Chemical and Sensorial Characterization of Tropical Syrah Wines Produced at Different Altitudes in Northeast of the Brazil

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Over the years, viticulture has expanded to new regions outside the temperate zones, such as Northeast Brazil, India, Thailand, Myanmar, Vietnam, Bangladesh and Venezuela, characterized by the production of tropical wines. It is important for the productive sector to comprehend the effects of grapevine interaction with the characteristics of each new region on wines composition. In this study, the composition of wines of Syrah from two regions with different altitudes in Northeast Brazil were analyzed by different methodologies to characterize chemical compounds as sugar, acids, minerals, phenolics (anthocyanins, flavonols, stilbenes and condensed tannins) and the sensory profile. The wines of the Bahia region (1100 m of altitude) obtained high concentrations for chemical parameters related to color, monomeric anthocyanins, stilbenes and monomeric and oligomeric tannins. Wines of the low altitude region, Pernambuco (350 m of altitude) were characterized by higher concentrations of flavonols (kaempferol, isorhamnetin, quercetin and rutin) and polymerized tannins. The chemical composition of wines from the two studied regions was influenced by altitude. A trend towards higher concentrations in most for phenolic compounds analyzed was observed in wines from the higher altitude region during the two years of study. Regarding the sensory profile, fruity, floral, herbaceous and empyreumatic attributes aromatic obtained highest scores in wines of the 350 m altitude region, the other attributes were dependent on the year of harvest.

INTRODUCTION

The traditional wine production in the world is located in temperate regions, between the 30-45° parallels in the Northern Hemisphere and between 29-42º in the Southern Hemisphere (Tonietto & Carbonneau, 1999). The knowledge of the physiology of the vine and the advances of the techniques of viticulture allowed the expansion of the production of grapes and wines to the regions located between the tropics, denominated regions of tropical viticulture (Tonietto & Pereira, 2011).

In the northeast of Brazil, in the Sub-middle region of the São Francisco Valley, the production of wines with *Vitis vinifera* L. varieties has been notable. It is located between parallels 8-9º of the Southern Hemisphere, with an altitude of 350 m, has a semi-arid tropical climate (average annual temperature of the region is 26 ºC). The soil and climatic characteristics allow staggering the production of grapes for wines throughout the year and a vine produces two annual harvest, mainly due to high temperatures, high insolation rates and water available in abundance for irrigation (Pereira *et al*., 2008a; Lima *et al*., 2011).

Another region of Northeast Brazil that is investing in the production of *Vitis vinifera* L. grapes is Morro do Chapéu, in state Bahia, located at 11° 33 'S and 41° 09 'W in the Chapada Diamantina, at 1100 m of altitude, where climatic conditions can be classified as tropical at altitude (average annual temperature is 19 ºC). In this region studies are being carried out on grapevines adaptation and wines production, as a new alternative for the development of agriculture and industry. Unlike the region of the São Francisco Valley, the production of grapes at Morro do Chapéu occurs only once a year, due to rainy periods during the winter in this region.

Some authors have studied the composition of wines

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in a tropical region: Jirayus *et al*. (2007) after evaluating five red wines among them Syrah, in Thailand, detected high concentrations of trans-resveratrol and gallic acid; Fernández *et al.* (2009) in a study with commercial wines in Venezuela, found high levels of minerals potassium, calcium, magnesium and sodium; Satisha *et al.* (2013) in the study of the influence of management practices on fruit composition and wine cultivation in the semi-arid tropical region of India, concluded that in tropical semi-arid conditions the concentration of tartaric acid and anthocyanins may decrease meanwhile the acid malic and potassium content may increase; Pereira *et al.* (2011) determined the physicochemical and aromatic characteristics of some tropical wines elaborated in Northeast Brazil, identified high concentrations of 2 methyl-1-butanol in Tempranillo and Syrah wines, methanol and 1-propanol in Petit Verdot, 1-propanol in Chenin Blanc and ethyl acetate in Sauvignon Blanc; Oliveira *et al.* (2012) when evaluating the influence of harvest, clone and rootstock on the chemical characteristics of tropical Syrah wine, found higher concentrations of myricetin, quercetin and kaempferol in wines made with clones in less vigorous rootstocks, as well as high concentrations of anthocyanins in grape wines of clone 525 (in rootstock IAC 313).

Tropical wines are considered recent in the current wine world, which represents a break in the pattern in world oenology. Since it is a few years old activity, when compared to the traditional producing regions, the potential of typicity, composition and quality of the wines is not yet fully unveiled. Considering the above and in the absence of publications with comparative studies on the composition of the wine elaborated with Syrah grapes, of tropical conditions with different altitudes in Northeastern Brazil, this work aims to carry out a broad characterization of these wines using different methodologies.

MATERIALS AND METHODS

Characterization of vineyards and grapes

The vineyards are located in two regions of the Brazilian Northeast, Morro do Chapéu (1100 m of altitude) in the Bahia and in the municipality of Lagoa Grande, in Pernambuco (350 m of altitude). The soils of the two areas are classified in argisols red-yellow in the region of Lagoa Grande and latosols red-yellow in Morro do Chapéu (Embrapa Solos, 2006).

Grapes *"Vitis vinifera* L." of the Syrah variety were harvested at both sites, the plants are cultivated in a trellis system and irrigated by drip irrigation. The vines of the region of Pernambuco are older (with an average of 10 years) and have two productive pruning. Vines from the highest altitude region are only four years old (in the first harvest of the study) and one annual production due to rainy periods at one time of the year. The grapes were harvested in the region of Bahia in September, year of 2014 (composition of the grape at harvest: pH 3.66; total soluble solids 21.2 ºBrix; total acidity 5.8 g L^{-1} of tartaric acid) and in October of 2015 (pH 3.76; total soluble solids 21.5 ºBrix; total acidity 5.1 g L^{-1} of tartaric acid). In Pernambuco, the harvests were in the months of December of 2014 (pH 4.29; total soluble solids 20.9 ºBrix; total acidity 5.6 g L^{-1} of tartaric acid) and September of 2015 (pH 3.44; total soluble solids 18.2 ºBrix; total acidity 6.4 g L^{-1} of tartaric acid), respectively. In each year and in both places, 40 kg of grapes were collected manually, in marked plants of different rows (25 vines) in the vineyard and in good sanitary condition and transported with plastic boxes. The decision of the harvest point was defined by the winery.

Production steps of monovarietal Syrah wines

The wines were elaborated, on an experimental scale (a sample composed of forty kg), the elaboration of the wines followed the traditional vinification for red wines, with the following steps: after harvesting, the grapes were guarded in a cold room (0-5°C) until vinified, it was removed from the stalks of the grapes with a semi-automatic equipment (Model DH150-DA, Recifer-Brazil), then 50 mg L^{-1} of sulfur dioxide and 20 g hL^{-1} of yeast (*Saccharomyces cerevisiae*, bayanus strain - Everintec, Italy) were added for the alcoholic fermentation which occurred at the temperature between 22 to 25ºC, the "remontage" was performed once a day with rack and return modality, the maceration time, the contact of the solid parts with the liquid, uniform in all treatments of seven days, with the intention of maintaining homogeneity of the extraction of the phenolic compounds. The end of the alcoholic fermentation was identified through the stability in the value of the density and analysis of alcohol content. The malolactic fermentation was without addition of bacteria, only with the native species, with temperature varying between 16 to 18ºC, identifying the end through paper chromatography (OIV, 2014). A tartaric stabilization in cold (0-5°C) was for 30 days, the amount of sulfur dioxide was corrected and then bottled in green bottles and the head space was replaced with nitrogen before closing. The wines elaborated were stored in the temperature of 16 ± 2ºC.

Classical chemical analysis

Wines were analyzed six months after the end of the tartaric stabilization, which the following classic parameters were evaluated: pH, total and volatile acidity, alcohol content, dry extract, free and total sulfur dioxide; residual sugar; minerals; paper chromatography (to accompany the malolactic fermentation) using the methods of OIV (2014).

In addition to spectrophotometric analysis: total anthocyanins (Somers & Evans, 1977); colored anthocyanin (Somers & Evans, 1977); total phenols (Ribéreau-Gayon, 1970); flavonoids and non-flavonoids (Kramling & Singleton, 1969); color intensity and tonality (OIV, 2014); total and polymeric pigments (Somers, 1971; Somers & Evans, 1977) and tanning power (De Freitas & Mateus, 2001), were performed according to the methods proposed and described in the references.

Quantification by high performance liquid chromatography of organic acids

The quantification of tartaric, malic, citric, lactic, acetic and succinic acids was performed by high performance liquid chromatography (HPLC) as described by Natividade *et al*. (2013) and using a chromatograph coupled with a diode detector (DAD) model Aliance e2695, Milford, USA. The pulp and wine samples were filtered through a 0.45 µm membrane and injected in triplicate. For determination, the

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DAD wavelength was maintained at 210 nm, with a run time of 15 min, flow rate 0.6 mL min^{-1}, temperature at 26°C and volume injection of 10 µL. The column used was a Gemini-NX C18 (150 mm x 4.60 mm, with internal particles 3 µm) and Gemini-NX C18 pre-columns (4.0 mm x 3.0 mm) both from Phenomenex, USA. The mobile phase comprised of a 0.025M KH_2-PO_4 solution acidified with H_3PO_4 to pH 2.6. The identification and quantification were performed based on standard curve using commercial standards of the corresponding acids.

Separation and quantification of monomeric anthocyanins by HPLC

For separation of the monomeric anthocyanins, a Perkin-Elmer HPLC (USA) was used, consisting of pump (Series 200) and detector (LC95 Uv/Visible), the separation occurred in a column C18 (250 mm x 4 mm), of reverse phase with 5µm of compaction, protected by a pre-column consisting of the same material, both from LichroCart, Merck-Germany. The solvents consisted of: A (40% formic acid), B (acetonitrile PA) and C (bidistilled water). Methanol / bidistilled water (50:50 v/v) was used to wash the column after the analyses. The initial conditions used were: 25% A, 6% B and 69% C for 15 min, followed by a 25% linear gradient of A, 25.5% B and 49.5% C for 70 min. The finishing with 20 min of 25% A, 25.5% B and 49.5% C. The flow was 0.7mL min^{-1}, using a detector with wavelength at 520nm. Both the samples and the solvents were filtered under the same conditions. The volume injected was 20 µL and the analyzes were performed in triplicate at a temperature between 20 to 25°C. Identification followed the method described by Roggero *et al*. (1986) and quantification based on the standard malvidin curve.

Separation and quantification of individual flavonols and stilbene by HPLC

Flavonols and stilbene were determined by HPLC on a Waters, USA (model Aliance e2695), chromatograph equipped with solvent pump and automatic injector, coupled with DAD, according to the methodology described by Natividade *et al*. (2013).

Data collection and analysis were performed using Empower™ 2 software (Milford, USA). In DAD, the detection of the compounds was performed at 320 nm for trans-resveratrol and 360 nm in the analysis of flavonols: kaempferol 3-*O*-glucoside, myricetin 3-*O*-glucoside, quercetin-3-*O*-glucoside, rutin (quercetin-3-*O*-rutiniside) and isorhamnetin 3-*O*-glucoside. The column used was a Gemini-NX C18, 150 mm x 4.60 mm, with internal particles 3 µm, and the pre-column was a Gemini-NX C18, 4.0 mm x 3.0 mm, both made by PhenomenexÒ. The oven temperature was maintained at 40°C, the injection volume of 10 µL (the wine being previously filtered through a 0.45 µm membrane) and the flow rate was 0.5 mL min^{-1}.

The mobile phase consisted of a solution 0.85% phosphoric acid (Solvent A) and acetonitrile (solvent B). The elution gradient was: 100% A; 0-10 min: 93% A and 7% B; 20 min: 90% A and 10% B, 30 min: 88% A and 12% B; 40 min: 77% A and 33% B; 45 min: 65% A and 35% B and 55 min: 100% B. The identification and quantification were performed based on standard curve using commercial standards of the corresponding flavonols.

Separation of proanthocyanidins in Sep-Pak C18 cartridges and quantification of the obtained fractions by the vanillin assay

The fractionation of the flavanols was performed using a Sep-Pak C18 cartridge (Waters, USA) according to their degree of polymerization in three fractions; monomeric, oligomeric and polymeric, respectively, following the method described by Sun *et al*. (1998a). The 3-flavanol content of each fraction was determined using the vanillin assay according to the method described by Sun *et al.* (1998b). The quantification is performed by means of standard curves prepared from 3-flavanol monomers, oligomers and polymers of grape seed isolates and as described by Sun *et al.* (1998 a, b); Sun *et al*. (2001). The separation was performed in triplicate for each sample.

Fractionation of low molecular weight flavanols into a polyamide column chromatography and further quantification by HPLC

Five milliliters of wine were fractionated on a polyamide column (Macherey-Nagel, Germany) as described by Ricardo-da-Silva *et al*. (1990) phenolic acids and other interferents compounds were first eluted with 80 mL of phosphate buffer, pH 7.0. The monomeric flavanols were eluted with 50 mL of ethyl acetate / water (30:70 v/v) and small oligomeric procyanidins with 50 mL of acetone / water (75:25 v/v). The fractions were brought to dryness, dissolved in 1.2 mL of methanol / water (50:50 v/v), filtered through a 0.45 µm membrane and finally injected onto the HPLC column. The new polyamide column was used for each preparation, with three replicates per sample. After column separation of polyamide, as described above, an HPLC equipment was used for analysis, consisting of a UV-Vis detector (Waters 2487) and a Merck L-7100 pump. Separation was performed on a C18 reverse phase column (LichroCart, Merck, Germany), dimensions 250 mm x 4.6 mm x 5 µm, at room temperature (25°C).

For monomeric flavan-3-ols, a gradient consisting of solvent A (water / acetic acid, 97.5: 2.5, v/v) and solvent B (acetonitrile / solvent A, 80:20, v/v) was applied at a flow rate of 0.9 mL min^{-1} as follows: 7-25% B linear from 0 to 31 min, followed by washing (methanol / water, 50:50 v/v) 32-50 min and the rebalancing of the column from 51 to 65 min under initial gradient conditions. For oligomeric procyanidins, a solvent gradient A (bidistilled water) and solvent B (bidistilled water / acetic acid, 90:10 v/v) was applied at a flow rate of 1.0 mL min^{-1} as follows: 10-70% linear B 0-45 min, 70-90% linear B 45-70 min, 90% B isocratic 70-82 min, 90-100% linear B 82-85 min, 100% B isocratic 85-90 min, followed by washing (methanol / water, 50:50 v/v) 91-100 min. And rebalancing the column from 101 to 120 min under initial conditions of the gradient. The detection being carried out at 280 nm and injections in triplicate.

The following flavanol molecules have been quantified: gallocatechin; (+)-catechin; (-)-epicatechin; (-) epigallocatechin; procyanidin dimers B1, B2, B3 and B4, B1-3-*O*-gallate, B2-3-*O*-gallate, B2 3'-*O*-gallate, trimer C1 and trimer T2. The identification of the compounds was done

according to the works of Rigaud *et al.* (1991) and Ricardo-da-Silva *et al*. (1991a) and later confirmed by Monagas *et al.* (2003). The quantification of monomeric flavan-3-ol and small oligomeric procyanidins (some dimers and trimers) were based on standard curves obtained with (+) catechin for the monomers and dimer B2 for the other compounds.

Characterization of the sensory profile of wines

Sensory evaluation was conducted in the sensory analysis laboratory of the Instituto Superior Agronomia in Lisbon by a panel of 12 oenology professionals, seven male and five females (from 22 to 55 years old). The panel was not trained for this study of sensory since they were professionals and were familiar with rating of the specific attributes.

The evaluation of the visual, olfactory and taste characteristics of the wines was carried out with Descriptive Analysis (DA), with 16 attributes: 4 visual sensations (color, color intensity, limpidity and fluidity), 5 aromatic attributes (fruity, floral, herbaceous, spices and empireumatic) and 7 taste attributes (sweetness, acidity, alcohol, bitterness, astringency, body and persistence). Being quantified by a scale with an unstructured intensity of 10 points, with minimum anchorage on the left and maximum on the right.

Each taster evaluated 2 samples per session, with two sections, one in the first half of 2015 (referring to wines from the 2014 harvest) and another in the first half of 2016 (wines from the 2015 harvest). The test room was composed of individual, white, illuminated booths. The volume of 50 mL of wine was individually served, randomising the sample position across tasters, in coded tasting glasses (ISO NORM 3591, 1977) with random 3-digit codes and temperature of 18º ± 2ºC (considered ideal for tasting red wines).

Statistical analysis

All chemical analyses of this study were performed in triplicate, to verify the differences between the samples, based on the two altitudes, an analysis of variance test (One-Way, ANOVA) and Principal Component Analysis (PCA) were determined. In the sensory analysis, an ANOVA test with 2-way of variation (samples and tasters) was performed. The Tukey test (HSD) with a significance level of 5% was used for chemical analysis and sensory profile. Both analyses were performed in STATISTIX 9.0 software (Florida, USA).

RESULTS AND DISCUSSION

Classic analysis

The results of the classic analysis are found in Table 1, there were significant differences ($p \leq 0.05$) in the chemical parameters analyzed between the two wine regions. The pH levels in all wine samples presented relatively high average values (Table 1), being from 3.84 to 4.32 in the region of highest altitude and 3.93 to 4.15 in the low altitude. According to Soares and Leão (2009), the soil-climatic conditions of region of the "São Francisco Valley", low altitude, prevail over the extraction of potassium, favoring high pH in wines also made with other grape varieties in this region. pH values between 3.6 and 4.5 have been observed in this region, which can be attributed to excessive soil fertilization with potassium fertilizers or even to the high natural concentration of this element in the soils of the region. High pH values in the regions of 1100 m altitude (4.32) and 350 m altitude (4.15) in the year 2014, may also be related to high potassium concentration in this harvest (Table 1).

The concentrations of total acidity in the wines varied with the harvest, being the year of 2014 with higher values, both in the region of higher altitude (Bahia) and in the lower altitude (Pernambuco), with values of 6.4 g L^{-1} and 5.7 g L^{-1} of tartaric acid, respectively. The highest total acidity content, in the higher-altitude (1100 m) region, may be related to high concentrations of succinic acid (Table 1). According to Coulter *et al*. (2004) higher concentration of succinic acid may result in a remarkable increase in acidity. However, the high total acidity in the 350 m altitude region, in 2014, due higher concentrations of malic, lactic and acetic acids present in these wines (Table 1).

The alcohol content varied from 11.6 to 12.3 v/v% in the states of Bahia and Pernambuco, in the years 2015 and 2014, respectively, the amount of alcohol in the wine depends on the concentration of initial sugar in the berries and the conditions under which alcoholic fermentation occurs (yeast, temperature, type of wine to be elaborated, among other factors).

Organic acids

Concentrations of tartaric acid in wines ranged from 1905.9 mg L^{-1} to 3302.1 mg L^{-1}, for the region of Bahia and Pernambuco (Table 1) being within the values found in the literature for wines, according to Curvelo-Garcia and Barros (2015), L (+) - tartaric acid is the specific acid of the grapes and the most important of the wine, are determinants of the values of fixed acidity and pH, its content is present between 1500 and 4000 mg L^{-1}. The highest concentrations of the tartaric acid were obtained in wines of the region at 350 m of altitude and are sourced grapes. In the study conditions, high concentrations may be related to the influence of climatic conditions (higher solar radiation, temperature and low thermal amplitude - data not shown), age of the plant, higher photosynthetic rate in the berries, high concentrations of calcium and potassium in this region. According to the literature, the ascorbic acid content and consequently of the tartaric acid in the grapes are influenced by some factors such as: light, time of day, plant age (Cruz-Rus *et al*., 2010); exposure of the bunches to the sun (DeBolt *et al*., 2006); formation of crystals in the berry during maturation, rendering the acid inert for metabolization (Iland & Coombe, 1988).

Succinic acid is formed during the process of alcoholic fermentation also from malolactic fermentation in amounts well dependent on the conditions in which it occurs, as well as the composition of the medium; the concentration in wine can range from 500 to 1500 mg L^{-1} (Curvelo-Garcia & Barros, 2015). The highest levels found in this study were in the higher altitude region with 582.0 and 481.6 mg L^{-1}, in the years of 2014 and 2015, respectively.

Potassium and calcium

Regarding the macronutrient, potassium, the concentrations in the wines of the region of low-altitude, obtained contents above 2.0 g L^{-1} (Table 1). According to the results presented by Pereira *et. al* (2007), for different red wines

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TABLE 1
Classical and spectrophotometric analysis of tropical Syrah wines from regions with different altitudes.

Region	Bahia (1100 m altitude)		Pernambuco (350 m altitude)		ANOVA
Harvest	2014	2015	2014	2015	(p-values)
Classic analyses					
pH	$4.32^{a} \pm 0.0$	$3.84^{c} \pm 0.0$	$4.15^{b} \pm 0.0$	$3.93^{c} \pm 0.0$	**
Total acidity (g L^{-1})	$6.4^{a} \pm 0.1$	$5.2^{c} \pm 0.1$	$5.7^{b} \pm 0.0$	$4.8^{d} \pm 0.1$	***
Volatile acidity (g L^{-1})	$0.41^{d} \pm 0.0$	$0.79^{a} \pm 0.0$	$0.65^{b} \pm 0.0$	$0.57^{c} \pm 0.0$	*
Alcohol content (v/v%)	$11.8^{b} \pm 0.1$	$12.3^{a} \pm 0.2$	$12.3^{a} \pm 0.0$	$11.6^{b} \pm 0.1$	*
Total dry extract (g L^{-1})	$27.6^{b} \pm 0.2$	$24.3^{c} \pm 0.0$	$29.7^{a} \pm 0.2$	$22.8^{d} \pm 0.1$	*
Density (g cm^{-3})	$0.9936^{c} \pm 0.001$	$0.9932^{d} \pm 0.0003$	$0.9953^{a} \pm 0.0001$	$0.9940^{b} \pm 0.0002$	***
Residual sugar (g L^{-1})	$1.6^{b} \pm 0.4$	$1.1^{c} \pm 0.7$	$2.6^{a} \pm 0.3$	$1.8^{b} \pm 1.1$	*
Free sulfur dioxide (mg L^{-1})	$25.9^{c} \pm 0.2$	$30.3^{b} \pm 1.2$	$33.3^{a} \pm 0.0$	$34.3^{a} \pm 1.1$	***
Total sulfur dioxide (mg L^{-1})	$36.7^{d} \pm 0.2$	$51.5^{b} \pm 1.1$	$48.1^{c} \pm 0.0$	$63.2^{a} \pm 1.3$	***
Organic acids (mg L^{-1})					
Tartaric	$2334.1^{c} \pm 6.7$	$1905.9^{d} \pm 1.8$	$2930.2^{b} \pm 5.8$	$3302.1^{a} \pm 11.2$	***
Malic	$16.3^{b} \pm 3.1$	$12.9^{b} \pm 1.2$	$39.7^{a} \pm 1.7$	$16.6^{b} \pm 1.4$	***
Lactic	$2792.8^{a} \pm 3.9$	$1882.6^{b} \pm 2.2$	$3242.7^{a} \pm 2.5$	$1905.6^{c} \pm 2.7$	*
Acetic	$283.6^{b} \pm 2.2$	$166.3^{c} \pm 4.6$	$489.3^{a} \pm 11.1$	$137.1^{d} \pm 4.9$	***
Citric	$64.1^{d} \pm 1.6$	$79.1^{c} \pm 0.9$	$131.3^{a} \pm 0.6$	$93.0^{b} \pm 3.0$	***
Succinic	$582.0^{a} \pm 1.4$	$481.6^{b} \pm 9.8$	$383.3^{c} \pm 5.7$	$408.0^{c} \pm 7.9$	**
Minerals (mg L^{-1})					
Potassium	$1982.2^{b} \pm 0.7$	$1827.8^{c} \pm 1.3$	$2423.3^{a} \pm 1.6$	$2025.1^{b} \pm 2.3$	**
Calcium	$45.3^{c} \pm 0.9$	$70.4^{b} \pm 0.4$	$42.0^{d} \pm 0.8$	$80.5^{a} \pm 0.2$	**

*Means followed by the same letter in the lines did not differ by Tukey test at 5% ($p \leq 0.05$). Standard deviation of triplicate analysis; n.s. (not significant); * (significant differences at a 95% confidence level); ** (significant differences at a 99.9% confidence level); *** (significant differences at a 99.99% confidence level).

from Northeast Brazil, with values between 1835.9 and 3671.8 mg L^{-1}. In general, the grapes and wines of the Sub-middle São Francisco Valley have high concentrations of potassium because some soils present high natural levels of this macronutrient, a fact related to the source material and processes of pedogenesis (Cunha *et al.*, 2010). Another explanation for the high potassium content is the use of the rootstock, Paulsen 1103, which tend to accumulate more potassium than in not grafted vines (Walker *et al.*, 1998).

The values identified for calcium are within those cited in the literature. ranging from 45.3 to 70.4 mg L^{-1} in the region of Bahia (1100 m) and 42.0 to 80.5 mg L^{-1} and Pernambuco (350 m), it is verified that there is no tendency in the calcium concentration for a particular region and the concentration varied in the study years. According to Amerine & Ough (1980) and Themelis *et al.* (1999) calcium levels are usually found in wines ranging from 30 to 200 mg L^{-1} and are strongly dependent on soil composition. Its presence affects some phases of the elaboration process and in high concentrations can cause precipitation after bottling and storage of wine (Amerine & Ough, 1980). The elevated levels of cations, as well as high pH values of the soil have contributed to the rapid chemical evolution of the wines elaborated in the region of Sub-middle São Francisco Valley (Pereira & Bassoi, 2008b).

Total phenols, flavonoids and non-flavonoids

The high-altitude wines, in 2014 followed by 2015, obtained the highest concentrations for the phenolic compounds here considered (Table 2): total phenols, flavonoids and non-flavonoids. Regarding total phenols, the highest concentrations were in the state of Bahia, with a minimum of 1676.9 mg L^{-1} of gallic acid (year 2015) and a maximum of 2142.9 mg L^{-1} of gallic acid (year 2014). The flavonoid compounds obtained the same behavior, with values of 1981.1 and 1486.0 mg L^{-1} of gallic acid, for the harvests of 2014 and 2015, respectively. For non-flavonoid compounds, the highest concentration was 194.7 mg L^{-1} of gallic acid for wines from 2015, a region of 1100 m altitude. The values found for total phenolics and flavonoids in this study, for wines of higher altitude, in 2014, were higher than those detected by Granato *et al.* (2010) for Brazilian Syrah

TABLE 2
Composition and concentration of anthocyanins, flavonols and tannins in tropical Syrah wines from different regions of the Northeast in two harvests.

Region	Bahia (1100 m altitude)		Pernambuco (350 m altitude)		ANOVA
Harvest	2014	2015	2014	2015	(p-values)
Global phenolic compounds					
Total phenols (mg L^{-1})	2142.9^{a} ± 0.1	1676.9^{b} ± 0.2	1456.9^{c} ± 0.2	1401.8^{c} ± 0.5	***
Non-flavonoids (mg L^{-1})	162.4^{c} ± 0.0	194.7^{a} ± 0.1	185.0^{b} ± 0.0	155.9^{d} ± 0.0	**
Flavonoids (mg L^{-1})	1981.1^{a} ± 0.2	1486.0^{b} ± 0.2	1272.4^{c} ± 0.1	1246.5^{d} ± 0.5	***
Color, anthocyanins and other pigments					
Total anthocyanins (mg L^{-1} of malvidin)	372.7^{a} ± 0.3	340.4^{b} ± 6.1	237.5^{d} ± 1.9	314.3^{c} ± 2.8	***
Colored anthocyanins (mg L^{-1} of malvidin)	74.3^{a} ± 0.8	50.5^{b} ± 0.8	35.1^{d} ± 0.3	38.4^{c} ± 0.3	***
Ionization index (%)	19.9^{a} ± 0.3	14.8^{b} ± 0.2	14.5^{b} ± 0.2	11.7^{c} ± 0.5	***
Total pigments (u.a)	13.1^{a} ± 1.6	11.6^{b} ± 0.9	9.2^{d} ± 0.9	10.6^{c} ± 1.2	**
Polymerized pigment (u.a)	4.2^{a} ± 0.2	2.9^{b} ± 0.5	1.8^{c} ± 0.8	1.9^{c} ± 0.3	**
Polymeric pigments index (%)	32.1^{a} ± 1.1	25.0^{b} ± 0.7	19.6^{c} ± 1.0	17.9^{d} ± 0.6	**
Color intensity (u.a)	16.590^{a} ± 0.067	11.540^{b} ± 0.026	7.900^{d} ± 0.053	8.480^{c} ± 0.081	***
Tonality (u.a)	0.732^{b} ± 0.002	0.711^{c} ± 0.003	0.753^{a} ± 0.005	0.665^{d} ± 0.001	**
Condensed tannins (mg L^{-1})					
Monomeric	23.6^{a} ± 1.1	23.9^{a} ± 1.3	16.3^{b} ± 0.4	12.6^{c} ± 0.4	***
Oligomeric	159.1^{a} ± 0.7	146.6^{b} ± 3.7	142.5^{bc} ± 0.4	139.3^{c} ± 0.3	**
Polymeric	302.8^{c} ± 0.9	249.0^{d} ± 1.3	665.4^{a} ± 1.0	400.0^{b} ± 4.4	***
Total tannins	485.5^{c} ± 1.7	419.5^{d} ± 17.0	824.3^{a} ± 1.2	551.9^{b} ± 4.5	***
Tannin power (NTU mL^{-1})	191.0^{c} ± 1.8	153.2^{d} ± 1.3	212.1^{a} ± 2.2	203.2^{b} ± 1.9	***

*Means followed by the same letter in the lines did not differ by Tukey test at 5% ($p \leq 0.05$). Standard deviation of triplicate analysis. Total phenols, non-flavonoids and flavonoids expressed as mg L^{-1} of gallic acid; u.a (absorbance unit); n.s. (not significant); * (significant differences at a 95% confidence level); ** (significant differences at a 99.9% confidence level); *** (significant differences at a 99.99% confidence level).

commercial wines, in different harvests. Regarding wines, in the year 2015, of both altitudes, the contents are in agreement to the same author. The "terroir" affects to a large extent the carbon flow to the different pathways in the metabolism of flavonoids from grape berries, and finally determine the phenol profiles in wines. The lower temperatures and the greater thermal amplitude in the region of 1100 m compared to the region of 350 m seem to favor the synthesis of these compounds.

Total anthocyanins, pigments and color

The harvest of 2014 in the region of higher altitude favored the composition of wines with high concentrations of total anthocyanins (372.7 mg L^{-1} of malvidin) and colored anthocyanins (74.3 mg L^{-1} of malvidin). According to Liang *et al.* (2012) altitude, temperature and precipitation play important roles in the accumulation of anthocyanins and flavonols compounds in *Vitis vinifera* L. vines. These compounds are extracted rapidly from the grapes during winemaking and reach a maximum concentration in the early days.

Ionization index of anthocyanins varied from 11.7% to 19.9%, being within the expected range for young wines, according to Riberéau-Gayon *et al.* (2006) the ionization index for young wines varies from 10 to 30% and increases during aging, reaching 80 to 90% in old wines. The highest percentage for the ionization index of anthocyanins was in the wine from the Bahia region (1100 m of altitude) with 19.9%, fact that is related to higher concentrations of total anthocyanins in these samples (372.7 mg L^{-1} of malvidin).

The total and polymerized pigments were higher in wines from the highest altitude region (1100 m), harvest of 2014 and 2015, respectively. High concentrations of total anthocyanins, monomeric and oligomeric tannins in wines from the 1100 m region may have favored anthocyanin and tannin reactions, increasing the pigmentation in these samples, these reactions already were reported by other authors (Dallas *et al.*, 1996; Riberéau-Gayon *et al.*, 2006; Zeng *et al.*, 2016).

The intensity of color obtained higher value in the region of high altitude (16.60) in the 2014 harvest, already the tonality was higher in Pernambuco, harvest 2014, with 0.753.

The color of red wines does not only depend on anthocyanin content but is closely dependent on the physicochemical characteristics of the pigments and the environment in which they are found (Ribéreau-Gayon, 1973; Timberlake and Bridle, 1976). In this study, it is possible to correlate the wines with higher color intensity (higher altitude) being those that have higher concentrations of anthocyanins and total pigments (Table 2).

Condensed tannins

Regarding the fractionation of the tannins, there were significant differences in the wines (Table 2). The monomeric fraction was higher in the two harvests for the wine of altitude 1100 m, with values of 23.6 and 23.9 mg L^{-1} for the years 2014 and 2015, respectively. Concentration of the oligomeric fraction was between 139.3 mg L^{-1} (Pernambuco, 2015) and 159.1 mg L^{-1} in the state of Bahia, harvest 2014. For polymeric tannins the highest concentrations were in Pernambuco (350 m altitude), with higher values in the 2014 harvest (665.4 mg L^{-1}) followed by the 2015 harvest (400.0 mg L^{-1}). The wines from the Pernambuco region had high concentrations of total tannins, with 824.3 mg L^{-1} in harvest 2014 and 551.9 mg L^{-1} in 2015. The monomeric and oligomeric condensed tannins of this study are below the values found by Sun *et al.* (1998b) in different red wines of Portuguese grape varieties; the polymers are among the concentrates found by the same author.

High concentrations of polymeric and total tannins were observed in wines from the lower altitude region, 350 m, which may be related to a characteristic of the altitude effect, as well as the better extraction capacity of the condensed tannins from the solid parts of the grapes of this region. Li *et al.* (2011) when evaluating Cabernet Sauvignon wines at different altitudes in China also found higher concentrations of polymeric tannins in low altitude region (214 m) when compared to the region with an altitude of 1214 m. The extraction capacity of wine tannins has been reported by other authors under traditional winemaking conditions (Vidal *et al.*, 2004; Adams and Scholz, 2008; Hanlin *et al.*, 2010), but other studies are still needed for tropical climate conditions.

In the tannin power analysis, a chemical parameter that intends to estimate the astringency of a wine (De Freitas and Mateus, 2001) the wines of low altitude obtained high concentrations ranging from 203.2 to 212.1 NTU mL^{-1}, for harvests of 2015 and 2014, respectively. According to the literature, polymeric procyanidins in the concentration of 250-1000 mg L^{-1} have a higher intensity of astringency than oligomeric procyanidins (Ribéreau-Gayon *et al*., 2006) the results obtained in this study are in agreement.

Individual monomeric anthocyanins

In the wines analyzed, it was possible to detect 14 anthocyanin compounds, which constitute three groups of substances: non-acylated anthocyanins 3-*O*-glucoside; anthocyanin esterified with acetic acid and anthocyanin esterified with p-coumaric acid. It is observed in the Table 3 that there is a variation of anthocyanins between regions, being able to be an indicator of altitude influence.

The group of monomeric anthocyanins in their 3-*O*-glucoside form (delphinidin, peonidin, petunidin and malvidin) obtained higher concentrations in wines from the high-altitude region, except for Cyanidin 3-*O*-glucoside. The cyanidin 3-*O*-glucoside was quantified only in the 2014 harvest in Pernambuco (2.3 mg L^{-1}), other studies had already identified and quantified these compounds in Syrah wines as reported by Gutièrrez *et al.* (2005) which found 0.9 to 2.8 mg L^{-1} in Syrah wine after analysis of 0 to 9 months of bottled and Andrade *et al.* (2013) quantified 6.58 - 9.24 mg L^{-1} in commercial wines from the São Francisco Valley and 4.7 to 10.8 mg L^{-1} in Chilean wines.

The malvidin 3-*O*-glucoside is actually the most abundant anthocyanin among those studied, the highest concentration was for the region of Bahia (43.2 mg L^{-1}). The values of malvidin in this study were lower than those found by Li *et al.* (2011) in a study of Cabernet Sauvignon wines of different altitudes in China in which they detected concentrations above 130 mg L^{-1}.

The anthocyanins group 3-*O*-acetylglucoside reached higher concentrations in the wines of the Pernambuco region. A situation also found by Andrade *et al.* (2013) when studying Syrah red wines from the San Francisco Valley and Chile. This can be explained based on the climatic conditions of this region (warm climate with high exposure of the grape to sunlight) that collaborate with the enzymatic activity of the anthocyanin acyltransferase, responsible for converting the glucoside forms to acetylate, improving pigment stability and fruit color (Fei He *et al.*, 2010; Andrade *et al.*, 2013) and consequently of the wines.

In the group of anthocyanins esterified as p-coumaric acid, the highest concentrations in the region of 1100 m of altitude for the compounds peonidin (1.7 mg L^{-1}), delphinidin (3.4 mg L^{-1}) and malvidin (3.6 mg L^{-1}) are found in agreement with those found by Li *et al.* (2011) for Cabernet Sauvignon wines at altitudes of 1214 m. However, there are no studies in the literature that prove a direct relationship between synthesis of anthocyanins coumarylated and the altitude.

In relation to the total monomeric anthocyanins, the highest concentration was for a region of 1100 m altitude with 71.3mg L^{-1}, in the vintage of the year 2014. It is possible to observe that there is no tendency for higher concentrations in a specific region and that the harvest year seems to be more significant.

Flavonols and stilbene

The flavonols detected and quantified during this study (Table 3) were formed by the five flavonoid structures commonly reported for *Vitis vinifera* L.: kaempferol, isorhamnetin, myricetin, quercetin and rutin, each in glucosylated. The low-altitude region was highlighted with higher concentrations for most of the compounds except for myricetin 3-*O*-glucoside. Quercetin 3-*O*-glucoside obtained the highest concentration (25.8 mg L^{-1}) among flavonols studied. This concentration was higher than those found by La Torre *et al.* (2006) for six commercial wines from Sicily and less than that found by Belmiro *et al.* (2017) for Syrah commercial wine from the São Francisco Valley, which found 125.5 mg L^{-1}.

Concentrations of myricetin ranged from 1.5 to 5.0 mg L^{-1}, the region of high-altitude in 2014, obtained

TABLE 3
Composition and concentration of anthocyanins, flavonols, stilbene, monomeric and small oligomeric procyanidins in tropical Syrah wines from different altitudes of the Northeast.

Region	Bahia (1100 m altitude)		Pernambuco (350 m altitude)		ANOVA
Harvest	2014	2015	2014	2015	(p-values)
Monomeric anthocyanins (mg L^{-1})					
Cyanidin 3-*O*-glucoside	$0.0^{b} \pm 0.0$	$0.0^{b} \pm 0.0$	$2.3^{a} \pm 0.1$	$0.0^{b} \pm 0.0$	***
Delphinidin 3-*O*-glucoside	$1.1^{d} \pm 0.2$	$5.9^{a} \pm 0.1$	$2.3^{c} \pm 0.1$	$4.6^{b} \pm 0.5$	*
Peonidin 3-*O*-glucoside	$3.3^{a} \pm 0.2$	$3.4^{a} \pm 0.1$	$1.3^{b} \pm 0.1$	$1.6^{b} \pm 0.2$	***
Petunidin 3-*O*-glucoside	$5.2^{a} \pm 0.4$	$4.5^{b} \pm 0.3$	$0.9^{d} \pm 0.1$	$3.6^{c} \pm 0.1$	***
Malvidin 3-*O*-glucoside	$43.2^{a} \pm 0.6$	$29.5^{c} \pm 0.9$	$20.9^{d} \pm 1.3$	$33.0^{b} \pm 0.2$	***
Peonidin 3-*O*-acetylglucoside	$0.0^{c} \pm 0.0$	$1.0^{b} \pm 0.2$	$1.8^{a} \pm 0.1$	$0.9^{b} \pm 0.0$	***
Petunidin 3-*O*-acetylglucoside	$1.1^{b} \pm 0.1$	$0.5^{c} \pm 0.1$	$1.5^{a} \pm 0.1$	$1.4^{a} \pm 0.1$	***
Cyanidin 3-*O*-acetylglucoside	$0.4^{b} \pm 0.1$	$0.3^{b} \pm 0.0$	$0.4^{b} \pm 0.0$	$1.1^{a} \pm 0.0$	***
Delphinidin 3-*O*-acetylglucoside	$1.2^{b} \pm 0.2$	$2.3^{a} \pm 0.2$	$1.3^{b} \pm 0.1$	$2.2^{a} \pm 0.1$	*
Malvidin 3-*O*-acetylglucoside	$5.4^{c} \pm 0.2$	$5.7^{c} \pm 0.1$	$12.6^{a} \pm 0.1$	$10.3^{b} \pm 0.3$	***
Peonidin 3-*O*-coumarylglucoside	$1.1^{b} \pm 0.1$	$1.7^{a} \pm 0.3$	$0.0^{c} \pm 0.0$	$0.9^{b} \pm 0.0$	**
Petunidin 3-O-coumarylglucoside	$0.4^{b} \pm 0.1$	$0.9^{a} \pm 0.1$	$1.1^{a} \pm 0.0$	$0.6^{b} \pm 0.0$	*
Delphinidin 3-*O*-coumarylglucoside	$3.4^{a} \pm 0.2$	$2.7^{b} \pm 0.2$	$0.0^{c} \pm 0.0$	$2.3^{c} \pm 0.1$	***
Malvidin 3-*O*-coumarylglucoside	$3.6^{a} \pm 0.1$	$2.8^{bc} \pm 0.1$	$3.0^{b} \pm 0.1$	$2.3^{c} \pm 0.0$	*
Total anthocyanins monomeric	$71.3^{a} \pm 0.9$	$61.8^{c} \pm 0.9$	$51.7^{d} \pm 1.2$	$64.1^{b} \pm 0.9$	**
Flavonols (mg L^{-1})					
Kaempferol 3-*O*-glucoside	$1.4^{b} \pm 0.0$	$1.10^{c} \pm 0.0$	$1.4^{b} \pm 0.1$	$3.5^{a} \pm 0.0$	***
Isorhamnetin 3-O-glucoside	$9.8^{b} \pm 0.2$	$4.6^{d} \pm 0.0$	$16.5^{a} \pm 0.1$	$13.9^{b} \pm 0.2$	***
Myricetin 3-*O*-glucoside	$5.0^{a} \pm 0.1$	$3.1^{c} \pm 0.0$	$1.5^{d} \pm 0.1$	$3.4^{b} \pm 0.0$	***
Quercetin-3-O-glucoside	$8.1^{c} \pm 0.1$	$6.0^{d} \pm 0.1$	$15.8^{b} \pm 0.2$	$25.8^{a} \pm 0.8$	***
Rutin (Quercetin-3-*O*-rutiniside)	$0.7^{b} \pm 0.0$	$0.6^{b} \pm 0.0$	$0.5^{c} \pm 0.0$	$1.3^{a} \pm 0.0$	***
Total flavonols	$25.0^{c} \pm 0.8$	$15.4^{d} \pm 0.1$	$35.7^{b} \pm 0.9$	$47.9^{a} \pm 1.1$	***
Stilbene (mg L^{-1})					
Trans-resveratrol	$3.5^{a} \pm 0.1$	$2.2^{b} \pm 0.0$	$1.3^{d} \pm 0.0$	$1.7^{c} \pm 0.1$	***
Flavanol monomeric and small oligomeric procyanidins (mg L^{-1})					
(+) Gallocatechin	$4.7^{a} \pm 0.1$	$0.9^{c} \pm 0.0$	$1.6^{b} \pm 0.3$	$0.6^{c} \pm 0.2$	**
(+) Catechin	$3.5^{b} \pm 0.1$	$1.7^{c} \pm 0.1$	$5.5^{a} \pm 0.1$	$1.5^{c} \pm 0.1$	***
(-) Epicatechin	$18.7^{a} \pm 0.4$	$8.8^{b} \pm 0.2$	$6.9^{c} \pm 0.0$	$6.2^{d} \pm 0.1$	***
(-) Epigallocatechin	$12.4^{a} \pm 0.2$	$7.1^{b} \pm 0.1$	$3.2^{c} \pm 0.4$	$12.6^{a} \pm 0.8$	***
B1	$13.8^{b} \pm 0.2$	$3.8^{d} \pm 0.1$	$20.8^{a} \pm 0.1$	$9.0^{c} \pm 0.1$	***
B2	$4.4^{a} \pm 0.3$	$1.2^{b} \pm 0.0$	$4.0^{a} \pm 0.3$	$1.3^{b} \pm 0.1$	*
B3	$8.2^{a} \pm 0.4$	$2.7^{c} \pm 0.1$	$4.8^{b} \pm 0.2$	$1.1^{d} \pm 0.2$	***
B1 3-*O*-gallate	$2.5^{b} \pm 0.2$	$3.9^{a} \pm 0.1$	$1.9^{c} \pm 0.0$	$3.0^{b} \pm 0.3$	***
B2 3-*O*-gallate	$0.9^{a} \pm 0.1$	$0.5^{b} \pm 0.1$	$0.6^{b} \pm 0.1$	$0.1^{c} \pm 0.0$	**
B2 3'-*O*-gallate	$2.5^{b} \pm 0.2$	$2.2^{b} \pm 0.1$	$6.0^{a} \pm 0.1$	$1.3^{c} \pm 0.0$	***
Epicatechin 3-*O*-gallate	$0.4^{a} \pm 0.1$	$0.3^{b} \pm 0.0$	$0.2^{b} \pm 0.0$	$0.2^{b} \pm 0.0$	**
C1	$2.9^{c} \pm 0.3$	$0.9^{d} \pm 0.0$	$4.8^{b} \pm 0.2$	$7.8^{a} \pm 0.3$	***
Trimer 2	$1.4^{a} \pm 0.2$	$0.2^{c} \pm 0.0$	$0.9^{b} \pm 0.0$	$0.0^{c} \pm 0.0$	*
Total flavanols	$76.5^{a} \pm 1.4$	$33.9^{d} \pm 0.3$	$60.2^{b} \pm 0.5$	$45.0^{c} \pm 0.2$	**

*Means followed by the same letter in the lines did not differ by Tukey test at 5% ($p \leq 0.05$). Standard deviation of triplicate analysis. Concentrations expressed in mg L^{-1}; n.s. (not significant); * (significant differences at a 95% confidence level); **(significant differences at a 99.9% confidence level); *** (significant differences at a 99.99% confidence level).

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higher value. This content is in accordance with the cited by Agatonovic-Kustrin *et al.* (2015) for commercial Syrah wines from Australia (0.0 to 9.4 mg L^{-1}) and below the values quoted by Granato *et al.* (2011) for commercial wines Syrah do Brazil, Argentina and Chile, with 18.0; 40.5 and 32.1 mg L^{-1}, respectively.

The highest concentration analyzed of rutin in this study was 1.3 mg L^{-1}, in Pernambuco, harvested in 2015. Being according to the cited in the literature: Fang Fang *et al.* (2008) found values of 0.0-3.7 mg L^{-1} after analysis of red wines from different varieties and regions of China. Granato *et al.* (2011) and Tauchen *et al.* (2015) when studying wines from different regions of Georgia, Czech Republic, France, Italy and Austria, identified concentrations varying from 0.9 to 4.5 mg L^{-1}.

High levels of trans-resveratrol present in the wine samples were for high- altitude region, with relevance for harvest of 2014 (3.5 mg L^{-1}). The results are in agreement with the literature for wines of the region with cold climate, as mentioned by Belmiro *et al.* (2017) with contents of 2.7 to 4.4 mg L^{-1} for Argentine wines and with Granato *et al.* (2011) studying Chilean and Brazilian Syrah wines (Rio Grande do Sul), cited concentrations of 3.1 and 2.8 mg L^{-1}, respectively. The low-altitude Syrah wines obtained values between 1.3 and 1.7 mg L^{-1}, higher than those mentioned by Padilha *et al.* (2016) for Syrah commercial wines from the same region. According to the literature, grape derivatives produced in tropical regions are potential sources of resveratrol, due to high temperature and light conditions, these compounds are present in cis form due to their greater chemical stability (Lucena *et al*., 2010). This fact explains the high concentrations in the region of lower altitude (350 m), indicating that in the wines from region the concentrations may be even higher.

Monomeric and small oligomeric procyanidins

The main Flavan-3-ols monomer in the wines are (+)-catechin and its isomer (-)-epicatechin, which can also be found in the form of gallic ester, verifying the presence of small amounts of epicatequin 3-*O*-gallate. Concentrations in this study, Table 3, of these compounds were influenced by the region. Concentrations (+)-catechin were higher in Pernambuco (5.5 mg L^{-1}) for (-)-epicatechin and (-)-epicatechin-3-O-gallate high concentrations were in wines of Bahia, with 18.7 and 0.4 mg L^{-1}, respectively.

In total, 13 individual flavan-3-ol molecules were detected and quantified in all tropical Syrah wines at different altitudes by HPLC (Table 3), including monomers, dimers and trimers. There were significant differences between the tropical Brazilian wines studied, the highest concentrations for the wines of the highest altitude region, except for catechin, B1 dimer, B2 3'-*O*-gallate and C1 trimer. According to Sun *et al.* (2001) the catechins and procyanidins of skins may be of greater critical importance in wines because of their location in the tissues, since they can be readily released during the maceration phase in the elaboration process. Extraction is influenced by the concentration of proanthocyanidins in the skin, the composition of the cell walls of the berry, which clearly affects the extraction capacity and processing methods (Ortega-Regules *et al.*, 2006). On the other hand, it has generally been accepted that the extraction of proanthocyanidins from the seeds requires longer maceration time because the lipids present in the seed should be eliminated first, which is usually done by increasing concentrations of ethanol (Glories & Saucier, 2000).

Among the procyanidins of the wine, B1 dimer has been found to have a higher content, according to previous studies (Ricardo-da-Silva *et al.*, 1992; Monagas *et al.*, 2003). The concentrations of B1 found under tropical conditions were lower than those reported by Leeuw *et al.* (2014) for Syrah wines in different regions of France (found from 45.83 to 70.56 mg L^{-1}).

Regarding total flavanols, concentrations in the highest altitude region (1100 m) ranged from 33.9 to 76.5 mg L^{-1}, while in the low altitude region (350 m) they ranged from 45.0 to 60.2 mg L^{-1}, the effect harvest season seems to be more significant than the region. According to Revilla *et al.* (1997) the climatic conditions and year to year can affect the total amount of catechins and procyanidins in grapes and consequently wines.

Principal component analysis (PCA)

The principal component analysis of the data matrix (chemical analysis vs. wines) was carried out to find relevant sources of variability and to highlight the relationships between the effects of altitude and on the phenolic composition harvest of tropical Syrah wines. The analysis of the main components applied on anthocyanins and flavonols is shown in Fig. 1. As can be seen, the main component 1 (PC1) represents 25.97% of the total variability of the original data and the second 50.70% (PC2), that is, together 76.67% of the total variance. Throughout the first component (PC1) there are three groups of larger sizes, corresponding to the Pernambuco wines (harvest 2015), Bahia (in the two years of harvest) and Pernambuco harvest of 2014. The group of high altitude wines, harvest 2014, is superimposed on the wine group from the 2015 harvest. This result is possibly due to the fact that there are significant similarities in concentrations of anthocyanins 3-*O*-coumarylglucoside in these two groups, such as cyanidin, malvidin and peonidin according to PCA. The discrimination between the three groups does not occur in the second component (PC2), where there is the formation of two groups only, broken down by region, in the positive axis Pernambuco and negative Bahia.

An inspection on the loadings chart, Fig. 1B, shows that the separation of wines in PC1 (negative axis) is essentially determined by the parameter sets: Malvidin 3-*O*-coumarylglucoside, cyanidin 3-*O*-coumarylglucoside, resveratrol, cyanidin 3-*O*-glucoside, petunidin 3-*O*-coumarylglucoside, Peonidin 3-*O*-acetylglucoside. The positive side being influenced by the other compounds. The second component PC2 (positive axis) is related to the variables cyanidin 3-*O*-acetylglucoside, petunidin 3-*O*-acetylglucoside, malvidin 3-*O*-acetylglucoside, peonidin 3-*O*-acetylglucoside, petunidin 3-*O*-coumarylglucoside, cyanidin 3-*O*-glucoside, quercetin, isorhamnetin and kaempferol.

The main component analysis (PCA) applied on the result of tannins means and flavanols in wines in the two

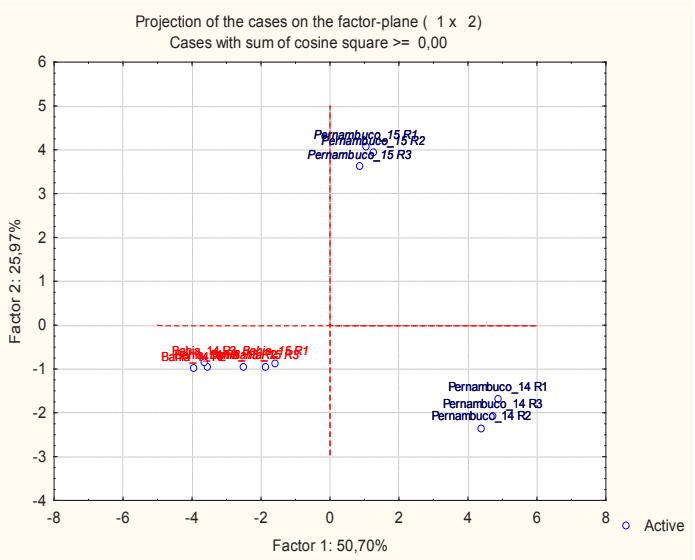

Figure 1A. Wine variation in PCA.

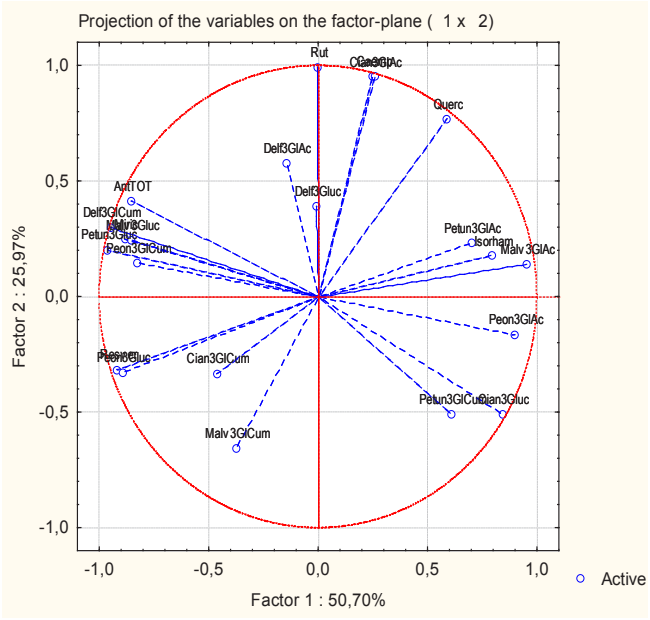

Figure 1B. Contribution of analytical parameters in variation of wines by principal component analysis.

FIGURE 1

Bahia (region with 1100 m of altitude); Pernambuco (region with 350 m of altitude); 14 and 15 (years of the experiment); R1 R2 and R3 (repetition of the analysis); Delf3Gluc Delphinidin 3-*O*-glucoside; Cian3Gluc Cyanidin 3-*O*-glucoside; Petun3Gluc Petunidin 3-*O*-glucoside; Malv3Gluc Malvidin 3-*O*-glucoside; Peon3GlAc Peonidin 3-*O*-acetylglucoside; Petun3GlAc Petunidin 3-*O*-acetylglucoside; Cian3GlAc Cyanidin 3-*O*-acetylglucoside; Delf3GlAc Delphinidin 3-*O*-acetylglucoside; Malv3GlAc Malvidin 3-*O*-acetylglucoside; Peon3GlCum Peonidin 3-*O*-coumarylglucoside; Petn3GlCum Petunidin 3-*O*-coumarylglucoside; Delf3GlCum Delphinidin 3-*O*-coumarylglucoside; Malv3GlCum Malvidin 3-*O*-coumarylglucoside; AntTOT Total anthocyanins; Quer Quercetin; Isorhm Isorhamnetin; Rut Rutin; Myr Myricetin.

harvests (Fig. 2) explained 85.35% of the total variability (PC1 x PC2). Principal component 1 (PC1) explained 39.02% while PC2, on the Y axis, illustrated 46.33% of the mathematical model. It is possible to observe that the altitude effects followed by the harvest date influence, are well representative. The first component (PC1) divided the treatments into two distinct groups, and on the positive side of PC1 (X-axis), wines from the low-altitude region and the negative ones were located at the highest altitude. The variables that are responsible for discrimination on the positive side of PC1 were: total tannins, polymeric tannins, B2 3'galate, B1, catechin and C1. While on the negative side of PC1 there is influence of the following parameters: monomeric tannins, oligomeric, gallocatechin, B2, B3, B2 3-gallate, T2, epicatechin 3-*O*-gallate, epigallocatechin, B1 3-*O*-gallate. The PC2 differentiated the wines in relation to the harvest year, located in the positive part of PC2, the wines from the harvest of 2015 discriminated due to higher concentrations for the C1, epigallocatechin and B1 3-*O*-gallate. In the negative part, are the samples of the region of higher-altitude, with higher values for the other parameters. As can be verified the results of the PCA are consistent with the analyses presented in Table 3. Through the PCA analysis it can be concluded that wines from the 2014 harvest had a higher tannin content than wines from the 2015 harvest, and wines from the region of 350 m altitude had higher concentrations of polymerized tannins than wines from the region at 1100 m altitude.

Sensory analysis of the wines

The result of the sensorial profile of the wines is described in Fig. 3 and in Table 4 the results of the average test of the notes on the attributes evaluated by the tasters. In the greater the distance of the center, the greater the intensity and the note assigned by the tasters to the attributes. It is observed that the wines are distinct from each other and that there is an influence of altitude and harvest in their sensorial characteristics, data confirmed by statistic of the notes attributed in the tests.

On the visual level, the Bahia wine, obtained higher grades for color (harvest of 2015, followed by 2014), limpidity, fluidity, with the exception of color intensity alone (Pernambuco wine, in 2015). Altitude wines obtained higher color scores, which coincides with color intensity analysis, and which can be explained by their high concentrations of anthocyanins (Table 2).

For the olfactory characteristics, the main aroma detected in all samples with high notes was fruity. But the wines of low-altitude also have as olfactory attribute, the floral (note 4.6), herbaceous (note 4.5), fruit (note 6.3) and

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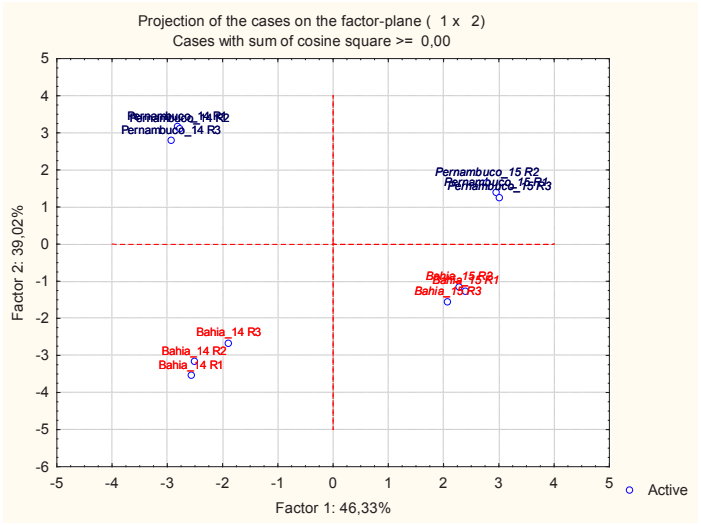

Figure 2A. Wines Syrah and regions.

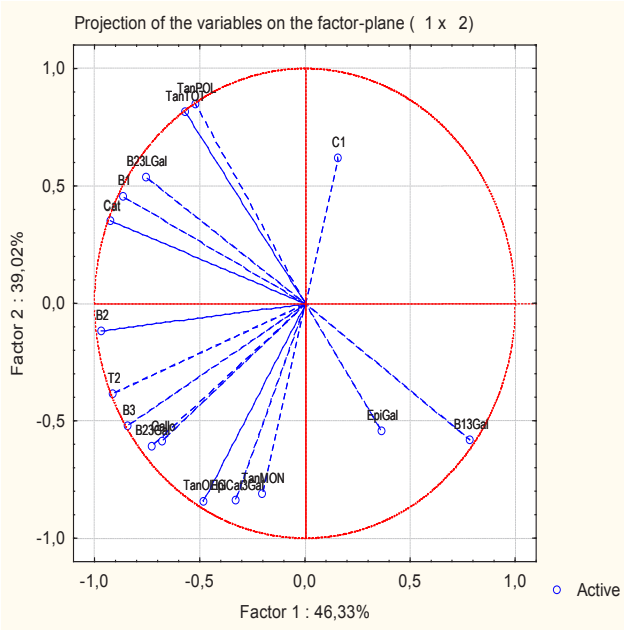

Figure 2B. Contribution of analytical parameters in variation of wines by principal component analysis.

FIGURE 2

Bahia (region with 1100 m of altitude); Pernambuco (region with 350 m of altitude); 14 and 15 (years of the experiment); R1, R2 and R3 (repetition of the analysis); Gall Gallocatechin; Cat Catechin; Epicat Epicatechin; Epigal Epigallocatechin; B1, B2 and B3 (Procyanidins dimer); B1 3 Gal B1 3-*O*-gallate, B2 3 Gal B2 3-*O*-gallate and B2 3LGal B2 3'-*O*-gallate (Procyanidin dimers gallate); Epicat_Gal Epicatechin 3-*O*-gallate; C1 and T2 (Procyanidins trimers); Tan MON monomeric tannins; Tan OLI oligomeric tannins; Tan POL polymeric tannins; Tan TOT Total tannins.

empireumatic aroma (note 5.1). Already the wines of high-altitude also obtained higher notes for the attribute spices. According to studies carried out by Geue *et al.* (2011) with Syrah wines from the hot and cold climate of Australia, in which they mentioned that the warm region wines had more fruity aromas and of the cold regions were described with notes of spices (mainly pepper).

Regarding the gustatory attributes, the wine of high altitude, in 2014, was characterized by higher notes for acidity (being according to the physicochemical analyzes, which also obtained a higher total acidity, Table 1), alcohol, bitterness, astringency, body and persistence. The sweetness attribute was higher in the wines of Pernambuco (2014), with 4.8 points, in the physical-chemical analysis, these wines also obtained higher values of residual sugar (Table 1).

There was no positive correlation between the note of the attribute astringency with the tannin content and tannin power in wines. Wines from the region of Bahia (harvest 2014) obtained a higher note, followed by the wines of Pernambuco also in the same harvest, with 5.3 and 4.7, respectively. Higher values for the Bahia wine samples followed by Pernambuco may be related to higher concentrations of total acidity, succinic acids (Table 1) and total flavanols (Table 3) in these wines. The perception of astringency results from complex phenolic profiles, as well as from other wine compounds the increase may be due, for example, the acidity of wine, that increasing the efficacy of bonding of polyphenols to salivary proteins (Perez-Maldonado *et al.*, 1995); the organic acids, that have astringent properties in their own right (Lawless *et al.*, 1996), which may result from pH mediated reduction in salivary viscosity (Nordbo *et al.*, 1984) and the flavanols which occur esterified with gallic acid (Singleton & Noble, 1976), conjugated with anthocyanins (Singleton & Trousdale, 1992) or free form (Ricardo-da-Silva *et al.*, 1991b).

The bitterness attribute obtained higher scores in wines from the Bahia region (year 2014), which may be related to a higher concentration of the flavonoids (Table 2) and monomeric tannins (Table 3) in the wines, the flavonoids phenols are the main cause of bitterness in wine (Singleton, 1995).

The sensory composition of the wine is complex, due to the quantity and importance of each compound involved. In this study, the characterization was influenced by factors such as grape composition in each region and harvest season.

CONCLUSIONS

The altitude and its peculiarities (day/night thermal amplitude, precipitation and solar radiation) had a significant effect on the chemical composition, principally in relation to the phenolic compounds and sensorial profile of the tropical wines of Northeast Brazil.

The low-altitude Syrah wines (Pernambuco) were characterized with high concentrations of tartaric acid, citric acid, potassium, quercetin, isorhamnetin, total flavonols, polymeric tannins and anthocyanins 3-O-acetylglucoside (petunidin and malvidin).

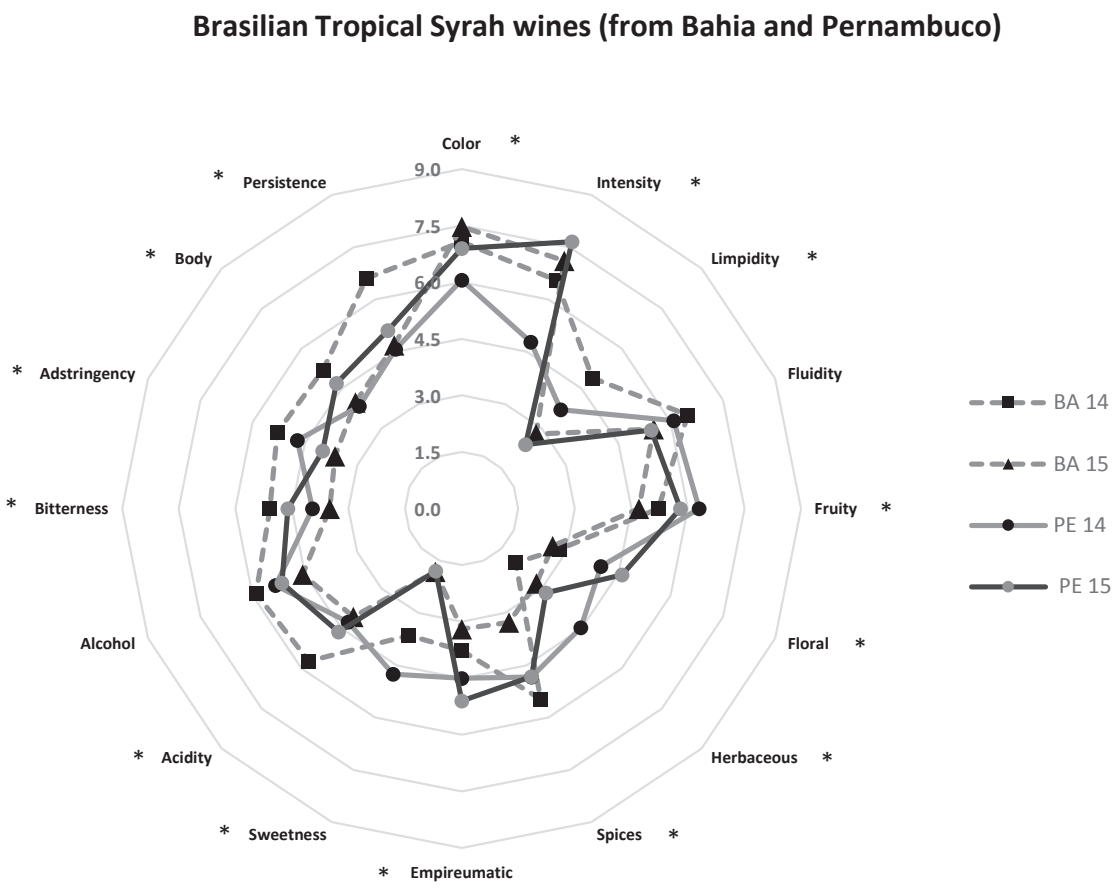

FIGURE 3
Influence of the region on the sensory profile of Brazilian tropical Syrah wines. BA 14 – Bahia state (1100 m altitude) year 2014; BA 15 – Bahia state (1100 m altitude) year 2015; PE 14 – Pernambuco state (350 m altitude) year 2014; PE 15 – Pernambuco state (350 m altitude) year 2015. * For most parameters significant statistical differences were observed.
(for more details, see Table 4)

TABLE 4
Descriptive analysis (0-10 scale) for the attributes of Syrah wines, from two tropical regions with different altitudes in Brazil (Bahia and Pernambuco regions).

Region	**Bahia (1100 m altitude)**		**Pernambuco (350 m altitude)**		**ANOVA**
Harvest	**2014**	**2015**	**2014**	**2015**	**(p-values)**
Visual profile					
Color	$7.1^{b} \pm 0.9$	$7.5^{a} \pm 1.0$	$6.1^{c} \pm 0.8$	$6.9^{b} \pm 1.1$	**
Intensity	$6.6^{c} \pm 1.3$	$7.1^{b} \pm 1.3$	$4.8^{d} \pm 1.8$	$7.7^{a} \pm 1.3$	***
Limpidity	$4.9^{a} \pm 1.7$	$2.8^{c} \pm 2.0$	$3.7^{b} \pm 2.0$	$2.4^{c} \pm 1.7$	*
Fluidity	$6.5^{a} \pm 1.3$	$5.5^{ab} \pm 1.9$	$6.1^{a} \pm 1.1$	$5.4^{ab} \pm 1.5$	n.s.
Aromatic attributes					
Fruity	$5.1^{b} \pm 1.8$	$4.7^{c} \pm 1.6$	$6.3^{a} \pm 1.9$	$5.8^{b} \pm 2.0$	*
Floral	$2.8^{c} \pm 1.9$	$2.6^{c} \pm 1.4$	$4.0^{b} \pm 1.6$	$4.6^{a} \pm 1.3$	***
Herbaceous	$2.0^{d} \pm 1.5$	$2.8^{c} \pm 2.7$	$4.5^{a} \pm 1.7$	$3.2^{b} \pm 2.2$	*
Spices	$5.5^{a} \pm 1.9$	$3.3^{c} \pm 1.8$	$4.8^{b} \pm 1.5$	$4.8^{b} \pm 1.3$	*
Empireumatic	$3.8^{c} \pm 1.3$	$3.2^{d} \pm 1.8$	$4.5^{b} \pm 1.6$	$5.1^{a} \pm 1.7$	*

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TABLE 4 (CONTINUED)

Region	Bahia (1100 m altitude)		Pernambuco (350 m altitude)		ANOVA
Harvest	2014	2015	2014	2015	(p-values)
Taste attributes					
Sweetness	$3.6^{b} \pm 1.8$	$1.8^{c} \pm 1.4$	$4.8^{a} \pm 1.5$	$1.8^{c} \pm 0.8$	***
Acidity	$5.7^{a} \pm 1.5$	$4.1^{c} \pm 1.8$	$4.3^{c} \pm 1.3$	$4.6^{b} \pm 1.8$	**
Alcohol	$5.9^{a} \pm 2.0$	$4.6^{b} \pm 1.4$	$5.3^{ab} \pm 2.1$	$5.2^{ab} \pm 1.3$	n.s.
Bitterness	$5.1^{a} \pm 1.7$	$3.5^{c} \pm 1.9$	$4.0^{bc} \pm 1.6$	$4.6^{b} \pm 2.2$	*
Astringency	$5.3^{a} \pm 1.3$	$3.6^{c} \pm 2.1$	$4.7^{b} \pm 1.8$	$3.0^{c} \pm 2.1$	*
Body	$5.2^{a} \pm 1.3$	$4.0^{c} \pm 1.3$	$3.8^{c} \pm 1.3$	$4.7^{ab} \pm 1.5$	*
Persistence	$6.6^{a} \pm 1.5$	$4.7^{c} \pm 1.7$	$4.6^{c} \pm 0.7$	$5.1^{b} \pm 1.8$	*

*Means followed by the same letter in the lines did not differ by Tukey test at 5% ($p \leq 0.05$). Standard deviation of triplicate analysis; n.s. (not significant); * (significant differences at a 95% confidence level); ** (significant differences at a 99.9% confidence level); *** (significant differences at a 99.99% confidence level).

The altitude of 1100 m (Bahia) provided wines with higher levels of succinic acid, total phenols, flavonoids, total and colored anthocyanins, ionization index of anthocyanins, total pigments, polymerized pigments, color intensity, monomeric and oligomeric tannins, trans-resveratrol, anthocyanins 3-*O*-glucoside (peonidin, petunidin and malvidin), three anthocyanins esterified with p-coumaric acid (peonidin, delphinidin and malvidin) and procyanidins B3, B1 3-O-gallate and Trimer 2.

Sensory attributes (spice, acidity, bitterness, astringency, body and persistence) are influenced by year of harvest, being the wine of the region of Bahia (1100 m) with highest values, in the year 2014. High scores to aromatic attributes (fruity, floral, herbaceous and empyreumatic) were obtained in 350 m altitude wines (Pernambuco), demonstrating an altitude effect, since there was the same behavior during the two years of study.

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