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Influences of the Harvest Season on Analytical Characteristics of Syrah Grapes and Wines Produced in the Northeast Region of Brazil

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Abstract The present study evaluated the main physical and chemical characteristics of Syrah grapes, coming from the tropical region of São Francisco river valley, harvested at different times and their relationship with analytical characteristics of resulting wines. Grapes came from the first half of 2009 harvest, collected at Casa Nova - Bahia, a semi-arid and hot region, comprising an interval from 84 days after pruning (84 dap) to the beginning of grape over-ripening, 133 days after pruning (133 dap). Harvests at 84, 91, 98, 105, 112, 119, 126 and 133 dap, were analyzed for pH, soluble solids and acidity in grapes, which were then processed for wine production. Maximum sugar/acidity ratio (s/a = 56) were observed in grapes harvested between 126 and 133 dap, coincided with the highest concentration of anthocyanins (851 mg L^{-1}) and total tannins (2.6 g L^{-1}) in the resulting wines, indicating that grapes collected between 126 and 133 dap showed the best potential for winemaking in the tropical climate of São Francisco river valley. This result was confirmed by the analytical characterization of wines, that, between 126 and 133 dap, showed 12.8% alcohol, 31 g L^{-1} dry extract, 5.6 g L^{-1} ashes and a TPI of 58, using only one pumping per day, for 5 days maceration. Syrah grapes considered in the present work presented a good evolution of maturation, and grapes harvested between 126 and 133 days after pruning, showed the best oenological potential for the development of red wine. The use of pH and soluble solids appeared useful parameters in the estimation of maturation degree and quality potential of grapes for winemaking.

Keywords Grape maturation, Characterization of wines, Tropical wine

1. Introduction

Tropical viticulture, aimed to winemaking and other grape and wine products, is a recent, worldwide diffused, activity. Brazil represents a pioneer in the area of tropical viticulture, currently producing around 5.0 million liters of wine per year, being the São Francisco river valley region responsible for the entire production (Mello, 2013). The region of São Francisco river valley is located in northeastern Brazil, between 8-9° latitude in the southern hemisphere, and has been developing rapidly in recent years, mainly near the cities of Petrolina, Lagoa Grande and Santa Maria da Boa Vista in Pernambuco State, and Juazeiro and Casa Nova in Bahia State (Lima et al., 2014). The region stands out on the national scene as the largest exporter of table grapes and the second largest producer of high quality wines (Lima et al., 2014). Wine grapes in this region are predominantly of European origin (*Vitis vinifera* L.) and, in particular, the Syrah red variety.

Syrah is one of the oldest cultivated varieties. Some authors suggested that it originates from the varieties "Dureza" and "Mondeuse blanche" in southeastern France. From France, it was exported in many countries and, today it is one of the most planted red grape cultivars in the world (Bowers et al. 2000; Vouillamoz and Grando, 2006). In the hot semi-arid conditions in northeastern Brazil (São Francisco river valley), the Syrah variety has shown excellent performances, where wine is distinctive for its aroma and bouquet (Giovannini, 2009).

One of the most important factor that differentiates São Francisco river valley from other traditional farming regions in the world, is the ability of plants to produce more than one crop per year. Due to the particular environmental conditions, hot climate, high luminosity and plenty of water for irrigation, winemakers in the region use to plan the period of

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grape harvest, adopting a scheduling system for plot pruning, and harvesting. This gives rise to different harvest periods, giving products with distinct characteristics (Teixeira et al., 2007; Lima et al., 2014). This fact means that smaller facilities can be used, that can be employed all over the year, reducing the need for inventory. Between one and another crop, irrigation is reduced to 15 to 20% of the crop coefficient, during dry periods by about 20 to 30 days (corresponding to the winter period in temperate regions), then pruning is carried out and hydrogen cyanamide application is used to homogenize the shooting. After this stage, irrigation is increased to supply 100% of the crop coefficient and a new production cycle starts. Generally, the periods of highest harvest concentration occurs between May and June and October and November (Teixeira et al., 2012). Wine production in the world is highly competitive, facing with countries with high experience, high quality and excellent image among consumer markets. Tropical wines, by contrast, have a low production volume if compared to world production. Certainly, tropical wines are unique in the world, with an identity that should be valued in the world market.

The quality of a wine depends on many factors, including variety and rootstock, which are influenced by environmental factors (climate and soils) and viticultural technology (systems of cultivation, fertilization and others), and finally, the technological choices will produce the final product, wine, which express the effect of all these factors (Orduna et al., 2010).

One of the key practices that interfere with the quality of wine is the determination of the right grape harvesting time. This step (desired maturation) must be indicated by easy to determine parameters, based on biochemical and/or morphological changes that occur during ripening. Some indicators are the simple count of the days after flowering or pruning, that, within a region, shows little variations for each cultivar, from year to year (Giovannini, 2009). Grape ripening analysis is one of the most effective controls that should be carried out for wine production, involving the evolution of sugars, acidity, polyphenols and aromatic compounds. More recently, in Europe the rate of phenolic maturation has been used. This gives an estimate of the best crop period and of grape destination, according to grape composition in terms of anthocyanins and tannins. Phenolic maturity takes into account the overall content of phenolic compounds, and also their structure and suitability for incorporation into wine during the maceration (Ribéreau-Gayon et al., 2003). Thus, differences appear from region to region and from different winemaking tradition, especially regarding climate, in particular in the tropical region (where the vine grows throughout the year, producing grapes in non-classical periods).

For these reasons, it is necessary to improve the research work, in order to contribute to the improvement of wine quality in these regions. The present study is aimed to determine the evolution of main chemical characteristics of Syrah grapes in different harvest periods and to correlate the results with the analytical composition of the resulting wines, generating information for winemakers in the São Francisco river valley, in order improve the quality of wines by deepening the knowledge about chemical composition and enological potential of the raw material.

2. Materials and Methods

2.1. Plant Material and Treatments

Syrah grapes were from an full production area for winemaking, located at Fazenda Ouro Verde, owned by MIOLO WINE GROUP, Santana do Sobrado, 40 BR 235 km, Casa Nova - Bahia, on the banks of the Sao Francisco river, at 09° 16' 20" South latitude and 40º 52' 8" West longitude, approximately 360 meters above sea level. The preparation of wines and the physico-chemical and spectrophotometric characteristics of grapes and wines were carried out at the Wine School (Enology Laboratory) of the Federal Institute of Sertão Pernambucano, Petrolina Campus, Rural Zone, located at 22 Km of BR 235 road, Senador Nilo Coelho Project, Nucleus 4, Petrolina (Pernambuco). Plants used, 5 years old, were derived from the Syrah 100 clone, grafted on IAC 766 rootstock with 2.2 x 1.0 m spacing, conducted on trellising system, 60 cm high, and led to a height of 1.20 m.

Plants received basic NPK fertilizer (30-30-30) once a year and a 4 liters per hour drip irrigation. The management of irrigation was used in accordance with the rate of evapotranspiration. The vines were pruned (production pruning) on February 18, 2009 and the grapes were harvested in the period from May 11 to June 29, 2009, in a weekly interval, which began 84 days after pruning (15 days after the color development) until the start of the grape over-ripening, characterized by the onset of withering of berries on the vine, 133 days after pruning (64 days after the color development).

Climatic data, in the region, averages per month, collected in the period February to June 2009, from pruning to last harvest completion (133 dap). They were: temperature 25.2°C, 89.4 mm rainfall, relative humidity 78.6%, 5.6 mm evaporation, illuminance 348.7 lx/day and 8.5 hours insolation, measured at the weather station of Mandacaru (Juazeiro – Bahia, 09° 24 'S, 40º 26' W).

The experimental design was completely randomized, involving 8 treatments and 3 replications, each plot comprised 20 plants. Treatments corresponded to different harvest seasons. The first harvest was 84 days after pruning (84 dap) (T1) and the others were collected at weekly intervals (91, 98, 105, 112, 119, 126 dap) until the beginning of grape over-ripening (133 dap) (T8). The results were subjected to variance analysis (ANOVA) and compared by Scott-Knott test at 5% probability using the SISVAR 4.2 statistical software (Sisvar, Brazil). Results were analyzed also by Pearson correlation at 5% probability using the SPSS 14.0 for Windows Evaluation Version (SPSS, USA).

2.2. Analytical Determinations of the Grape Must Samples

Grape samples were subjected to physical and chemical analysis. Grape berries (n = 200) were randomly collected from different parts of the grape and from different plants, in order to be representative. The plot consisted of 20 plants, totaling 480 plants used and distributed in eight treatments and three replications. Analysis were: berry juice pH, determined by a digital bench pH-meter (Tecnal, Brazil); soluble solids (SS), using a digital Abbé type bench refractometer, and total acidity (TA) by titration following the methodology described by OIV (2011). The determination of tartaric acid was carried out on grape juice or wine in acetic acid containing ammonium vanadate, and the van do-tartrate complex was evaluated using a UV/VIS bench spectrophotometer (mod. T60, PG instruments, England) at 530 nm, following the methodology described by Matissek et al. (1998). The soluble solids/total acidity ratio (SS/TA) was calculated according to the methodology described by Togores (2006).

2.3. Analytical Determinations of Wine Samples

Wine samples were analyzed as regard pH and titrable acidity, according to the methodology described by OIV (2011). Dry extracts were determined by sample evaporation in a water bath, followed by drying at 105°C, and ashes were determined by incineration of the solid samples at 550°C in a digital furnace (Jung, Brazil), according to the method described by AOAC (2005). Volatile acidity was determined by titration of volatile acids obtained from current vapor sample extracts, followed by rectification, using a semi-automatic volatile acidity analyzer (Tecnal, Brazil). Sample density was measured by a hydrometer for specific gravity (range 0.900 to 1.000 g cm^{-3}, reslution = 0.001 g cm^{-3}) at 20°C by comparison with water at 20°C. Alcohol content was evaluated by measuring the refractive index of sample distillate, at 20°C, using an Abbé type benchtop digital refractometer, as described by OIV (2011). Anthocyanins were determined according to the bisulfite bleaching technique, followed by reading the absorbance at 520 nm, using a 10 mm path length cuvette. Tannins were determined by color development, at 550 nm in 10 mm cuvettes. Total polyphenol index was measured by diluting wine samples with water (1:100) followed by reading the absorbance at 280 nm in 10 mm cuvettes (Ribéreau-Gayon et al. 2003).

2.4. Winemaking

For each treatment used for physico-chemical analysis, grapes (20 kg) were collected to perform a micro-vinification process, which was conducted at the Wine School of SERTÃO IF-Pernambuco. Grapes were weighed, crushed, destemmed and squeezed, then potassium metabisulfite (60 mg L^{-1}) and selected active dry yeast (*Saccharomyces cerevisiae* var. Bayanus) (200 mg L^{-1}) were added. Grape juice was incubated in 20 L glass bottles. Maceration was carried out for 5 days at 25°C, 1 pumping per day. At the end of maceration, a hand press was used, peels were eliminated, and the wine was inserted in glass bottles for continuing the fermentation, at 25°C. After the alcoholic fermentation occurrence, wines were transferred and the natural malolactic fermentation occurred, at 25°C. At the end, wine was transferred again and a correction by 30 mg L^{-1} sulfur dioxide was added. The clarification was carried out just by cold incubation, keeping the bottles at 8°C for 5 days, where the natural settling of the sludge occurred. After the clarification, a new wine transfer was carried out and the level of free sulfur dioxide was corrected to 30 mg L^{-1}. Then, wines were bottled by hand in 750 mL amber glass bottles, closed with agglomerated cork stoppers using a semi-automatic corker (Ricefer, Brazil) and stored 60 days for stabilization. After the stabilization period, wine analytical determinations were performed.

3. Results and Discussion

3.1. Analytical Results on Syrah Grapes

An increase of pH values was observed in grapes during berries maturation, starting from pH 2.64 at 84 dap, and reaching a stabilization before the over-ripening appearance at 126 dap, pH 3.8 (Table 1). The increase in pH values was accompanied by a decrease of titrable acidity (Table 1). The more pronounced reduction of acidity occurred between 84 and 105 dap, with a significant decrease from 334 to 95 mEq L^{-1}. After 105 dap, this decline was slower, reaching a constant value starting from 119 dap with a value of 67 mEq L^{-1}, while that in the early over-ripening (133 dap) it reached 56 mEq L^{-1}.

Sugars increased with the advance of the harvest season reaching values of 23.4° brix at 133 dap, showing the good potential of Syrah variety to produce wines with good alcohol content and without the necessity of external sugaring. In this study, we found an accumulation of tartaric acid (Table 1) in grapes from 84 to 105 dap, reaching a value of 5.0 g L^{-1}. Tartaric acid concentration then decreased until 133 dap, with final value of 2.8 g L^{-1}.

Values of pH in Syrah grapes during the maturation were generally higher than those normally found in other wines coming from other Brazilian regions (pH around 3.3) (Orlando et al., 2008, Mota et al., 2009). The pH values, found in the present study on ripe Syrah grapes, were similar to those mentioned by Busse-Valverde et al. (2010) in the Jumilla region, southeast Spain, during 2009 harvest. Sigler (2008) mentioned that in hot weather (with temperature close to 30°C), the pH of grapes was near 4.0, differing from the values measured in other traditional wine regions of the world. Teixeira et al. (2007) reported that the average annual temperature in the region of São Francisco river valley varies between 24° and 30°C, which could explain the high pH values found in the present study.

Table 1. Analytical parameters of Syrah musts, coming from grapes collected in the São Francisco river valley, Brazil, harvested at different times during the first half of 2009

Collection time	Average values				
	pH	Titrable acidity (mEq L^{-1})	SS (°Brix)	SS/AT	Tartaric acid (g L^{-1})
84 dap	2.64^{f}	334^{a}	12.4^{f}	5^{e}	3.4^{c}
91 dap	2.83^{e}	230^{b}	14.6^{e}	8^{e}	3.9^{b}
98 dap	2.95^{d}	176^{c}	15.7^{d}	12^{d}	5.0^{a}
105 dap	3.29^{c}	95^{d}	18^{c}	26^{c}	5.0^{a}
112 dap	3.49^{b}	88^{d}	19.4^{c}	29^{c}	3.9^{b}
119 dap	3.72^{b}	67^{e}	20.8^{b}	41^{b}	3.2^{c}
126 dap	3. 81^{a}	56^{e}	22.4^{a}	53^{a}	3.0^{c}
133 dap	3.87^{a}	56^{e}	23.4^{a}	56^{a}	2.8^{c}
CV%	*1.99*	*12.9*	*2.94*	*9.2*	*7.26*

Means followed by the same letters in the same column do not differ by Scott-Knott test at 5% probability.
Legend: dap - days after pruning.

The knowledge of the pH values of grapes is of extreme importance, as they will reflect on the final pH of wines. Among the factors determining the increase of pH, the salification of organic acids due to the high potassium content (Gawel et al., 2000, Mpelasoka et al., 2003), the physiological breathing process and the dilution of acids due to water accumulation during the increasing of berry size, stand out (Togores, 2006).

The increase in pH values was accompanied by a decrease of titrable (Table 1). Results similar to those found in the present study were described on Syrah grapes, at different phases of maturation in Jumilla region (southeast Spain), where the acidity (expressed in g L^{-1} tartaric acid) ranged from 89 to 59 mEq L^{-1} (Garde-Cerdán et al., 2011). Similar titrable acidity values, as well, ranging from 177 to 75 mEq L^{-1}, and pH 2.82 to 3.28, were found in Cabernet Sauvignon, seven weeks after the color development period in Tarragona (Spain) (Kontoudakis et al. 2011).

The increase of sugars in Syrah grape could mean the good potential of Syrah variety to produce wines, without the necessity of external sugaring. Keller (2009) suggested that a Soluble Solid (Brix degree value, °Brix) higher than 24 - 25, are not the result of photosynthesis and sugar transport from leaves to berries, or of concentration due to evaporative loss. Garde-Cerdan et al. (2011) found values of soluble solids similar to those found in the present work in Merlot and Syrah grapes, in the 2007/2008 harvest in Jumilla region (Spain). Busse-Valverde et al. (2010), as well, reported values of 29° Brix in ripe Syrah grapes harvested in the Jumilla region (Spain) in 2009. Orlando et al. (2008), studying the behavior of Syrah grapes on different rootstocks in Jundiaí, São Paulo (Brazil), found values of soluble solids of 17.6º Brix on IAC 766, the same rootstock used in the present experiment. According to Togores (2006), grape sugars are synthesized in the green part of the grapevine and migrate to the various parts of the plant, primarily in the berries. Besides the translocation process, the accumulation of sugars in the berry is due to the transformation of malic acid into sugars via respiratory metabolim, being these biochemical processes influenced by several factors, among them, solar irradiation and temperature. In the present work on Syrah grapes, higher soluble solids and lower acidity were obtained, when compared to products from other Brazilian regions, which could be attributed to the high availability of light and temperatures found in the São Francisco river valley, Brazil.

3.2. Analytical Results on Syrah Wine

The increase of grape pH during the onset of grape maturation resulted in an increased of pH of the resulting wine, reaching values of pH 3.92 in wine made from harvest at 133 dap, in early over-ripening (Table 2). At the beginning of the harvest (84 and 91 dap), wines presented a large amount of dry extracts (31.6 and 27.3g L^{-1} respectively), but this extracts were composed mainly by organic acids, confirmed by high acidity of grapes and wines (titrable acidity 307 and 206 mEq L^{-1}, respectively). With the evolution of grape maturation, organic acid concentration decreased, thus reducing the dry extracts. However, there was an increase in soluble solids in the period from 98 to 133 dap.

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The values of ashes found in the present study increased with advancing maturity of the wine, starting from 3.7 g L^{-1} at 84 dap to 5.6 g L^{-1} at 133 dap and there was an increased concentration of alcohol in wine, starting from 5.6% at 84 dap to 12.8% at 133 dap. The amount of ethyl alcohol in Syrah grapes harvested starting from 105 dap (Table 2). The results about volatile acidity in all the analyzed wines were found less than 8 mEq L^{-1}. In the period from 112 to 133 dap a small reduction of tartaric acid in wine (Table 2) was observed in comparison to grape must content (Table 1).

A significant accumulation of tannins from 112 dap (1.96 g L^{-1}), reaching a peak maximum at 133 dap (2.61 g L^{-1}) is evident. The accumulation of anthocyanins in Syrah wine was constant and proportional to the grape maturation. At 112 dap, the wine obtained presented a higher concentration of anthocyanins. In our experimental Syrah grapes and wines, the total polyphenol index (TPI) increased with grape maturation, demonstrating the best values between 119 and 132 dap.

This increase in pH observed in this study is reflected by the decrease of wine acidity with increasing maturity of the grape, and is considered a peculiar point for Syrah grapes in the São Francisco river valley, since at pH around 4.0, the conservation and stability of wine become more sensitive (Peynoud, 1984, Orduna et al., 2010). According to Rankine (1989), it is recommended that in red wines the pH is between 3.3 and 3.7 for proper conservation and wines presenting pH values above these limits should be corrected by adding tartaric acid. Dallas et al. (2003) mentioned that at pH 3.2, low molecular weight procyanidins are more resistant to chemical and physical degradation. This could represent an important information in studies of wine stability in the tropical regions. In Syrah wines resulting from ripe fruits (119 to 133 dap), pH values were higher than those found in other wine regions (Orlando et al. 2008, Cosme et al., 2009, Garde-Cerdán et al., 2011), confirming the need of adopting specific actions to reduce wine pH in São Francisco river valley, possibly by chemical acidification with tartaric acid, modification of grape handling to maintain a higher concentration of acids in the ripe berries or decreasing the concentration of available potassium in the soil, through the reduction of potassium fertilizers, suggesting to perform chemical analysis of the soil, periodically. Viviani et al. (2007) studying the different varieties of wine in southern Spain, found pH values around 3.9 in Syrah wines, similar to those obtained in the present work.

The wines studied presented a large amount of dry extracts and this extracts were composed mainly by organic acids. With the evolution of grape maturation, organic acid concentration decreased, thus reducing the dry extracts. However, there was an increase in soluble solids in this period, probably due to the accumulation of phenolic compounds in grapes and to their higher extractability in the resulting wines. The amount of extract (soluble solids, excluded sugars) determines the body of the wine. Wine containing less than 2% extract is considered as a light wine, when compared with other degusting wines, which show extracts up to 3 (Peynoud, 1984).

The values of ashes found in the Syrah wine studied increased with advancing maturity. The ash content found in wines were higher than those reported by Mota et al. (2009) in Syrah wine from Três Corações, Minas Gerais State, (Brazil), a temperate region, and suggesting that wines from São Francisco river valley would be characterized by a good body.

Table 2. Analytical parameters of wines resulting from Syrah grapes harvested at different times in the São Francisco river valley during the first half of 2009

parameter	Days after pruning								*CV%*
	84	91	98	105	112	119	126	133	
pH	2.59f	2.76e	3.35d	3.55c	3.59c	3.69b	3.70b	3.92a	*1.4*
Titrable acidity (mEq L^{-1})	307d	206c	104a	84a	75a	70a	68a	65a	*6.2*
Volative acidity (mEq L^{-1})	2.5c	2.5c	6.2b	6.3b	6.4b	6.7b	7.6a	7.8a	*6.4*
Tartaric acid (g L^{-1})	1.3b	1.4b	1.5b	1.5b	1.8a	1.9a	1.9a	2.1a	*23.2*
Density (g mL^{-1})	1.007e	0.998d	0.995c	0.994b	0.993a	0.993a	0.993a	0.992a	*0.1*
Alcohol %v/v	5.6h	7.0g	8.9f	10.0e	10.5d	11.1c	12.3b	12.8a	*1.2*
Dry extract (g L^{-1})	32.6a	27.3b	21.4f	23.3e	24.4d	25.8c	27.6b	31.8a	*1.0*
Ashes (g L^{-1})	3.7d	2.7e	3.9d	4.6c	4.5c	5.0b	5.2b	5.6a	*2.8*
Total tannins (g L^{-1})	0.93c	1.03c	1.08c	1.22c	1.96b	2.08b	2.06b	2.61a	*7.4*
Total anthocyanins (mg L^{-1})	55e	203d	322c	421c	538b	586b	669b	851a	*18.4*
Total polyphenols index	20d	24d	26d	33c	41b	45b	54a	58a	*8.3*

*Means followed by the same letters in the same column do not differ by Scott-Knott test at 5% probability.

With the advance of maturation and accumulation of sugars in the grapes, there was an increased concentration of alcohol in wine, starting from 5.6% at 84 dap to 12.8% at 133 dap. The amount of ethyl alcohol in the wines studied starting from 105 dap, showed that there is no need of external sugaring in order to obtain marketable wines, according to the Brazilian legislation (Brazil, 2004), and concomitantly presenting a good stability. Some authors referred about the approximate alcohol content of Syrah wines from different regions of Spain and Portugal (Cosme et al. 2009, Kontoudakis et al., 2011, Garde-Cerdán et al., 2011), reporting values similar to those found in the present work.

The results about volatile acidity in all the analyzed wines, demonstrating that the winemaking process was successful in relation to undesirable microbial contamination. It was noted, during the period in which analysis were carried out, an increase of volatile acidity with the advance of grape ripening, which can be attributed to the formation of acetic acid, one of the secondary metabolites of alcoholic fermentation. Garde-Cerdán et al. (2011) described an increase in volatile acidity in wines with the progress of fermentation. According to Peynaud (1984), the amount of acetic acid produced during a pure alcoholic fermentation should be in the order of 3 to 6 mEq L^{-1}, depending on the yeast strain, must composition and fermentation conditions.

Comparing the concentration of tartaric acid in grapes and in the resulting wines, it is clear that, as maturation proceeded, tartaric acid in wines was conserved. The loss of tartaric acid in Syrah wines (Table 2) obtained in this experiment decreased with the progression of grape maturation (Table 1), with a consequent increase in pH and alcohol concentration.

Depending on the grape variety, its maturation degree and winemaking technique, the content of tannins in red wines range from 1 to 4 g L^{-1} (Peynoud 1984). The results observed in all the experimental wines produced were within this range. In this study there was a significant accumulation of tannins and of anthocyanins, showing that the accumulation and extraction of these pigments in this variety, in the São Francisco River Valley, was increasing with maturation. The anthocyanins concentration at 112 dap, was higher than that reported by Cabanis and Cabanis (2000) (500 mg L^{-1}), reaching 851 mg L^{-1} in the 133 dap, showing the good color potential of this variety.

Studies on the influence of plant pruning in high altitude grown vineyards on Syrah wine quality in São Joaquim - SC (Brazil) showed that the highest concentration of extractable anthocyanins in grape berries was found after 64 days from the appearance of fruit color, in the 2005/2006 harvest and after 74 days in the 2006/2007 season (Silva et al., 2009). Similar values were observed in the present study, where the highest anthocyanins value was found in the 133 dap wine (64 days after the appearance of grape color). Studies on the influence of different maturation phases in the polyphenolic composition and wine quality of Cabernet Sauvignon in the region Tarragona (Spain) found an increase in anthocyanin concentration seven weeks after the color appearance period, reaching a value of 1108 mg L^{-1} (Kontoudakis et al., 2011).

In order to obtain a good wine color, the accumulation of anthocyanins in grape skins is a necessary condition. However, it is not always enough. It is necessary that cell maturation proceed as these molecules will be easily extracted by gentle technology (Gachons and Kennedy, 2003, Canals et al. 2005, Regules et al. 2006, Busse-Valverde et al. 2010). This characteristic was fully observed in Syrah grapes evaluated in the present work. As an example, the 112 dap wine, with only one pumping per day and five days of maceration, showed the highest anthocyanin concentration.

The TPI increased linearly with grape maturation. According to Hernández (2004), values of wine TPI over 60 should be devoted to vintage wines, while TPI values between 55 and 45 give rise to young wines, and wines with TPI under 40 are considered mediocre. These data show that, in the São Francisco river valley, the potential quality of Syrah wine, as regards total polyphenols, increased with the maturation of grapes. According to the TPI values found in the Syrah wines (Table 2), it is clear that, up to 112 dap, wines can be classified as mediocre, while as young Syrah wines, with TPI values above 40, only from 119 to 133 dap. Kontoudakis et al. (2011), on Sauvingnon Cabernet wine, found TPI values ranging from 39 to 51, according to grapes ripeness, and Viviane et al. (2007) cited TPI values of 80 in Syrah wines from southeast Spain.

Possible correlations should be noted in Table 3, among different variables, such as pH, soluble solids and acidity regarding Syrah grapes during the maturation progress, and among pH, titrable acidity, alcohol content, anthocyanins, tannins and ashes regarding wines.

The correlations noted in Table 3, among different variables show a good maturation of Syrah variety in the São Francisco river valley. Several authors stated that during grape ripening the concentrations of sugars, amino acids, phenolic compounds and potassium tend to increase, while organic acids, particularly malic acid, decrease. This could explain the mathematical correlations found in the present study (Coombe, 1987, Ollat et al. 2002, Adams, 2006). Kontoudakis et al. (2011) found that the higher the density of grape juice, which is highly influenced by the concentration of soluble solids, higher will be the values of ethanol, pH, TPI, anthocyanins and proanthocyanidins, and lower the acidity of wines. These results were similar to those obtained in the present study, and strengthen the evidence for the usefulness of the measurement of juice soluble solids, as a parameter in the estimation of the main chemical components of wine.

Table 3. Correlation matrix between analytical variables of Syrah grapes and wines from different harvesting times in the São Francisco river valley, during the first half of 2009

	grape pH	grape TarA	grape TA	grape SS	wine pH	Wine TA	wine DS	wine TT	wine TAC	wine TPI	wine AC	wine VA	wine DE	Wine AS	wine TarA
grape pH	1														
grape TarA	-0.49*	1													
grape TA	-0.92*	0.18	1												
grape SS	0.99*	-0.43*	-0.93*	1											
wine pH	0.91*	-0.17	-0.95*	0.93*	1										
wine TA	-0.83*	-0.01	0.95*	-0.84*	-0.95*	1									
wine DS	-0.58*	-0.17	0.78*	-0.62*	-0.68*	0.85*	1								
wine TT	0.93*	-0.64*	-0.78*	0.91*	0.81*	-0.69*	-0.44*	1							
wine TAC	0.92*	-0.41*	-0.87*	0.94*	0.91*	-0.82*	-0.60*	0.88*	1						
wine TPI	0.95*	-0.57*	-0.85*	0.96*	0.85*	-0.74*	-0.50*	0.93*	0.94*	1					
wine AC	0.97*	-0.34	-0.95*	0.98*	0.97*	-0.91*	-0.68*	0.88*	0.94*	0.93*	1				
wine VA	0.76*	0.01	-0.86*	0.74*	0.88*	-0.90*	-0.62*	0.63*	0.70*	0.65*	0.81*	1			
wine DE	0.02	-0.76*	0.30	0.02	-0.24	0.48*	0.59*	0.23	0.03	0.17	-0.10	-0.50*	1		
wine AS	0.88*	-0.42*	-0.78*	0.88*	0.88*	-0.71*	-0.29	0.84*	0.84*	0.88*	0.88*	0.74*	0.11	1	
wine TarA	0.18	0.46*	-0.39*	0.18	0.40*	-0.49*	-0.41*	0.03	0.07	0.04	0.25	0.55*	-0.62*	0.20	1

*Pearson correlations significant at 5 % probability.
Legend: TarA - tartaric acid; TA – titrable acidity; SS – soluble solids; DS – density; TT – total tannins; TAC – total anthocyanins; TPI – total polyphenol index; AC – alcohol content; VA – volatile acidity; DE – dry extract and AS – ashes.

Grapes used in the winemaking process are harvested according to various criteria, depending on the country or region of production, the type of wine being produced and the natural conditions prevailing in a particular harvest period. In Brazil, the most commonly used criterion is the sugar content, because wine is ultimately a product of the transformation of grape sugar into alcohol and other by products. Depending on the environment and climate, the highest wine anthocyanin content may coincide with the maximum ratio of sugar soluble/total acidity (SS/TA), being considered as the optimal ripeness parameter (Ribéreau-Gayon et al. 2003). The maximum SS/TA in evaluated Syrah grapes was 56 (see Table 1), and it was found in dap between 126 and 133, and coincided with the highest concentrations of anthocyanins (851 mg L^{-1}) and total tannins (2.6 g L^{-1}) in wine (Table 2), being an indicator of the ideal harvest time for the Syrah variety in the tropical climate of São Francisco river valley. This was confirmed by the analytical composition of wines, that between 126 and 133 dap, showed approximate values of 12.4% alcohol, 30 g L^{-1} of dry extract, 5.2 g L^{-1} ashes, and TPI = 56, with only one pumping daily for a five days maceration.

4. Conclusions

Syrah grapes considered in the present work presented a good evolution of maturation, and grapes harvested between 126 and 133 days after pruning, showed the best oenological potential for the development of red wine. The use of pH and soluble solids appeared useful parameters in the estimation of maturation degree and quality potential of grapes for winemaking.

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