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Integrated analyses of phenolic compounds and minerals of Brazilian organic and conventional grape juices and wines: Validation of a method for determination of Cu, Fe and Mn

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ABSTRACT

The phenolic profile and antioxidant activity (AOX) of "organic vs. conventional" Brazilian wines and grape juices were analyzed. A simple method for the determination of minerals Cu, Fe and Mn by F-AAS was validated and used to characterize the samples studied. In the validation of the Cu, Fe and Mn determination method, the protocol for samples preparation by hot digestion with HNO_3 + H_2O_2 proved to be more suitable for the grape juice and wine matrices. The validation parameters were considered satisfactory. Conventional products presented higher anthocyanins content, and no significant differences were observed on other phenolic compounds, AOX and Cu, Fe and Mn minerals. All the evaluated samples presented similar results between the same cultivars and in products from grapes of the two cultivation systems. The AOX of juices and wines, organic and conventional, was high, and correlated with procyanidin B1, petunidin-3-glucoside and cyanidin-3,5-diglucoside.

1. Introduction

Grape-derived beverages such as juices and wines are important sources of phenolic compounds beneficial to consumer health (Granato, Carrapeiro, Fogliano, & van Ruth, 2016). Several studies mention grape juice and wines as a functional beverages with good bioactive content and high antioxidant activity *in vitro* and *in vivo*, associated with their phenolic compounds content (Dani et al., 2009; Karnopp, Margraf, Maciel, Santos, & Granato, 2017; Lima et al., 2014; Padilha, Miskinis, et al., 2017; Silva et al., 2015).

The cultivation of wine under stress condition may favor the concentration of phenolic compounds in the grape (Dani et al., 2007). In this way, it is possible that the organic crop system produces greater amount of phenolic compounds, because in this type of agriculture the plant is more susceptible to the action of pathogens due to the non-use of pesticides, which can increase plant stress condition (Olsson, Anderson, Oredsson, Berglund, & Gustavsson, 2006). In the literature we find studies that mention a higher amount of phenolic compounds in organic grape juice compared to the juice obtained from traditional grapes, but the comparative samples were from different grape varieties (Rodrigues et al., 2012; Toaldo et al., 2015). Another study shows that there is no significant difference in the phenolic content and *in vitro* antioxidant activity of organic and conventional grape juices from different cultivars and regions of origin (Margraf, Santos, de Andrade, Van Ruth, & Granato, 2016). Grape variety, region of origin and processing technique may influence the chemical composition of juices and wines (Granato et al., 2016; Granato, Margraf, Brotzakis, Capuano, & van Ruth, 2015), in conventional and organic product comparisons it is not always possible to standardize these factors.

Grape-derived beverages are complex matrices that, in addition to the broad phenolic profile, also have an abundant mineral composition (Toaldo et al., 2015). Some minerals such as Mg, Ca, Mn, Fe, Cu, Zn, Si, S and Cl are associated with antioxidant and antimutagenic effects and may contribute to the prevention of some diseases caused by oxidative stress such as arteriosclerosis and neurodegenerative diseases (Dani et al., 2012). However, high concentrations of elements such as Fe, Mn and Cu, and other heavy metals can cause harm to consumers' health (Tariba, 2011).

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Minerals such as Fe, Mn and Cu are transition metals that are normally quantified by means of flame atomization (F-AAS), graphite furnace (GF-AAS) or plasma optical emission spectrometry inductively coupled (ICP-OES) and mass spectrometry (ICP-MS) (Selih, Sala, & Drgan, 2014; Toaldo et al., 2015). According to Boschetti et al. (2013) F-AAS technique has good sensitivity, simplicity and low cost. The main techniques of sample preparation for determination of metals in grape juices and wines by F-AAS range from simple dilution in water (Bora, Bunea, Rusu, & Pop, 2015), dilution in nitric/hydrochloric acid or hot digestion with acid and the hydrogen peroxide for decomposition of organic matter (Alkış et al., 2014; Boschetti et al., 2013; Vystavna, Rushenko, Diadin, Klymenko, & Klymenko, 2014). However, studies comparing the performance of these techniques of preparation in both matrices: grape juice and wine, which have different physical-chemical nature, were not found in the literature.

The sub-region São Francisco Valley (SFV) is a new Brazilian region that has invested in the production of wines and grape juice, and its products are recognized by the high antioxidant activity associated with phenolic compounds (Padilha, Biasoto, Corrêa, Lima, & Pereira, 2017; Padilha, Miskinis, et al., 2017). Recently, some companies in the SFV have invested in the production of fine organic wines (*Vitis vinifera* L.) and organic grape juices (*Vitis labrusca* L. and hybrids) (Dutra et al., 2018).

In this context, the objective of this work was to evaluate the phenolic compounds profile, minerals and *in vitro* antioxidant activity of Brazilian "organic vs. conventional" grape juices and wines, comparing products of the same grape variety, harvest and region of origin. Additionally, a simple method for the determination of transition metals Cu, Fe and Mn by F-AAS was validated and used to characterize the samples studied.

2. Material and methods

2.1. Standards and reagents

Standard solutions of copper, iron and manganese were obtained from Quimlab (São Paulo, SP, Brazil). Hydrogen peroxide was supplied by Chemical Kinetics (Monterrey City, Mexico). Nitric acid, Folin-Ciocalteu reagent, ethanol, potassium persulfate, phosphoric acid and potassium phosphate monobasic were purchased from Merck (Darmstadt, Germany). Trolox (6-hydroxy-2,5,7,8-tetramethylchromate-2-carboxylic acid) and the 2,2-diphenyl-1-picrylhydrazyl (DPPH) radicals and 2,2-azino-bis (3-ethylbenzthiazoline-6 sulfonic acid) (ABTS) were supplied by Sigma-Aldrich (St. Louis, MO, USA). Methanol from J.T. Baker (Phillipsburg, NJ, USA). Ultrapure water was obtained in a Marte Científica purification system (São Paulo, SP, Brazil). External standards of gallic acid, syringic acid, hesperidin, naringenin, procyanidin B_1, catechin, procyanidin B_2, *trans*-caftaric acid, chlorogenic acid, caffeic acid, *p*-coumaric acid, cyanidin 3,5-diglucoside, pelargonidin 3,5-diglucoside, malvidin 3,5-diglucoside, cyanidin 3-glucoside and perlagonidin 3-glucoside were purchased from Sigma-Aldrich (St. Louis, MO, USA). Epigalocatechin gallate, epicatechin, epicatechin gallate, procyanidin A_2, quercetin 3-glucoside, rutin, kaempferol 3-glucoside, delphinidin 3-glucoside, peonidin 3-glucoside, malvidin 3-glucoside and petunidin 3-glucoside from Extrasynthese (Genay, France). *Trans*-resveratrol and *cis*-resveratrol were obtained from Cayman Chemical Company (Michigan, EUA).

2.2. Samples

The monovarietal juices were elaborated in three replicates and each commercial label consisted of three bottles, where each bottle corresponded to one repetition. A total of 10 products were evaluated (n = 3), being 4 monovarietal grape juices, 3 commercial grape juices and 3 commercial red wines, totalizing 30 samples.

Organic and conventional monovarietal grape juices of the Isabel Precoce (*V. labrusca*) (IPO and IP, respectively) and BRS Violeta (*V. labrusca* × *V. vinifera*) (BVO and BV respectively) were handcrafted by the craft hot press method (Morris & Striegler, 2005) with grapes obtained in Petrolina PE (09°21′S; 40°40′W) and Lagoa Grande PE (8°59′S; 40°16′W), Northeast of Brazil, and harvested in 2017 May.

Three samples of SFV commercial grape juices were donated by local companies and elaborated by mixing the grapes: Isabel Precoce + BRS Violeta from organic cultivation coded as OGJ and conventional cultivation denominated GJA and GJB, all processed in May 2017. Three labels of commercial wines elaborated with the varieties (*V. vinifera*) organic Tempranillo, conventional Tempranillo and Barbera organic (denominated OTW, TW and OBW, respectively), all of the harvest 2016 and originated from Lagoa Grande PE (SFV), were acquired in the local market.

2.3. Basic analysis of quality

To obtain basic analytical characteristics of the samples, classical pH analyzes (potentiometer pH Analyzer – Tecnal (Brazil)) were carried out; soluble solids (°Brix) (digital refractometer HI 96801 Hanna, USA), alcohol (%v/v) and titratable acidity (TA), following the methodologies described in International Organization of Vigne et du Vin (2011). All determinations were performed in triplicate. The results are shown in Table 1.

2.4. Total phenolic content and in vitro antioxidant activity

The total phenolic content of the samples was measured by the colorimetric method with Folin-Ciocalteu according to Singleton and Rossi (1965). Gallic acid was used as standard and the phenolic concentrations in wine and juice samples were expressed as mg of gallic acid equivalents (GAE)/L. Total monomeric anthocyanins were

Table 1
Characteristics of samples studied.

Samples	Codification	Classical analysis				
		pH	°Brix	TA (%)	Ratio °Brix/TA	Alcohol (% *v/v*)
Grape juice: Isabel Precoce + BRS Violeta	GJA	3.42 ± 0.02	20.7 ± 0.04	0.67 ± 0.007	30.9 ± 0.29	–
Grape juice: Isabel Precoce + BRS Violeta	GJB	3.47 ± 0.008	20.3 ± 0.0	0.70 ± 0.007	28.9 ± 0.29	–
Organic grape juice: Isabel Precoce + BRS Violeta	OGJ	3.12 ± 0.009	18.5 ± 0.04	0.64 ± 0.007	29.1 ± 0.36	–
Grape juice: BRS Violeta	BV	3.87 ± 0.009	24.1 ± 0.04	0.54 ± 0.007	44.0 ± 0.65	–
Organic grape juice: BRS Violeta	BVO	3.22 ± 0.02	18.4 ± 0.04	0.87 ± 0.03	21.1 ± 0.90	–
Grape juice: Isabel Precoce	IP	3.60 ± 0.01	22.0 ± 0.12	0.49 ± 0.01	44.5 ± 1.05	–
Organic grape juice: Isabel Precoce	IPO	3.40 ± 0.005	19.0 ± 0.05	0.63 ± 0.02	30.2 ± 1.37	–
Organic Tempranillo wine	OTW	3.76 ± 0.18	–	0.57 ± 0.002	–	12 ± 0.1
Tempranillo wine	TW	3.78 ± 0.004	–	0.66 ± 0.007	–	13 ± 0.1
Organic Barbera wine	OBW	3.22 ± 0.0	–	0.76 ± 0.01	–	12 ± 0.2

The results are expressed as mean ± standard deviation (independent samples, n = 3). TA = titratable acidity.

determined by the pH difference method as described by Lee, Durst and Wrolstad (2005) and the results expressed as equivalent to mg of malvidin 3-glucoside L^{-1} of juice/wine. The samples were diluted with buffer solutions of KCl 0.025 M (pH 1.0) and CH_3COONa 0.4 M (pH 4.5) and absorbance measurements were performed at 520 and 700 nm, respectively.

In vitro antioxidant activity was determined by free radical sequestration with DPPH (1,1-diphenyl-2-picrylhydrazyl) and ABTS 2,2-azinobis (3-ethylbenzthiazoline-6-sulfonic acid) (Kim, Guo, & Packer, 2002; Re et al., 1999), and by elimination of hydrogen peroxide (H_2O_2) (Ruch, Cheng, & Klaunig, 1989). The Trolox analytical standard was used to build the calibration curves and the results were expressed as Trolox equivalents per liter of juice/wine (mM TEAC L^{-1}).

The ABTS radical (1 mM) was formed through the reaction of 7 mM ABTS in 140 mM potassium persulfate in the absence of light for 16 h. The solution was then diluted in ethanol until an absorbance of 0.700 ± 0.05. The ABTS radical scavenging activity of the samples was determined through the rate of decay in the absorbance at 734 nm determined at time t = 0 min and at time t = 6 min after the addition of samples.

The DPPH method of the samples was assessed through the rate of decay in the absorbance at 517 nm. A solution of DPPH 1.0 mmol was prepared in ethanol and diluted to an absorbance of 0.900 ± 0.050 (100 μmol L^{-1}). The absorbance of the DPPH solution was determined at time t = 0 min and 30 min after the addition of sample.

H_2O_2 method: A solution 0.4 mol L^{-1} of hydrogen peroxide was prepared in phosphate buffer (pH 7.4) and its concentration was determined spectrophotometrically at 230 nm. The grape juice and red wine samples (0.4 mL) were mixed with hydrogen peroxide solution (0.6 mL), and the final volume was completed to 3 mL with the phosphate buffer. The absorbance value of the reaction mixture was recorded at 230 nm and determined 10 min later against a blank solution containing the phosphate buffer. All determinations were performed in triplicate.

2.5. Profile of phenolic compounds by HPLC-DAD

The individual phenolic compounds were determined following the methodology validated by Padilha, Miskinis, et al. (2017), with adaptations on gradient and runtime for quantification of stilbenes, flavonols and flavanones, using an Agilent 1260 Infinity LC System (Agilent Technologies, Santa Clara – USA) liquid chromatograph coupled to a diode arrangement detector (DAD) (model G1315D). Data were processed using the OpenLAB CDS ChemStation Edition software (Agilent Technologies, Santa Clara – USA). The column used was Zorbax Eclipse Plus RP-C18 (100 × 4.6 mm, 3.5 μm) and the pre-column was Zorbax C18 (12.6 × 4.6 mm, 5 μm) (Zorbax, USA). The oven temperature was 35 °C and the injection volume was 20 μL of the sample, previously diluted in phase A, and filtered through 0.45 μm membrane (Millex Millipore, Barueri, SP, Brazil). The solvent flow was 0.8 mL min^{-1}. The new gradient used in the separation was 0–5 min: 5% B; 5–14 min: 23% B; 14–30 min: 50% B; 30–33 min: 80% B where solvent A was a solution of phosphoric acid (0.1 M, pH = 2.0) and solvent B was methanol acidified with 0.5% H_3PO_4. Detection of the compounds was done at 220, 280, 320, 360 and 520 nm, and the identification and quantification by comparison with external standards. Typical chromatograms of grape juice Isabel Precoce (*V. labrusca*) and Tempranillo wine (*V. vinifera* L.) are available at Supplementary Material (Figs. S1 and S2).

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.foodchem.2018.07.014.

2.6. Preparation of the samples for determination of the minerals

Two protocols for sample preparation for determination of Cu, Fe and Mn were tested. In the first method the samples were prepared by simple dilution of 10 mL of wine/grape juice in 30 mL of 2% nitric acid, followed by filtration on qualitative filter paper with porosity < 14 μm (J. Prolab, PR, Brazil), as described by Gadzhieva (2014).

In the second method the samples were subjected to hot digestion with nitric acid and hydrogen peroxide. A solution composed of 5 mL of juice/wine, 2 mL of 30% H_2O_2 and 1 mL of 65% HNO_3 was heated to a temperature of 75 °C in a thermodigester block for tubes (Bioplus IT-2002 (Barueri, SP, Brazil)) until discoloration of the sample. After discoloration the liquid was filled to 20 mL with ultrapure water and filtered on qualitative filter paper, following the methodology described by Boschetti et al. (2013).

2.7. Determination of Fe, Cu and Mn contents

The determination of the metals was done using an AA500 atomic absorption spectrum equipped with flame atomizer (F-AAS), graphite furnace (GF-AAS) and automatic sample injector, manufactured by PG Instruments (Alma Park, Leicestershire, UK). The determination of Cu, Fe and Mn was performed only on F-AAS. The data were processed using the software AAWin (PG Instruments). The detection of the studied metals was in air-acetylene flame, with high purity acetylene (99.0%v/v) (White Martins, Brazil) as fuel. The wavelengths of the lamps were 327.4, 372 and 403.1 nm, for Cu, Fe and Mn respectively. The lamp currents were 4, 5 and 5 mA for Cu, Fe and Mn, respectively. Fuel flow rate 1.5 L/min and measurement time of 5 s.

2.8. Method validation for determination of Cu, Fe and Mn

The validation parameters were in accordance with the validation and quality control guide of the Brazilian Ministry of Agriculture, Livestock and Supply (Brasil, 2011). Standard solutions, white samples and fortified samples were used. The validation parameters were linearity, precision, recovery and limits of detection and quantification.

2.8.1. Linearity, precision and recuperation

Linearity was obtained by a calibration curve of the compounds in five concentrations. The external Cu, Fe and Mn standards were diluted in 2% HNO_3 and aspirated. Concentration versus absorbance calibration curves were determined from regression analysis using the least squares method.

The precision was evaluated through the coefficient of variation (CV %) obtained from the results of six replicates of grape juice samples and red wines fortified with the studied metals. The recovery was calculated by comparing the values obtained for each fortified compound in relation to the initial value contained in the sample.

2.8.2. Limit of detection (LOD) and limit of quantification (LOQ)

LOD and LOQ were obtained following the method of Hubaux and Vos (1970), in which three standards of the test compounds were prepared, with concentrations close to the estimated LODs. An analytical curve was built by plotting the values obtained from the analysis of the standards versus the current values, obtaining the slope of the curve, intercept and coefficient of correlation. The residual standard deviation (RSD) was calculated by comparing the values obtained in the analysis of the current values. LOD and LOQ were established at 3 and 10 times the RSD, respectively, added with the intercept of the curve.

2.9. Statistical analysis

The results obtained from the analysis of the samples were submitted to analysis of variance (one-way ANOVA) and compared by the Tukey test at 5% of error probability, with the aid of the R-Studio program (R-Studio Inc., Version 1.0. 143, Boston, USA).

Table 2
Phenolic profile of grape juices and wines, organic vs conventional, originated from the São Francisco Valley, Northeast Brazil.

Phenolic compounds	Grape Juices							Wines		
	GJA	GJB	OGJ	BV	BVO	IP	IPO	OTW	TW	OBW
Phenolic acids										
Gallic acid	ND	2.14 ± 0.05^{c}	2.80 ± 0.3^{c}	4.02 ± 0.04^{c}	4.40 ± 0.4^{c}	ND	2,97 ± 0.6^{c}	22.70 ± 1.6^{b}	29.51 ± 4.6^{b}	73.89 ± 2.74^{a}
Syringic acid	1.26 ± 0.2^{bcd}	2.14 ± 0.5^{bc}	0.42 ± 0.02^{d}	3.93 ± 0.1^{a}	2.41 ± 0.9^{b}	0.88 ± 0.04^{cd}	0.79 ± 0.01^{cd}	1.18 ± 0.04^{bcd}	1.85 ± 0.3^{bc}	2.18 ± 0.02^{bc}
Caftaric acid	114.98 ± 19.0^{abc}	91.34 ± 3.4^{abc}	120.72 ± 9.5^{abc}	148.03 ± 8.6^{a}	136.32 ± 5.9^{ab}	144.24 ± 8.2^{ab}	169.05 ± 37.9^{a}	38.69 ± 1.5^{c}	33.58 ± 3.2^{C}	49.89 ± 0.7^{bc}
Chlorogenic acid	9.30 ± 1.5^{ab}	7.54 ± 0.3^{ab}	8.81 ± 0.6^{ab}	17.03 ± 0.9^{a}	14.17 ± 0.5^{ab}	10.45 ± 0.6^{ab}	10.36 ± 0.2^{ab}	11.60 ± 0.5^{ab}	5.93 ± 0.4^{b}	7.76 ± 0.5^{ab}
Cafeic acid	3.20 ± 0.5^{ab}	5.24 ± 1.3^{ab}	1.52 ± 0.2^{b}	9.63 ± 0.4^{a}	6.64 ± 1.5^{ab}	2.25 ± 0.1^{ab}	2.00 ± 0.3^{ab}	2.62 ± 0.2^{ab}	8.56 ± 0.3^{ab}	ND
p-Coumaric acid	1.16 ± 0.2^{b}	1.90 ± 0.6^{ab}	0.78 ± 0.03^{b}	1.38 ± 0.1^{ab}	0.65 ± 0.02^{b}	1.19 ± 0.05^{ab}	1.22 ± 0.2^{ab}	1.15 ± 0.03^{b}	5.23 ± 1.1^{a}	ND
Σ phenolic acids	129.9 ± 21.4	110.30 ± 6.15	135.05 ± 10.65	184.02 ± 10.14	164.59 ± 9.22	159.01 ± 9.0	186.39 ± 39.21	77.94 ± 3.87	84.66 ± 9.92	133.72 ± 3.96
Flavanols										
Catechin	4.36 ± 0.6^{c}	1.55 ± 0.3^{c}	3.21 ± 0.1^{c}	3.97 ± 0.1^{c}	2.30 ± 0.8^{c}	7.22 ± 0.2^{bc}	0.87 ± 0.1c	18.83 ± 1.0^{ab}	23.68 ± 3.6^{a}	27.95 ± 1.2^{a}
Epicatechin gallate	ND	ND	ND	0.69 ± 0.04	1.72 ± 0.2	ND	ND	ND	ND	ND
Procyanidin A2	2.23 ± 0.2^{b}	ND	ND	1.76 ± 0.2^{b}	4.70 ± 0.2^{ab}	ND	ND	10.39 ± 0.3^{a}	9.57 ± 1.6^{a}	ND
Procyanidin B1	3.80 ± 0.4^{b}	3.19 ± 0.6^{b}	2.17 ± 0.5^{b}	5.04 ± 0.1^{b}	2.29 ± 0.5^{b}	5.19 ± 0.4^{b}	2.88 ± 0.4^{b}	ND	24.79 ± 5.8^{a}	ND
Procyanidin B2	12.03 ± 1.6^{c}	10.54 ± 2.0^{c}	2.81 ± 0.4^{c}	59.37 ± 2.6^{a}	41.92 ± 1.5^{ab}	6.23 ± 0.7^{c}	1.98 ± 0.3^{c}	16.60 ± 0.6^{c}	21.16 ± 1.5^{bc}	21.04 ± 0.3^{bc}
Σ Flavanols	22.42 ± 2.8	15.28 ± 2.9	8.19 ± 1.0	70.83 ± 3.04	52.93 ± 3.2	18.64 ± 1.3	5.73 ± 0.8	45.82 ± 1.9	79.20 ± 12.5	48.99 ± 1.5
Flavonols										
Quercitin 3-glucoside	1.81 ± 0.2^{cd}	1.97 ± 0.5^{cd}	3.42 ± 0.1^{abc}	2. 36 ± 0.1^{bcd}	1.24 ± 0.4^{d}	2.25 ± 0.02^{bcd}	3.28 ± 0.7^{abc}	4.16 ± 0.02^{a}	3.62 ± 0.6^{ab}	2.54 ± 0.04^{bcd}
Rutin	0.24 ± 0.01^{bc}	0.24 ± 0.08^{bc}	ND	0.74 ± 0.06^{a}	0.35 ± 0.1^{abc}	0.63 ± 0.2^{ab}	0.32 ± 0.08^{abc}	0.23 ± 0.02^{bc}	0.15 ± 0.01^{c}	0.19 ± 0.008^{bc}
Kaempferol glucoside	0.71 ± 0.08^{bc}	0.74 ± 0.02^{bc}	0.32 ± 0.01^{c}	2.26 ± 0.1^{a}	1.47 ± 0.5^{ab}	0.21 ± 0.01^{c}	0.26 ± 0.05^{c}	0.88 ± 0.06^{bc}	0.49 ± 0.01^{c}	0.25 ± 0.02^{c}
Σ Flavonols	2.76 ± 0.29	2.95 ± 0.6	3.74 ± 0.11	5.36 ± 0.23	3.06 ± 1.0	3.09 ± 0.23	3.86 ± 0.83	5.27 ± 0.1	4.26 ± 0.62	2.98 ± 0.068
Anthocyanins										
Cyanidin 3,5 diglucoside	9.83 ± 1.2^{bc}	7.47 ± 0.7^{c}	ND	53.40 ± 2.4^{a}	27.85 ± 1.8^{b}	ND	0.72 ± 0.1^{c}	ND	ND	ND
Delphinidin 3 glucoside	2.45 ± 0.2^{c}	1.31 ± 0.2^{c}	0.59 ± 0.4^{c}	10.28 ± 0.6^{a}	5.85 ± 0.3^{b}	2.27 ± 0.2^{c}	1.85 ± 0.4^{c}	0.19 ± 0.008^{c}	0.81 ± 0.1^{c}	ND
Malvidin 3,5 diglucoside	45.20 ± 6.2^{bc}	31.80 ± 2.9^{bcd}	5.10 ± 0.3^{d}	191.98 ± 8.5^{a}	64.89 ± 2.4^{b}	28.86 ± 2.2^{cd}	25.18 ± 0.5^{cd}	ND	ND	ND
Cyanidin 3 glucoside	0.84 ± 0.05^{ab}	0.94 ± 0.01^{ab}	2.94 ± 0.6^{ab}	ND	3.61 ± 0.1^{a}	1.46 ± 0.3^{ab}	ND	ND	0.61 ± 0.1^{b}	ND
Pelargonidin 3 glucoside	1.72 ± 0.1^{ab}	ND	1.36 ± 0.1^{ab}	ND	2.56 ± 0.6^{ab}	4.50 ± 0.3^{a}	2.99 ± 0.4^{ab}	1.31 ± 0.02^{ab}	3.50 ± 0.7^{ab}	0.39 ± 0.008^{b}
Peonidin 3 glucoside	1.26 ± 0.1^{bc}	0.46 ± 0.01^{bc}	1.01 ± 0.2^{bc}	ND	0.50 ± 0.03^{bc}	5.18 ± 0.4^{a}	2.80 ± 0.5^{abc}	3.99 ± 0.8^{ab}	0.48 ± 0.01^{bc}	0.19 ± 0.01^{c}
Malvidin 3 glucoside	9.46 ± 0.8^{b}	1.78 ± 0.5^{b}	6.11 ± 0.4^{b}	4.20 ± 0.2^{b}	1.36 ± 0.3^{b}	36.92 ± 3.2^{a}	18.04 ± 3.6^{ab}	6.05 ± 0.03^{b}	25.07 ± 2.4^{ab}	1.67 ± 0.02^{b}
Petunidin 3 glucoside	38.94 ± 4.4^{b}	33.35 ± 1.5^{b}	3.60 ± 0.5^{b}	209.45 ± 19.5^{a}	172.23 ± 7.1^{a}	ND	2.14 ± 0.5^{b}	ND	ND	ND
Σ anthocyanins	109.70 ± 13.05	77.11 ± 5.82	20.71 ± 2.5	469.31 ± 31.2	278.85 ± 12.63	79.19 ± 6.6	53.72 ± 6.0	11.54 ± 0.86	30.47 ± 3.31	2.25 ± 0.04
Total monomeric anthocyanins[¥]	409.1 ± 0.7^{c}	270.3 ± 3.7^{d}	103.4 ± 9.8^{efg}	1532.3 ± 67.6^{a}	1322.5 ± 9.4^{b}	152.2 ± 3.8^{e}	121.0 ± 3.4^{ef}	38.7 ± 3.3^{g}	85.9 ± 2.09^{efg}	40.3 ± 1.8^{fg}
Stilbenes										
Trans-resveratrol	0.22 ± 0.01^{b}	0.30 ± 0.02^{ab}	0.55 ± 0.008^{ab}	0.50 ± 0.01^{ab}	0.28 ± 0.01^{ab}	0.35 ± 0.004^{ab}	0.45 ± 0.1 ab	0.47 ± 0.02^{ab}	0.67 ± 0.07^{a}	0.67 ± 0.02^{a}
Cis-resveratrol	3.52 ± 0.3^{c}	3.33 ± 0.1^{c}	ND	17.94 ± 1.5^{a}	10.24 ± 0.4^{b}	ND	ND	ND	ND	ND
Σ Stilbenes	3.74 ± 0.31	3.63 ± 0.12	0.55 ± 0.008	18.44 ± 1.51	10.52 ± 0.41	0.35 ± 0.004	0.45 ± 0.1	0.47 ± 0.02	0.67 ± 0.07	0.67 ± 0.02
Flavanones										
Hesperidin	ND	ND	ND	4.04 ± 0.3^{b}	ND	ND	ND	ND	4.93 ± 0.5^{a}	4.32 ± 0.05^{ab}
Naringenin	0.90 ± 0.1^{b}	0.46 ± 0.03^{b}	ND	5.64 ± 0.8^{a}	5.36 ± 0.6^{a}	0.42 ± 0.004^{b}	0.27 ± 0.01^{b}	ND	0.72 ± 0.05^{b}	ND
Σ Flavanones	0.90 ± 0.1	0.46 ± 0.03	ND	9.68 ± 1.1	5.36 ± 0.6	0.42 ± 0.004	0.27 ± 0.01	ND	5.65 ± 0.55	4.32 ± 0.05
Total phenolics[Ψ]	1614.2 ± 87.4^{e}	2023.0 ± 62.1^{d}	1375.7 ± 99.0^{e}	4846.3 ± 114.8^{a}	3842.9 ± 155.7^{b}	1626.6 ± 34.2^{e}	1580.1 ± 37.42^{e}	2242.9 ± 137.88^{d}	3333.1 ± 177.43^{c}	3373.3 ± 90.5^{c}

The results are expressed as mean ± standard deviation (n = 3). Means followed by equal letters, in lines. Do not difer among themselves by the Tukey test at 5% of error porbability.

[¥] Total monomeric anthocyanins quantified by the technic of difference of pH and expressed as equivalent to malvidin 3-glucoside.

[Ψ] Total phenolics measured with Folin–Ciocalteu expressed as mg L^{-1} equivalent to gallic acid. ND – not detected.

3. Results and discussion

3.1. Phenolic compounds

In commercial grape juices the total phenolic content (TPC) varied from 1375.7 (OGJ) to 2023 mg L^{-1} (GJB) (see Table 2). In the monovarietal grape juices the results were 1580.1 and 4849.3 mg L^{-1} in the IPO and BV samples, respectively. In the wines these values ranged from 2242.9 (TW) to 3373.3 mg L^{-1} (OBW). The values found for TPC in the studied samples agreed with the mentioned in the literature for wines and grape juice of the SFV, Northeast of Brazil, which varied from 749 to 4036 mg L^{-1} (Lima et al., 2014; Silva et al., 2015; Padilha, Biasoto, et al., 2017; Padilha, Miskinis, et al., 2017). In general, SFV wines and juices, originating from conventional agriculture, presented higher TPC values than organic ones. The results obtained in this study are similar to those found by Margraf et al. (2016) when comparing 37 organic and 25 conventional grape juice samples from different varieties and regions of origin, whose mean TPC values were 2011 and 1914 mg L^{-1} for conventional and organic, respectively.

3.1.1. Phenolic acids

The averages of the sum of phenolic acids quantified in grape juice ranged from 110.3 to 186.4 mg L^{-1} in the GJB and IPO samples, respectively (Table 2). In the wines the sum of phenolic acids ranged from 77.9 to 133.7 mg L^{-1} in the OTW and OBW samples. Comparing all organic and conventional products, there was no significant difference in the total number of phenolic acids quantified or in the profile of individual phenolic acids. In the work of Margraf et al. (2016) there were also no significant differences in the individual and total phenolic acid profile of organic and conventional grape juice. In all grape juice samples *trans*-caftaric acid was the major phenolic acid, whose mean values ranged from 91.3 to 169 mg L^{-1}. In the studied wines, the *trans*-caftaric acid was also one of the main phenolic acids found, but in smaller values (33.6–49.9 mg L^{-1}) compared to the samples of grape juice. Other studies that characterized organic and conventional grape juices (Toaldo et al., 2015), and commercial grape juices and wines from the SFV (Padilha, Miskinis, et al., 2017) also showed *trans*-caftaric acid to be one of the main phenolic compounds present, with values from 6.6 to 366 mg L^{-1}. The second main phenolic acid present in the analyzed juices was chlorogenic acid, with values varying from 7.5 to 17 mg L^{-1}. The values of gallic acid in the wines (*V. vinifera*) studied were also highlighted, with values varying from 22.7 to 73.9 mg L^{-1}.

3.1.2. Flavanols and flavonols

In the commercial and monovarietal grape juice samples the sum of quantified flavanols ranged from 5.73 mg L^{-1} in the IPO sample to 70.83 mg L^{-1} in the BV juice, and the conventional juices presented the highest values (Table 2). Procyanidin B2 was the predominant flavanol, with values between 1.98 and 59.37 mg L^{-1}. Other studies also report the procyanidins B1 and B2 as being the main flavanols present in grape juice, with values from 20.8 to 38.6 mg L^{-1} (Lima et al., 2015; Padilha, Miskinis, et al., 2017; Silva et al., 2015). Conventional wine also presented higher values of flavanols compared to organic ones, with values varying from 45.82 mg L^{-1} in the OTW sample to 79.20 mg L^{-1} in TW wine, with catechin and procyanidin B2 being the main quantified compound. Samples TW and OTW were from different companies. It is well known that the winemaking process can also result in differences in the phenolic profile of wines. Based on this, we cannot affirm in a conclusive way that the conventional wine presents higher flavanols concentrations that organic one.

The total of flavonols ranged from 2.76 to 5.36 mg L^{-1} in grape juice samples, and these results were in accordance with other grape juice characterization, where the values varied from 0.5 to 14.6 mg L^{-1} (Lima et al., 2014; Toaldo et al., 2015). For quantified flavonols, quercetin 3-glucoside was found among all the juices as the main flavonol present among the analyzed samples, except for OBW, where kaempferol 3-glucoside was the main compound. In the wines the sum of quantified flavonols was 2.98, 4.26 and 5.27 mg L^{-1} in the samples OBW, TW and OTW, respectively. Quercetin 3-glucoside was also the main quantified flavonol in wine samples. The values obtained in the individual flavonols, in all wine samples studied, agrees with those mentioned by Padilha, Biasoto, et al. (2017) for monovarietal wines (*V. vinifera*) trades produced in the SFV with the varieties Tempranillo and Barbera.

In general, there was no significant difference in the amount and profile of flavanols and flavonols in organic and conventional juices and wines. These values are also in agreement with the study by Granato, Koot, Schnitzler, and van Ruth (2015), comparing 65 grape juice samples from several Brazilian regions, of which 19 were organic and 46 conventional, and there was also no significant difference in total phenolic content, catechin, quercetin and rutin.

3.1.3. Anthocyanins

The average total monomeric anthocyanins (TMA) in grape juice ranged from 103.4 to 1532.3 mg L^{-1} in the OGJ and BV samples, respectively (Table 2). These results demonstrate considerable variation in TMA content between the different grape varieties. The sum of the anthocyanins quantified by HPLC in grape juice ranged from 20.71 to 469.31 mg L^{-1}, the compounds malvidin 3.5-diglucoside and petunidin 3-glucoside being the major anthocyanins in grape juices, with values from 5.1 to 192 mg L^{-1} (malvidin) and 2.1 to 209.5 mg L^{-1} (petunidin). In the study by Granato, Koot, et al. (2015) the main anthocyanin present in Brazilian organic and conventional grape juices was also malvidin 3,5-diglucoside, in average values of 55.53 and 71.42 mg L^{-1} for conventional and organic juices, respectively. In *V. vinifera* wines the TMA values ranged from 38.68 to 85.94 mg L^{-1} in the OTW and TW samples, respectively. In relation to total anthocyanins quantified by HPLC, the values ranged from 2.25 to 30.47 mg L^{-1} in the OBW and TW samples, respectively. Malvidin 3-glucoside was the main anthocyanin present in the studied wines, which was already expected because it was *V. vinifera* wines (Ribéreau-Gayon, Glories, Maujean, & Dubourdieu, 2003).

Comparing organic and conventional SFV juices and wines, the values of TMA and individual anthocyanins were notably higher in conventional products. These results may be associated with better nutrition of the vines in conventional cultivation, since the conventional viticulture practiced in this region is highly technified, with controlled irrigation, fertilization by fertigation and scheduling of the productive cycles of the grapevine to be harvested in every month of the year.

In the study of Granato, Koot, et al. (2015), several samples (N = 97) of Brazilian, European, organic, biodynamic and conventional grape juice samples were compared, and differences in TMA and anthocyanin profile were not observed. In this same study, the main anthocyanin present in Brazilian organic and conventional grape juices was malvidin 3,5-diglucoside.

3.1.4. Stilbenes and flavanones

The *trans*-resveratrol was present in all the samples evaluated, where the grape juice values varied from 0.22 to 0.55 mg L^{-1} in the samples GJA and OGJ, respectively. In the wines the variations were 0.47–0.67 mg L^{-1} in the OTW, and TW & OBW samples, respectively. Cis-resveratrol was present only in grape juice samples ranging from 3.33 to 17.94 mg L^{-1} in samples GJB and BV, respectively. Regarding *trans*-resveratrol, there was no significant difference between organic and conventional wines, but *cis*-resveratrol was present in larger amounts in conventional grape juice.

We also highlight the high values of *cis*-resveratrol in the studied juices, with great emphasis on the BRS Violeta variety. According to Lima et al. (2014), it was expected that *cis*-resveratrol would be present in greater amounts than *trans*-resveratrol in SFV grape juice.

In relation to flavanones, hesperidin was present only in grape juice

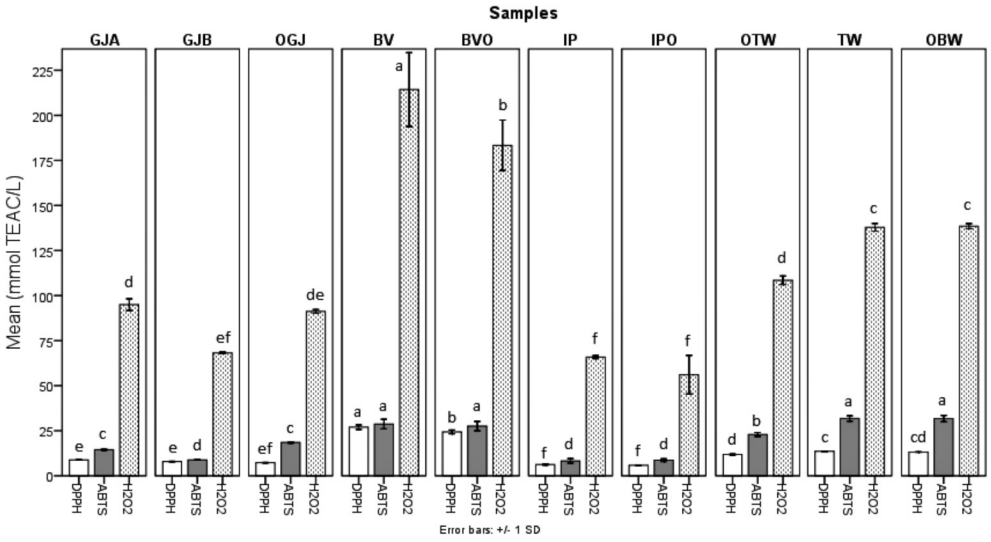

Fig. 1. Mean values of the *in vitro* antioxidant activity of organic and conventional grape juices and wines of the SFV, northeastern Brazil. *Legend:* GJA and GJB = conventional "Isabel Precoce + BRS Violeta" grape juice; OGJ = organic "Isabel Precoce + BRS Violeta" grape juice; BV and BVO = conventional and organic "BRS Violeta" grape juices, respectively; IP and IPO = conventional and organic "Isabel Precoce" grape juices, respectively; OTW and TW = organic and conventional "Tempranillo" wines, respectively; OBW = organic "Barbera" wine. Averages bars followed by equal letters do not differ from each other by the Tukey test at 5% of error probability.

samples BV (4.04 mg L^{-1}), TW wines (4.93 mg L^{-1}) and OBW (4.32 mg L^{-1}). Naringenin presented values ranging from 0.27 to 5.64 mg L^{-1} in the evaluated juices and wines. In general, naringenin was present in conventional products, with the exception of IPO and BVO organic juices. Flavanones are compounds little explored in characterization of beverages derived from grapes, and are usually studied in citrus fruits, and are associated with antioxidant, blood cholesterol and obesity (Vinueza, Faria, & César 2008; Domínguez, 2016).

3.2. In vitro antioxidant activity

In vitro antioxidant activity (AOX) was measured in the samples under study by free radical sequestration methods (DPPH and ABTS) and inhibition of hydrogen peroxide (H_2O_2), and the results are presented in Fig. 1.

In grape juices the AOX had averages varying from 5.83 to 26.98 mM TEAC L^{-1} for DPPH, and from 8.24 to 28.70 mM TEAC L^{-1} for ABTS. In wines the mean AOX ranged from 11.83 to 13.59 mM TEAC L^{-1} (DPPH) and from 22.93 to 31.79 mM TEAC L^{-1} (ABTS). Regarding AOX for the H_2O_2 method, values for grape juice varied from 56.10 to 214.29 mM TEAC L^{-1}, and for wines ranged from 108.50 to 138.47 mM TEAC L^{-1}. The values found in the samples studied are in accordance with those reported by Padilha, Miskinis, et al. (2017) for commercial juices and wines (*V. labrusca* and hybrids) of the SFV, with emphasis on the high AOX obtained in the H_2O_2 method which is a reactive oxygen species.

Comparing organic and conventional products, in general, no significant differences were observed in AOX quantified by the three methods. Margraf et al. (2016) also did not find differences comparing organic and conventional grape juices from different Brazilian regions using the AOX *in vitro* method with ABTS (ferric-reducing antioxidant power (FRAP) and reducing potential of the hydrophilic phenolic compounds (RPHPC).

3.3. Validation of the method for determination of Cu, Fe and Mn

The method was validated using two sample preparation protocols: direct dilution in 2% nitric acid, and hot digestion in HNO_3 + H_2O_2. The two protocols of sample preparation led to satisfactory results in the validation parameters for wine. However, in the recovery of Cu to grape juice matrix using dilution in nitric acid, the values were considered unsatisfactory (recovery of 68.8%). Boschetti et al. (2013) also compared two protocols for the preparation of "dry" wines for metal determination by direct dilution in 1% hydrochloric acid and hot digestion with H_2O_2 + HNO_3 and concluded that the two protocols were adequate. In the current study, low recovery of Cu in grape juice preparation by simple dilution in 2% nitric acid presented low recovery, possibly due to the presence of large amounts of sugar in the matrix, which can be evidenced by the °Brix of studied samples (values from 18.4 to 24.1) (Table 1).

For purposes of results and discussion of this work, only the characterization of the samples was considered using the preparation protocol by hot digestion with nitric acid + hydrogen peroxide.

3.3.1. Linearity, precision and recuperation

The results obtained for linearity, precision and recovery are presented in Table 3. Precision was measured by the coefficient of variation (CV%). In the grape juice matrices, the CV% ranged from 0.43 to 1.77 for determination of Cu and Mn elements, respectively. In the wines the CV% ranged from 1.18 to 12.9 for the Mn and Cu elements, respectively.

The CV% values for the three transition metals studied indicate satisfactory accuracy for the method, since they are below the

Table 3
Results of the parameters obtained in the validation of the method of determination of minerals Cu, Fe and Mn in wines and grape juices by F-AAS.

Transition metals	Calibration range (mg L^{-1})	Calibration curve	Correlation coefficient (R)	Recovery (%)		Precision (CV%)		RSD	LOD	LOQ
				Juices	wines	juices	wines		(mg L^{-1})	(mg L^{-1})
Cu	0.25–5	$A = 0.108 \times C\left(\frac{mg}{L}\right) + 0.0085$	0.9995	108.9	100.6	0.43	12.9	0.017	0.05	0.18
Fe	0.25–5	$A = 0.0659 \times C\left(\frac{mg}{L}\right) - 0.002$	0.9999	104.3	101.6	1.08	1.23	0.034	0.12	0.23
Mn	0.25–5	$A = 0.1015 \times C\left(\frac{mg}{L}\right) - 0.0105$	0.9996	110.4	108.2	1.77	1.18	0.0084	0.021	0.11

*A = Absorbance and C = mass concentration.

maximum limit established by Brazilian legislation, which is 20% (Brasil, 2011).

The results obtained for the percentage recovery of the compounds (RC%) ranged from 104.3 to 110.4 in the grape juice matrix, for the Fe and Mn elements, respectively. In the wine the RC% ranged from 100.6 to 108.2 in the Cu and Mn elements, respectively. The RC% values obtained in this study were considered acceptable for use of this methodology in scientific research with these matrices, since the RC% established by the Brazilian legislation for analytical methods, with analytes in the concentration range studied, vary from 80% to 107% (Brasil, 2011). Other validated methods for the determination of transition metals mention RC% ranging from 96 to 112 (Vystavna et al., 2014; Boschetti et al., 2013).

3.3.2. Limit of detection (LOD) and limit of quantification (LOQ)

The results obtained for LOD were 0.021, 0.05 and 0.12 mg L^{-1} for Mn, Cu and Fe, respectively. The LOQ values were 0.11, 0.18 and 0.23 mg L^{-1} for Mn, Cu and Fe, respectively (Table 3). The LOD and LOQ values of this work were considered acceptable for use of this methodology in grape and wine juice analyzes, since in another validated method for determination of metals in wines by F-AAS, the LOD values were 0.04 mg L^{-1} (Boschetti et al., 2013), and the LOQ 0.15 and 0.14 mg L^{-1} for copper and manganese, respectively. For the determination of copper by ICP-OES in grape juice and wine the LOD was approximately 1.0 μg L^{-1} (Vystavna et al., 2014). In the determination of transition metals in wines by GF-AAS, LOQ values were 0.06 mg L^{-1} (Fe), 1.3 μg L^{-1} (Cu) and 1.5 μg L^{-1} (Mn) (Alkış et al., 2014).

The limits of detection and quantification obtained in this study were higher than those normally found for determination of the same elements by GF-AAS and ICP-OES. However, they were considered satisfactory because several studies characterizing these elements in wines and juices mention values varying from 0.01 a 9.663 mg L^{-1} (Alkış et al., 2014; Boschetti et al., 2013; Fiket, Mikac, & Kniewald, 2011; Šeruga, Tomac, & Laslavić, 2008; Vystavna et al., 2014).

The present methodology can be considered as a simple and adequate protocol for the determination of Cu, Fe and Mn in beverages derived from grapes, which showed good performance even in matrices with different physical-chemical characteristics such as juices and wines.

3.4. Determination of Cu, Fe and Mn in the organic and conventional wines and grape juices

The results obtained in the Cu, Fe and Mn analyzes are shown in Fig. 2. In grape juice and wine evaluated Cu was only detected in the BV sample, presenting a mean concentration of 0.05 mg L^{-1}. Other studies that evaluated Cu in grape juices and wines mentioned values ranging from 0.01 to 6.827 mg L^{-1} for this element (Alkış et al., 2014; Boschetti et al., 2013; Kment et al., 2005; Šeruga, et al., 2008; Vystavna et al., 2014).

The mean values of Fe in grape juice ranged from 0.17 to 2.02 mg L^{-1} in the GJB and IPO samples, respectively. For the Mn values ranged from 0.19 to 0.29 mg L^{-1} in the OGJ and IPO samples, respectively. In wines the mean Fe concentrations ranged from 0.55 to 0.89 mg L^{-1} in the OTW and TW samples, respectively. The Mn ranged from 0.57 to 1.01 mg L^{-1} in the TW and OTW samples, respectively.

The results for Fe and Mn are in agreement with other studies, which report values varying from 0.31 to 9.663 mg L^{-1} for Fe, and from 0.032 to 8.59 mg L^{-1} for manganese (Alkış et al., 2014; Boschetti et al., 2013; Fiket et al., 2011; Kment et al., 2005).

Comparing the organic and conventional BRS Violeta juices, the Fe concentration was higher in the conventional (1.65 mg L^{-1}). For Isabel Precoce juices the highest Fe content was obtained in organic juice (2.03 mg L^{-1}). In the Tempranillo wine the Fe content was also higher in the conventional samples (0.88 mg L^{-1}). For the Mn mineral the monovarietal and commercial juices did not differ between organic and conventional, where all presented approximate values of 0.25 mg L^{-1}. In relation to Tempranillo wines, the organic samples showed higher values of Mn (1.15 mg L^{-1}) than the conventional ones (0.56 mg L^{-1}).

In general, comparing the evaluated juices and wines, in relation to Fe, Cu and Mn, the results obtained are varied, and it is not possible to affirm that there are considerable differences between organic and conventional products. Minerals Fe, Cu and Mn, even in small amounts, are important micronutrients in the human diet because they also exert an antioxidant effect, mainly related to the reduction of oxidative stress (Dani et al., 2012).

3.5. Correlation between phenolic compounds, minerals and antioxidant activity

The results of the Pearson correlation analysis between phenolic compounds, minerals and antioxidant activity (AOX) of organic and conventional wines and juices are presented in Table 4. The correlation

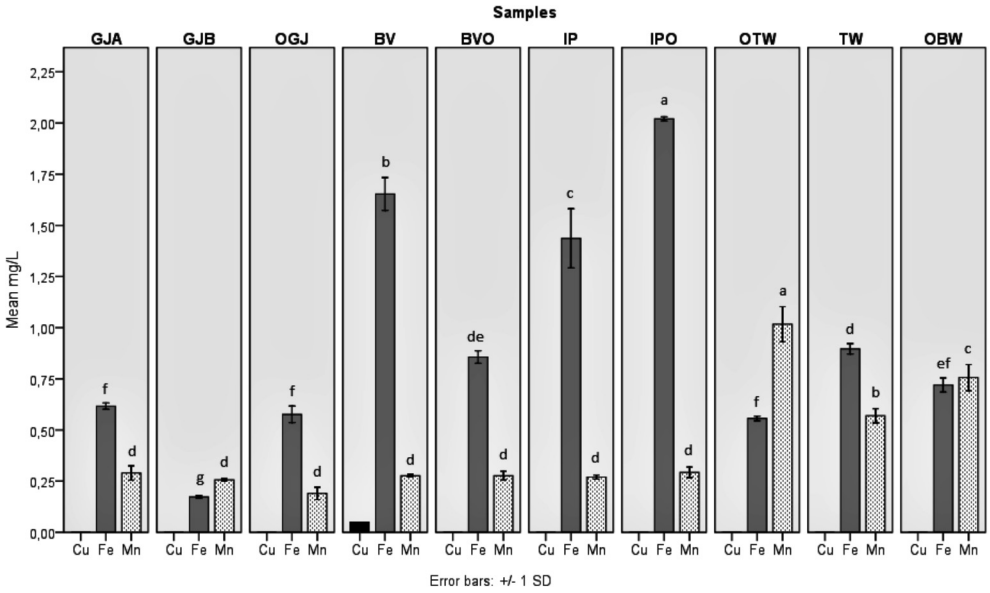

Fig. 2. Mean values of the Cu, Fe and Mn minerals in organic and conventional grape juices and wines of the SFV, northeastern Brazil. *Legend:* GJA and GJB = conventional "Isabel Precoce + BRS Violeta" grape juice; OGJ = organic "Isabel Precoce + BRS Violeta" grape juice; BV and BVO = conventional and organic "BRS Violeta" grape juices, respectively; IP and IPO = conventional and organic "Isabel Precoce" grape juices, respectively; OTW and TW = organic and conventional "Tempranillo" wines, respectively; OBW = organic "Barbera" wine. Averages bars followed by equal letters do not differ from each other by the Tukey test at 5% of error probability.

Table 4
Pearson correlations between phenolic compounds, minerals and antioxidant activity of Brazilian organic and conventional grape juices and wines.

Variable	Pearson (*r*-value)		
	DPPH*	ABTS*	H_2O_2*
Phenolic acids			
Gallic acid	0.07	0.62[a]	0.22
Syringic acid	0.82[a]	0.53[a]	0.81[a]
Trans-Caftaric acid	0.04	−0.41	−0.06
Chlorogenic acid	0.54[a]	0.16	0.46
Caffeic acid	0.57[a]	0.33	0.52[a]
p-Coumaric acid	−0.01	0.15	0.02
Flavanols			
Catechin	0.02	0.60[a]	0.18
Epicatechin gallate	0.69[a]	0.34	0.64[a]
Procyanidin A_2	0.27	0.48[a]	0.31
Procyanidin B_1	0.05	0.26	0.11
Procyanidin B_2	0.91[a]	0.64[a]	0.88[a]
Flavonols			
Quercetin 3-glucoside	−0.31	0.12	−0.21
Rutin	0.39	−0.06	0.29
Kaempferol 3-glucoside	0.83[a]	0.40	0.75[a]
Stilbenes			
Trans-Resveratrol	0.02	0.50[a]	0.17
Cis-Resveratrol	0.83a	0.33	0.75[a]
Flavanones			
Hesperidin	0.45	0.75[a]	0.59[a]
Narigenin	0.83[a]	0.40	0.75[a]
Anthocyanins			
Cyanidin 3,5-diglucoside	0.84[a]	0.34	0.81[a]
Malvidin 3,5-diglucoside	0.71[a]	0.18	0.63[a]
Delphinidin 3-glucoside	0.76[a]	0.23	0.67[a]
Cyanidin 3-glucoside	0.13	0.02	0.09
Pelargonidin 3-glucoside	−0.27	−0.27	−0.31
Peonidin 3-glucoside	−0.45	−0.40	−0.45
Malvidin 3-glucoside	−0.36	−0.30	−0.35
Petunidin 3-glucoside	0.85[a]	0.36	0.81[a]
Minerals			
Cu	0.68[a]	0.31	0.65[a]
Fe	0.15	0.12	0.09
Mn	0.02	0.47	0.11
Total bioactive content			
Total monomeric anthocyanins (TMA)	0.88[a]	0.33	0.81a
Total phenolic contente (TPC)	0.94[a]	0.81[a]	0.94a
Antioxidant activity			
DPPH		0.70[a]	0.96[a]
ABTS			0.83[a]

[a] Pearson correlation significant at 1% of probability of error ($p < 0.01$).
* DPPH, ABTS and H2O2 = Antioxidant methods.

coefficient (r) is a measure that shows the degree of association between both variables. The correlation between two variables is positive if high values for one variable are associated with high values for the other variable. For discussion purposes, we consider only Pearson correlation coefficients (r) greater than 0.80 ($p < 0.05$), which according to Granato, Calado and Jarvis (2014) correspond to strong correlations. For AOX measured with DPPH, the variables that presented a relevant positive correlation, in decreasing order of r-values were: TPC > TMA > procyanidin B2 > petunidin 3-glucoside > cyanidin 3,5-diglucoside > narigenin, *cis*-resveratrol & kaempferol 3 -glucoside > syringic acid. For the ABTS method only the TPC variable showed r > 0.80. For the H_2O_2 method, the variables that presented a relevant positive correlation were: TPC > procyanidin B2 > TMA, petunidin 3-glucoside, cyanidin 3,5-diglucoside & syringic acid. The significant correlation of the greater number of phenolic compounds with AOX with DPPH is due to the better sensitivity that this method possesses for grape matrices and derived products, which the International Grape and Wine Organization (OIV) mentions when recommending the method with DPPH for studies with beverages derived from grapes (Lima et al., 2014). The high correlations between AOX (DPPH and H2O2) and petunidin 3-glucoside & cyanidin 3,5-diglucoside are explained by the fact that these compounds were prominent in the monovarietal grape juice BV and BVO, which were the samples with the highest antioxidant activity *in vitro*. However, the strong correlations between AOX and procyanidin B2 can be explained by the high values of this compound in the samples BV, BVO, TW, OTW and OBW, which were the most antioxidant products in general (see Table 2 and Fig. 1). In relation to the Cu, Fe and Mn minerals, there were no significant correlations with AOX, only Cu presented a moderate positive correlation because it was present in the BRS Violeta grape juice sample (Fig. 2). As in this study, strong correlations (r > 0.80) between TPC and TMA with *in vitro* antioxidant activity were also obtained in studies that characterize organic, biodynamic and conventional Brazilian grape juices (Granato, Koot, et al., 2015; Granato, Margraf, et al., 2015).

4. Conclusions

In the present study, except for anthocyanins, no significant differences were found in the phenolic profile, *in vitro* antioxidant activity and Cu, Fe and Mn minerals between organic and conventional juices and wines. All the evaluated samples presented similar results among the same cultivars in the products originating from grapes from different cultivation systems. The protocol of preparation of the samples by hot digestion with $HNO_3 + H_2O_2$ showed to be more suitable for the grape juice and wine matrices. The validation parameters evaluated were considered satisfactory for the established purpose. The antioxidant activity of organic and conventional juices and wines was high, and was correlated with the contents of procyanidin B1, petunidin-3-glucoside and cyanidin-3,5-diglucoside of the samples.

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