *Vitis vinifera* L. grape varieties in São Joaquim, Southern Brazil: a new South American wine growing region. *Cien Inv Agr* 37:61–75
- Gris EF, Mattivi F, Ferreira EA, Vrhovsek U, Filho DW, Pedrosa RC, Bordignon-Luiz MT (2011) Stilbenes and tyrosol as target compounds in the assessment of antioxidant and hypolipidemic activity of *Vitis vinifera* red wines from Southern Brazil. *J Agric Food Chem* 59:7954–7961
- Gris EF, Mattivi F, Ferreira EA, Vrhovsek U, Filho DW, Pedrosa RC, Bordignon-Luiz MT (2013) Phenolic profile and effect of regular consumption of Brazilian red wines on in vivo antioxidant activity. *J Food Compos Anal* 31:31–40
- Hall A, Jones GV (2010) Spatial analysis of climate in wine grape-growing regions in Australia. *Aust Soc Vitic Oenol* 16:389–404
- Jackson RS (2008) *Wine science—principles and applications*, 3rd edn. Academic Press, London, p 789
- Jackson DI, Lombard PB (1993) Environmental and management practices affecting grape composition and wine quality—a review. *Am J Enol Viti* 44:409–430
- Jones GV, Davis RE (2000) Climate influences on grapevine phenology, grape composition, and wine production and quality for Bordeaux, France. *Am J Enol Viti* 51:249–261
- Kelebek H, Canbas A, Jourdes M, Teissedre P (2010) Characterization of colored and colorless phenolic compounds in Öküzgözü wines from Denizli and Elazığ regions using HPLC-DAD-MS. *Ind Crops Prod* 31:499–508
- Kim YK, Guo Q, Packer L (2002) Free radical scavenging activity of red ginseng aqueous extracts. *Toxicology* 172:149–156
- Lorenz DH, Eichhorn KW, Bleiholder H, Klose R, Meier U, Weber E (1995) Phenological growth stages of the grapevine (*Vitis vinifera* L. ssp. *vinifera*)—codes and descriptions according to the extended BBHC scale. *Aust J Grape Wine Res* 1:100–103
- Protas JFS, Camargo UA (2011) *Viticultura brasileira: panorama setorial de 2010*. Embrapa Uva e Vinho, Brasília, p 110
- Re R, Pellegrini N, Proteggemnte A, Pannala A, Yang M, Rice-Evans C (1999) Antioxidant activity applying and improved ABTS radical cation de colorization assay. *Free Rad Biol Med* 26:1234–1237
- Revilla I, Pérez-Magarinó S, González-Sãojose ML, Beltrán S (1999) Identification of anthocyanin derivatives in grape skin extracts and red wines by liquid chromatography with diode array and mass spectrometric detection. *J Chromatogr A* 847:83–90
- Singleton VL, Rossi JA (1965) Colourimetry of total phenolics with phosphomolybdic phosphotungstic acid reagent. *Am J Enol Viti* 16:144–158
- Stockham K, Sheard A, Paimin R, Buddhadasa S, Duong S, Orbell JD, Murdoch T (2013) Comparative studies on the antioxidant properties and polyphenolic content of wine from different growing regions and vintages, a pilot study to investigate chemical markers for climate change. *Food Chem* 140:500–506
- Winkler AJ, Cook JA, Kliewer WM, Lider LA (1974) *General Viticulture*. University of California, Berkeley, p 710