ORIGINAL PAPER



Phytochemicals, Monosaccharides and Elemental Composition of the Non-Pomace Constituent of Organic and Conventional Grape Juices (*Vitis labrusca* L.): Effect of Drying on the Bioactive Content

Isabel Cristina da Silva Haas¹ · Isabela Maia Toaldo¹ · Jefferson Santos de Gois^{2,3} · Daniel L. G. Borges^{3,4} · Carmen Lúcia de Oliveira Petkowicz⁵ · Marilde T. Bordignon-Luiz¹

Published online: 13 October 2016 © Springer Science+Business Media New York 2016

Abstract Grape and grape derivatives contain a variety of antioxidants that have gain increasing interest for functional foods applications. The chemical composition of grapes is mainly related to grape variety and cultivation factors, and each grape constituent exhib its unique characteristics regarding its bioactive properties. This study investigated the chemical composition and the effect of drying on the bioactive content of the non-pomace constituent obtained in the processing of organic and conventional grape juices from V. labrusca L. The nonpomace samples were analyzed for polyphenols, monosaccharides, antioxidant activity and elemental composition and the effect of drying on the bioactive composition was evaluated in samples subjected to lyophilization and drying with air circulation. The analyses revealed high concentrations of proanthocyanidins, flavanols and anthocyanins, and high antioxidant capacity of the organic and conventional samples. The drying processes reduced significantly (P < 0.05) the total

Marilde T. Bordignon-Luiz marilde.bordignon@ufsc.br

¹ Department of Food Science and Food Technology, Federal University of Santa Catarina, Admar Gonzaga Rd., 1346, 88034-001 Florianópolis, SC, Brazil

- ² Department of Analytical Chemistry, Rio de Janeiro State University, São Francisco Xavier, 524, Maracanã, 20550-900 Rio de Janeiro, RJ, Brazil
- ³ Department of Chemistry, Federal University of Santa Catarina, Des., Vitor Lima Av., 476, 88040–900 Florianópolis, SC, Brazil
- ⁴ Present address: INCT de Energia e Ambiente do CNPq, Brasília, Brazil
- ⁵ Department of Biochemistry and Molecular Biology, Federal University of Paraná, CP 19046, 81531-980 Curitiba, PR, Brazil

phenolic content that ranged from 13.23 to 36.36 g/kg. Glucose, xylose, and mannose were the predominant monosaccharides, whereas K, Ca and Mg were the most abundant minerals. Variations in the chemical composition of organic and conventional samples were associated with cultivation factors. Nevertheless, this non-pomace constituent is a promising source of nutrients and polyphenols with bioactive potential.

Keywords Grape juice · Polyphenols · Dehydration · Elemental composition · Monosaccharides · Bioactive potential

Abbreviations

ANOVA	analysis of variance
CDS	conventional dried with air circulation sample
CFS	conventional fresh sample
FID	flame ionization detector
FRAP	ferric ion reducing antioxidant power
ICP-MS	inductively coupled plasma mass spectrometry
LCS	lyophilized conventional sample
LOS	lyophilized organic sample
NPP	non-polymerized polyphenols
ODS	organic dried with air circulation sample
OFS	organic fresh sample
PAC	proanthocyanidins
PP	polymerized polyphenols
TEAC	Trolox equivalent antioxidant capacity
TMA	total monomeric anthocyanins
TF	total flavanols
ТР	total polyphenols

Introduction

Grape (*Vitis* sp.) and grape derivatives are important sources of polyphenols with bioactive properties [1]. Recently, efforts have been dedicated to identifying grape constituents as potential sources of natural antioxidants, macro and micronutrients [2], as well as functional ingredients to enrich foods [3]. The antioxidant properties of grapes have been extensively studied in *V. vinifera* L. varieties, which are mainly destined for the production of wines [4, 5]. American varieties *V. labrusca* L. are widely cultivated in North and South America and are mainly used for the production of grape juices. Grape juice is a natural and non-alcoholic beverage that contains the nutrients present in grapes, such as sugars, minerals and phenolic compounds [6, 7]. The chemical composition of grape juices is influenced by factors such as grape variety, soil, and climate conditions, and cultivation practices [8].

During processing of grape juices, the grape marc consisting mainly of seeds and skins is obtained after pressing of the grapes. The grape marc is rich in antioxidants and has been studied for its bioactive properties [5]. After the pressing stage, grape juices are clarified through centrifugation, with the separation of a highly-colored non-pomace constituent that corresponds to 4-8 % of the volume of the processed juice. The removal of this constituent produces grape juices with low turbidity [7]. As a consequence of modern demands, the utilization of grape constituents for nutritional purposes may be a good alternative to fulfill the expectations of consumers, and a valuable approach regarding functional foods.

Phytochemicals in grapes are extensively reported in seeds, skins, and pomaces obtained from wine processing, mainly from *V. vinifera* L. grapes. However, differently than in wine processing, grape juices are not subjected to fermentation, which may lead to particular properties of grape juice co-products. Therefore, the aim of this study was to investigate the chemical composition and the effect of drying on bioactive polyphenols, monosaccharides, elemental profile and antioxidant activity of the non-pomace constituent of organic and conventional grape juices from *V. labrusca* L.

Material and Methods

Grape Juice Preparation and Non-Pomace Samples Organic *V. labrusca* L. grapes (var. Bordo) cultivated in organic system in the region of Rio do Sul, Santa Catarina, Brazil, and conventional Bordo grapes (*V. labrusca* L.) cultivated in conventional system in the region of São Marcos, Rio Grande do Sul, Brazil, were used for the production of grape juices and obtention of the non-pomace samples. The grapes were harvested at technical maturity, when total soluble solids were 15–17 °Brix. The organic and conventional grape juices were processed separately in an industrial-scale process.

Initially, the grapes were destemmed and crushed using a mechanical crusher (EDA, São Paulo, Brazil). The extraction of grape juices was carried out on an 800 kg capacity stainless steel tank with controlled temperature (85 ± 1 °C, 10 s) (Boff, Vacaria, Brazil). This temperature-time condition was used for pasteurization of grape juice and the short-time (10 s) was intended to prevent or reduce degradation of phenolic compounds at the applied temperature, specifically anthocyanins and flavonols that confer color and flavor to grape juice. Subsequently, pectinases (Coavin LX, AB Enzymes, Germany) were used to improve maceration and extraction of grape juice (2 g/L, 40 °C, 60 min). Following the mechanical pressing (EDA, São Paulo, Brazil), the grape marc was removed and grape juice was pumped into a 600 Pieralisi decanter centrifuge (Jesi, Italy) for clarification (5000 rpm, 10 min). At this stage, the samples of the non-pomace constituent were collected from the compartment on the bottom of the centrifuge and immediately stored at -18 °C until the analyses. The samples of the non-pomace constituent of the organic and conventional grape juices were analyzed in three different states: fresh (after thawing at 10 °C); lyophilized; and dried with air circulation at temperatures of 45, 55 and 65 °C. All lyophilized and dried samples were produced in triplicates from their respective fresh samples.

Lyophilization and Drying with Air Circulation For the lyophilization process, organic and conventional samples were frozen at -80 °C in an UFV 37 ultra-freezer (Terroni, São Carlos, Brazil) and lyophilized in a countertop lyophilizer (Terroni, Brazil) for 24 h until the moisture content was 5 % (*w*/w). For the drying process, fresh samples were dried until moisture content of 8 % (w/w) in an oven with air circulation (Model TE-394/2, Tecnal®, Piracicaba, Brazil) at temperatures of 45, 55 and 65 °C for 4 h and 55 min, 3 h and 15 min and 2 h and 45 min, respectively. Drying with air was carried out using round trays of 40 cm diameter and 0.7 cm height. The thickness of the sample was 0.5 cm and the air velocity was set at 0.78 m/s. Both lyophilized and dried samples were triturated and sieved through a 20-mesh sieve, and stored at -20 °C until the analyses.

Phenolic Contents and Antioxidant Activity Extracts of fresh, lyophilized and dried with air samples were prepared mixing 4 g of sample with 15 mL of 80 % (ν/ν) acetone solution acidified with 0.1 % (ν/ν) HCl in a shaker (500 rpm, 120 min), followed by centrifugation at 3000 rpm for 10 min. The supernatants were collected for the analyses. The total polyphenols (TP) content was determined according to Singleton and Rossi [9] and expressed as gallic acid equivalents (GAE). The content of non-polymerized polyphenols (NPP) was determined by the vanillin method [10]. The polymerized polyphenols (PP) were determined by calculating the difference between the total phenolic content and the content

of non-polymerized polyphenols and expressed as catechin equivalents. The total monomeric anthocyanins (TMA) were quantified using the pH differential method [11] and expressed as malvidin 3.5-diglucoside equivalents. The total flavanols (TF) were determined using the DMACA (pdimethylaminocinnamaldehyde) method [12], and total proanthocyanidins (PAC) were determined using the HClbutanol method [13]. Results were expressed as equivalent of catechin. The antioxidant capacity was determined using the free radical scavenging methods ABTS [2,2'-azino-bis(3ethylbenzothiazoline-6-sulphonic acid)] [14] and DPPH (2,2diphenyl-1-picrylhydrazyl) [15], and the ferric ion reducing antioxidant power (FRAP) method [16], with absorbance readings at 754 nm, 517 nm and 620 nm, respectively. Results were expressed as Trolox (6-hydroxy-2,5,7,8tetramethylchroman-2-carboxylic acid) equivalent antioxidant capacity (TEAC) µmol/g of dry basis. The spectrophotometric analyses were carried out in triplicates on a UV-VIS spectrophotometer (Hitachi U 2010, CA, USA).

Gas Chromatography Analysis for Monosaccharides The non-pomace samples were treated for removal of pigments and low-mass compounds using 80 % (ν/ν) ethanol at 65 °C. The solid fraction was separated by centrifugation (3000 rpm for 10 min), dried in a vacuum oven at 25 °C, and prepared for the chromatographic analysis. For the determination of neutral monosaccharides, the samples were hydrolyzed with sulfuric acid 72 % (v/v) for 1 h, followed by dilution to 8 % (v/v) and then kept at 100 °C for 8 h. The monosaccharides were reduced by adding sodium borohydride and the alditols formed were acetylated by reaction with acetic anhydride and pyridine [17]. The alditol acetates formed were then analyzed in a Trace GC Ultra chromatograph (Thermo Electron Corporation, Waltham, USA) equipped with a DB-225 capillary column (30 m \times 0.25 mm). The temperatures of the injector and flame ionization detector (FID) were 250 °C and 300 °C, respectively. The oven temperature was increased from 100 °C to 215 °C at a rate of 40 °C/min. Helium was used as carrier gas at a flow rate of 1.0 mL/min. The determination of acid monosaccharides was performed according to Blumenkrantz and Asboe-Hansen [18], with absorbance read at 520 nm. The analyses were performed in triplicates and results were expressed as a percentage of individual sugars.

Mutielemental Analysis by ICP-MS The elemental composition of the organic and conventional lyophilized samples was determined by inductively coupled plasma mass spectrometry (ICP-MS) on an ELAN 6000 spectrometer (PerkinElmer, Thornhill, Canada). Argon (99.996 % purity) was used to create the plasma and aerosol carrier gas. The analyses were performed according to Millour et al. [19]. The lyophilized samples were analyzed in triplicates and pretreated by microwave-assisted digestion using an MLS 1200 Mega station with closed PTFE vessels (Milestone, Italy). The isotopes monitored were ²⁷Al, ⁴³Ca, ⁵⁹Co, ⁶³Cu, ⁵⁷Fe, ²⁴Mg, ⁵⁵Mn, ⁶⁰Ni, ³⁹K, ²³Na, ²⁰⁸Pb, ⁸⁵Rb, ¹⁰³Rh, ⁸⁸Sr, ¹³⁷Ba, ⁵²Cr, ¹¹¹Cd and ⁶⁶Zn.

Statistical Analysis The analysis of variance (ANOVA) and Tukey's HSD *post hoc* test were performed using the Statistica 6.0 software (StatSoft Inc., Tulsa, USA). Data homoscedasticity and normality were verified using Hartley test (F max). Statistical differences were regarded at P < 0.05, at the confidence level of 95 %.

Results and Discussion

The phenolic composition of the non-pomace constituent of grape juices was determined in fresh, lyophilized and dried samples (Table 1). The antioxidant activity of samples is shown in Fig. 1. The main phenolic classes were quantified in all the organic and conventional samples. The total phenolic content ranged between 13.23 and 36.36 g/kg in the lyophilized organic sample and the fresh conventional sample, respectively. Both conventional and organic samples showed high antioxidant capacity, low concentrations of nonpolymerized polyphenols and elevated levels of polymerized phenolics. When comparing the phenolic composition of the fresh materials, the conventional samples showed higher concentrations of total polyphenols, monomeric anthocyanins, flavanols, polymerized polyphenols, proanthocyanidins and higher antioxidant activity in comparison with the organic samples. These phytochemicals are related to defense mechanisms in plants. In the organic cultivation, in which the use of pesticides is not permitted, there is an increased need for polyphenols synthesis [8]. Conversely, in this study, the lower contents of phenolic compounds verified in the organic samples may be explained by differences between the growing locations, or also by the stage of ripening during the harvest of V. labrusca grapes. Thus, specific factors related to climate and soil conditions not evaluated in this study may have contributed to the observed differences between samples. In fact, these factors exert a strong influence on polyphenols production in plants [20]. Similarly, Granato et al. [21], when evaluating the chemical composition of purple grape juices, reported that the multivariate analysis showed no clear separation between organic, biodynamic and conventional juices, indicating that the production region exerted a stronger influence on this parameters than crop system. According to Margraf et al. [22], there is no consensus regarding the differences between chemical compounds and antioxidant properties of conventional and organic plant-derived products; however, apart from their geographical origin and phenological characteristics, the distinction between crops is attainable based on their specific compounds or phytochemical markers.

425

Table 1 Phenolic contents in fresh, lyophilized and dried with air circulation samples of the non-pomace constituent of Bordo juices

Samples	TP	TMA	NPP	PP	TF	PAC
CFS	$36.36^{a} \pm 0.72$	$9.51^{a} \pm 0.27$	$0.030^{\mathrm{a}} \pm 0.005$	$32.76^{a} \pm 0.60$	$4.09^{a} \pm 0.21$	$34.62^{a} \pm 0.52$
LCS	$18.05^{\text{c}}\pm0.76$	$9.13^{\rm a}\pm0.54$	$0.006^{b} \pm 0.001$	$15.25^{c} \pm 0.64$	$2.98^{b}\pm0.49$	$18.72^b\pm0.42$
CDS 45 °C	$18.20^{\circ} \pm 0.22$	$5.82^{b}\pm0.33$	$0.006^{b} \pm 0.000$	$15.70^{\rm c} \pm 0.40$	$2.94^{b}\pm0.23$	$17.86^{\circ} \pm 0.62$
CDS 55 °C	$19.53^{\circ} \pm 0.25$	$6.20^{b}\pm0.22$	$0.005^{b}\pm 0.000$	$17.22^{b} \pm 0.13$	$2.78^{b}\pm0.10$	$18.82^b\pm0.74$
CDS 65 °C	$17.27^{\rm c} \pm 0.21$	$5.86^{\rm b}\pm0.18$	$0.006^{b} \pm 0.001$	$16.66^{b} \pm 0.20$	$2.43^{c} \pm 0.21$	$18.06^{\circ} \pm 0.53$
OFS	$\mathbf{27.24^b} \pm 0.56$	$2.00^{\rm c}\pm0.02$	$0.031^{a}\pm 0.004$	$22.21^{a}\pm0.32$	$2.73^b\pm0.12$	$30.24^{a}\pm0.70$
LOS	$13.23^d\pm0.43$	$1.16^{\rm e} \pm 0.01$	$0.002^{b} \pm 0.000$	$11.00^{e} \pm 0.46$	$1.93^{d}\pm0.10$	$14.61^{e} \pm 0.33$
ODS 45 °C	$13.81^{d}\pm0.41$	$1.51^{d}\pm0.15$	$0.005^{b} \pm 0.001$	$11.79^{d} \pm 0.11$	$2.17^d \pm 0.15$	$14.75^{e} \pm 0.51$
ODS 55 °C	$16.42^{\circ} \pm 0.51$	$1.46^{d} \pm 0.14$	$0.007^{b} \pm 0.001$	$14.11^{c} \pm 0.50$	$2.32^{c} \pm 0.13$	$15.78^d\pm0.43$
ODS 65 °C	$17.00^{\rm c}\pm0.18$	$1.77^{c} \pm 0.10$	$0.007^{b} \pm 0.001$	$14.88^b\pm0.17$	$2.09^{d} \pm 0.11$	$15.89^d\pm0.58$
*P-value	0.920	0.897	0.067	0.588	0.979	0.659
#P-value	<0.001	<0.001	0.007	<0.001	< 0.001	< 0.001

Results (g/kg) expressed as mean ± SD

TP total polyphenols, *TMA* total monomeric anthocyanins, *NPP* non-polymerized polyphenols, *PP* polymerized polyphenols, *TF* total flavanols, *PAC* proanthocyanidins, *CFS* conventional fresh sample, *LCS* lyophilized conventional sample, *CDS* conventional dried with air circulation sample, *OFS* organic fresh sample, *LOS* lyophilized organic sample, *ODS* organic dried with air circulation sample

*Probability values obtained by Hartley test

[#]Probability values obtained by one-way ANOVA

The dehydration process affected the polyphenols content of both organic and conventional samples, and the antioxidant activity, which was reduced upon lyophilization and drying. When compared to the fresh material, the antioxidant activity of the non-pomace samples assayed by ABTS and DPPH methods was reduced up to 41.1 and 54.6 % (ABTS) and up to 72.1 and 40.6 % (DPPH) in lyophilized and dried with air samples, respectively. Using the FRAP assay, the antioxidant activity of these samples was reduced up to 45.4 and 24.4 %, respectively. The total monomeric anthocyanins in organic samples were reduced significantly in both lyophilized (42 %) and dried with air (27 %) samples. Contrarily, for the conventional samples, concentrations of anthocyanins in the lyophilized sample were higher than those of the dried with air samples. When comparing the dried samples, it was verified that concentrations of polymerized polyphenols, total monomeric anthocyanins and proanthocyanidins were greatly decreased in comparison with the fresh samples upon drying at 45 °C, with values up to 46.9 and 52 % (PP), 24.5 and 38.8 % (TMA), and 51.2 and 48.4 % (PAC) for the organic and conventional samples, respectively. The mean reduction in the total phenolic content was 49.3 % for the organic samples and 49.9 % for the conventional samples. This may be explained by the prolonged time at this temperature (4 h 55 min) in comparison with treatments at 55 °C (3 h 15 min) and 65 °C (2 h 45 min). In fact, according to Khanal et al. [23], the stability of anthocyanins and proanthocyanidins depends on the nature of these molecules, pH of medium and, to a greater extent, the temperature and duration of heating. The pH of samples was similar to that of grape juice, approximately 3.0–3.4. In fact, these compounds are more stable in acidic media. At this low pH, the flavylium cation of anthocyanins is predominant and the compounds are present in their characteristic red-purple color. At higher pH (5–7), anthocyanins assume their carbinol pseudo-base form or the colorless chalcone form, more susceptible to oxidation [24].

Regardless of the dehydration process, the non-pomace samples showed the most abundant content of polyphenols and high antioxidant activity. Also, the total phenolics quantified in samples were similar to that of grape juices from other *V. labrusca* L. varieties, such as Isabel, Concord and BRS Cora [22, 25]. According to Granato et al. [26], the total polyphenols, specifically anthocyanins, flavonols, gallic acid, *p*coumaric acid, and flavanols are responsible for the antioxidant activity of fruit juices. These are the main phenolics reported in *V. labrusca* L. grape juices [27]. Further, our findings support that this non-pomace constituent is a polyphenol-rich matrix with antioxidant potential comparable to that of grape juices.

The monosaccharide profile and elemental composition of the non-pomace samples are presented in Table 2 and Table 3, respectively. Glucose was the most abundant monosaccharide in both conventional (475 g/kg) and organic (512.3 g/kg) samples, followed by xylose and mannose. These last monosaccharides are produced from the breakdown of polysaccharides xylans and mannans by enzymes xylanase and mannanase and comprise two groups of hemicellulose compounds that are structurally important in the cell wall of plants. Hemicelluloses are naturally present along with cellulose in



Fig. 1 Antioxidant activity of conventional **a** and organic **b** samples of the non-pomace constituent of *V. labrusca* L. grape juices assayed by ABTS, DPPH and FRAP methods, expressed as Trolox equivalent antioxidant capacity (TEAC). CFS = conventional fresh sample, LCS = lyophilized conventional sample, CDS = conventional dried with air circulation sample, OFS = organic fresh sample, LOS = lyophilized organic sample, ODS = organic dried with air circulation sample. Samples dried with air at temperatures of 45, 55 and 65 °C. Data expressed as mean \pm SD. For each method, bars with different letters are significantly different (P < 0.05)

vegetal cells [28]. Thus, the results indicate that these are the major components of insoluble fiber in the non-pomace constituent of *V. labrusca* L. juices. The concentrations of

 Table 2
 Monosaccharide profile of the non-pomace constituent of conventional and organic grape juices

Monosaccharides (g/kg)	Organic	Conventional	
Rhamnose	$18.3^{a} \pm 0.3$	15.7 ^a ± 0.1	
Fucose	$17.3^{\rm a} \pm 0.4$	$17.0^{\rm a} \pm 0.4$	
Arabinose	$36.3^{a}\pm0.3$	$33.3^{\mathrm{a}}\pm0.3$	
Xylose	$137.0^b\pm0.3$	$177.3^{\rm a} \pm 0.5$	
Mannose	$144.3^a\pm0.2$	$138.7^{b}\pm0.1$	
Galactose	$73.7^b\pm0.2$	$82.7^{a} \pm 0.3$	
Glucose	$512.3^{a} \pm 1.2$	$475.0^{b}\pm0.8$	
Galacturonic acid	$60.7^{\rm a}\pm0.1$	$60.3^{\rm a}\pm0.1$	

Results expressed as mean \pm SD. Different letters in the same line indicate statistical difference between cultures (Tukey's HSD test, P < 0.05)

 Table 3
 Elemental composition of organic and conventional samples of the non-pomace constituent of *V. labrusca* L. grape juices

Elements (mg/kg)	Organic	Conventional
Macroelements		
Na	$21.10^{a}\pm0.24$	$11.40^b\pm0.58$
K	$8830.50^b \pm 14.53$	$9695.71^{a}\pm13.12$
Mg	$300.91^{a}\pm 10.67$	$326.00^a\pm4.78$
Ca	$1167.19^{a}\pm 2.98$	$1228.11^{a}\pm15.39$
Microelements		
Fe	$211.21^{a}\pm 0.39$	$156.92^b\pm2.81$
Mn	$12.90^{a}\pm0.02$	$10.80^{a}\pm0.14$
Zn	$4.70^{a}\pm0.01$	$3.92^{a}\pm0.04$
Rb	$13.30^b\pm0.01$	$25.11^{a}\pm0.35$
Trace elements		
Со	nd	nd
Sr	$3.52^{a}\pm0.01$	$5.10^{\mathrm{a}}\pm0.07$
Ba	$2.40^b\pm0.01$	$6.60^{a} \pm 0.10$
Cr	nd	nd
Al	$16.9^{\rm a}\pm0.68$	$11.20^{b} \pm 1.57$
Cu	$3.19^b \pm 0.01$	$6.51^{a}\pm0.82$
Ni	nd	nd
Pb	nd	nd
Cd	nd	nd

Results expressed as mean \pm SD. Values for each element followed by different letters are significantly different (Tukey's HSD test, P < 0.05) *nd* not detected

mannose, galactose, xylose and glucose varied significantly, with the highest contents of galactose (82.7 g/kg) and xylose (177.3 g/kg) in the conventional sample. The samples showed similar contents of acidic monosaccharides, and rhamnose and fucose were quantified in small concentrations (< 18 g/kg). The mannose quantified in samples can be attributed to the presence of hemicelluloses such as mannans, galactomannans, and galactoglucomannans, functionally present in the vegetal cell wall. In addition, the presence of glucose, xylose, galactose and fucose indicates the presence of xyloglucans [28]. Importantly, these monosaccharides contribute to the high fiber content of the non-pomace constituent of the V. labrusca L. grape juices, corroborating its functional properties. Similarly, other grape constituents such as grape pomace and grape marc are good sources of soluble and insoluble dietary fiber [3].

The elemental analysis revealed the presence of many macro- and microelements, and of trace elements (Table 3). Calcium and K were the most abundant elements, and Fe was the predominant microelement. Copper and Al were the main trace elements quantified. Concentrations of Ca ranged from 1167.19 to 1228.11 mg/kg and concentrations of K ranged from 8830.50 to 9695.71 mg/kg in the organic and conventional samples, respectively. The non-pomace constituent

showed considerable amounts of Mg and Mn, and low content of Zn, while concentrations of Na, K, Ca, Rb and Fe varied significantly between organic and conventional samples. The micronutrients determined in samples are consistent with those previously verified in grapes and grape juices [6, 29].

The content of essential minerals such as K, Mg and Ca was slightly higher in the conventional samples, which was obtained from grapes cultivated in the conventional system. These minerals are macroelements extracted from soil by plants and are present in high concentrations in grape products [29]. Concerning the content of elements, differences verified between organic and conventional samples obtained from the same grape variety are probably attributed to grapevine location and cultivation factors. In the conventional system, the application of pesticides, fertilizers or synthetic nutrients is allowed [8], which contributes to the supply of minerals to the plants. Indeed, geographical origin, environmental conditions as well as cultivation practices, which determine the availability of elements in the soil, are major factors that influence the elemental composition of grapes and its derivatives [27, 30]. Granato et al. [31] demonstrated the distinction between organic and conventional grape juices and between conventional and organic/ biodynamic juices using an authentication model based on polyphenols composition and antioxidant properties of these juices. Further, in addition to phenolic markers, the elemental profile can generate useful information to characterize growing locations and grape cultivars, as well as to identify and monitor the quality of grape products.

Conclusions

The non-pomace constituent of grape juice was demonstrated to be a rich source of different classes of polyphenols, monosaccharides and minerals. There were significant variations in phenolic concentrations upon dehydration. Drying with air circulation and lyophilization reduced the concentrations of bioactive polyphenols. The fresh samples had the highest contents of anthocyanins, flavanols and proanthocyanidins, whilst the highest concentration of total polyphenols was verified in the conventional fresh sample (CFS). In samples subjected to drying with air at 45 °C or lyophilization a decrease in the contents of polymerized and total polyphenols was observed when compared with drying at 55 and 65 °C for shorter periods. Moreover, results showed that glucose, xylose and mannose were the predominant monosaccharides in samples, whereas K and Fe were the most abundant macro- and microelements, respectively. This grape co-product showed high phenolic content and antioxidant activity and may represent a promising alternative as a food ingredient for functional foods.

Acknowledgments The authors gratefully acknowledge the Poggere Winery for providing the raw material. This work was supported by the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), Brazil.

Compliance with the Ethical Standards

Conflict of Interest The authors declare that they have no conflict of interest.

References

- 1. Giovinazzo G, Grieco F (2015) Functional properties of grape and wine polyphenols. Plant Foods Hum Nutr 70(4):454–462
- Dumitriu D, Peinado RA, Peinado J, Lerma NL (2015) Grape pomace extract improves the *in vitro* and *in vivo* antioxidant properties of wines from sun light dried Pedro Ximénez grapes. J Funct Foods 17:380–387
- Mildner-Szkudlarz S, Bajerska J, Zawirska-Wojtasiak R, Gorecka D (2013) White grape pomace as a source of dietary fiber and polyphenols and its effect on physical and nutraceutical characteristics of wheat biscuits. J Sci Food Agric 93:389–395
- Sri Harsha PSC, Gargana C, Simonetti P, Spigno G, Lavelli V (2013) Characterization of phenolics, *in vitro* reducing capacity and anti-glycation activity of red grape skins recovered from winemaking by-products. Bioresour Technol 140:263–268
- Rockenbach II, Gonzaga LV, Rizelio VM, Gonçalves AESS, Genovese MI, Fett R (2011) Phenolic compounds and antioxidant activity of seed and skin extracts of red grape (*Vitis vinifera* and *Vitis labrusca*) pomace from Brazilian winemaking. Food Res Int 44:897–901
- Toaldo IM, De Gois JS, Fogolari O, Hamann D, Borges DLG, Bordignon-Luiz MT (2014) Phytochemical polyphenol extraction and elemental composition of *Vitis labrusca* L. grape juices through optimization of pectinolytic activity. Food Bioprocess Technol 7: 2581–2594
- 7. Rizzon LA, Meneguzzo J (2007) Grape Juice. Embrapa Technological Information, Brasília
- Mulero J, Pardo F, Zafrilla P (2010) Antioxidant activity and phenolic composition of organic and conventional grapes and wines. J Food Compos Anal 23:569–574
- Singleton VL, Rossi JA (1965) Colourimetry of total phenolics with phosphomolybdic-phosphotungstic acid reagent. Am J Enol Vitic 16:144–158
- 10. Panoretto L (1977) Polifenoli e tecnica enological. Selepress, Milan
- Giusti MM, Wrolstad RE (2001) Anthocyanins: characterization and measurement with UV-visible spectroscopy. In: Wrolstad, RE (ed) Current protocols in food analytical chemistry, 1st edn. Wiley, New York, pp. F1.2.1–F1.2.13
- Arnous A, Makris D, Kefalas P (2002) Correlation of pigment and flavanol content with antioxidant properties in selected aged regional wines from Greece. J Food Compos Anal 15:655–665
- Porter LJ, Hrstich LN, Chan BG (1986) The conversion of procyanidins and prodelphinidins to cyaniding and delphinidin. Phytochemistry 25:223–230
- Re R, Pellegrini N, Proteggemnte A, Pannala A, Yang M, Rice-Evans C (1999) Antioxidant activity applying an improved ABTS radical cation decolorization assay. Free Radic Biol Med 26:1231–1237
- Kim YK, Guo Q, Packer L (2002) Free radical scavenging activity of red ginseng aqueous extracts. Toxicology 172:149–156

- Benzie IFF, Strain JJ (1996) The ferric reducing ability of plasma (FRAP) as a measure of antioxidant power: the FRAP assay. Anal Biochem 239:70–76
- 17. Wolfrom ML, Thompson A (1963) Reduction with sodium borohydride. Methods. Carbohydr Chem 2:65–68
- Blumenkrantz N, Asboe-Hansen G (1973) New method for quantitative determination of uronic acids. Anal Biochem 54:484–489
- Millour S, Noel L, Kadar A, Chekri R, Vastel C, Guérin T (2011) Simultaneous analysis of 21 elements in foodstuffs by ICP-MS after closed vessel microwave digestion: method validation. J Food Compos Anal 24:111–120
- Garrido J, Borges F (2013) Wine and grape polyphenols a chemical perspective. Food Res Int 54:1844–1858
- Granato D, Margraf T, Brotzakis I, Capuano E, van Ruth SM (2015) Characterization of conventional, biodynamic, and organic purple grape juices by chemical markers, antioxidant capacity, and instrumental taste profile. J Food Sci 80:C55–C65
- 22. Margraf T, Santos ENT, Andrade EF, van Ruth SM, Granato D (2016) Effects of geographical origin, variety and farming system on the chemical markers and *in vitro* antioxidant capacity of Brazilian purple grape juices. Food Res Int 82:145–155
- Khanal RC, Howard LR, Prior RL (2010) Effect of heating on the stability of grape and blueberry pomace procyanidins and total anthocyanins. Food Res Int 43:1464–1469
- Jackson RS (2008) Chemical constituents of grapes and wine. In: Jackson RS (ed) Wine science: Principles and applications, 3rd edn. Elsevier, Boston, pp 270–331
- Lima MS, Dutra MCP, Toaldo IM, Correa LC, Pereira GE, Oliveira D, Bordignon-Luiz MT, Ninow JL (2015) Phenolic compounds,

organic acids and antioxidant activity of grape juices produced in industrial scale by different processes of maceration. Food Chem 188:384–392

- Granato D, Karnopp AR, van Ruth SM (2015) Characterization and comparison of phenolic composition, antioxidant capacity and instrumental taste profile of juices from different botanical origins. J Sci Food Agric 95:1997–2006
- 27. Toaldo IM, Cruz FA, Lima Alves T, de Gois JS, Borges DLG, Cunha HP, Bordignon-Luiz MT (2015) Bioactive potential of *Vitis labrusca* L. grape juices from the southern region of Brazil: phenolic and elemental composition and effect on lipid peroxidation in healthy subjects. Food Chem 173:527–535
- Caffall KH, Mohnen D (2009) The structure, function, and biosynthesis of plant cell wall pectic polysaccharides. Carbohydr Res 344: 1879–1900
- Panceri CP, Gomes TM, De Gois JS, Borges DLG, Bordignon-Luiz MT (2013) Effect of dehydration process on mineral content, phenolic compounds and antioxidant activity of cabernet sauvignon and merlot grapes. Food Res Int 54:1343–1350
- 30. Dutra SV, Adami L, Marcon AR, Carnieli GJ, Roani CA, Spinelli FR, Leonardelli S, Vanderlinde R (2013) Characterization of wines according the geographical origin by analysis of isotopes and minerals and the influence of harvest on the isotope values. Food Chem 141:2148–2153
- Granato D, Koot A, Schnitzler E, van Ruth SM (2015) Authentication of geographical origin and crop system of grape juices by phenolic compounds and antioxidant activity using chemometrics. J Food Sci 80:C584–C593