



## Chemical characterization of winemaking byproducts from grape varieties cultivated in Vale do São Francisco, Brazil

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### Abstract

The recovery of agroindustry byproducts can bring opportunities for the development of new products. The objective of this study was to characterize chemical compounds contents in the byproducts generated during winemaking from different grape varieties cultivated in Vale do São Francisco, Brazil. The grapes and their byproducts (skins and seeds) from four wineries (w1, w2, w3 and w4) were evaluated. The varieties studied were: Viognier, Chenin Blanc, Moscato Canelli, Italia, Arinto+Fernão Pires, Tempranillo, Grenache, Mourvèdre, Verdejo and Sauvignon Blanc, used in the processing of white/sparkling wines, and also Tempranillo, Cabernet Sauvignon, Syrah and Alicante Bouschet, used in the processing of red wines. High ascorbic acid contents were found in the skin and seed byproducts, the latter also presenting high protein and pectin contents. The skin byproduct obtained in the process of elaborating white/sparkling wines from 'Tempranillo' grapes presented relatively higher ascorbic acid, pectin and protein contents. In the elaboration of red wines by w1, the 'Syrah' skin byproduct showed high ascorbic acid, soluble solids, sugars and protein contents. The seed byproduct from the 'Syrah' grapes used to elaborate red wines by w1 showed a more favorable composition for reuse, as did those of red wines of 'Tempranillo' grapes from w3.

**Keywords:** tropical viticulture; agroindustrial byproducts; chemical composition; *Vitis vinifera* L.

**Practical Application:** The chemical composition of winemaking byproducts was characterized for their reuse.

### 1 Introduction

In 2016, 984,481 tons of grapes were produced in Brazil, covering 77,132 ha, and approximately 50% was destined for processing (Instituto Brasileiro de Geografia e Estatística, 2016). Agroindustrial activities related to grape production have been developing in Vale do São Francisco (Brazil) area mainly over the last fifteen years. With proper irrigation and cultural management practices, the farmers in that region can produce grapes and wine at any time of the year due to the availability of sunlight, which favors the complete maturation of the grapes, providing the conditions for obtaining well-structured wines. In addition, it is possible to produce a variety of quality wines as a result of the intra-annual climatic variability, with reasonable constancy of the conditions year after year (Camargo et al., 2011; Teixeira et al., 2007).

Part of grape quality is due to the byproducts, constituted mainly of skins and seeds. Two types of byproducts are generated in wineries: sweet bagasse and red or fermented bagasse. It has been estimated that these byproducts represent 20% of the production (Barcia et al., 2014), causing economic and ecological problems. Making use of the byproducts could subsidy a parallel activity, supported by the appeal of generating new products, reducing environmental waste, and instigating a greater use

of the consumables and infrastructure, amongst other factors (Lavelli et al., 2017a; Silva et al., 2014; Souza et al., 2014).

With a view to giving technical and scientific support to such initiatives, studies have been carried out with various types of agroindustrial byproducts, identifying compounds of interest, especially functional ones (Barcia et al., 2014; Correia et al., 2012; Durante et al., 2017). The perspectives are also favorable for their use in human feeding, such as using grape byproducts to provide phenolic enrichment to the juices of the fruit itself (Toaldo et al., 2013) and others beverages (Lavelli et al., 2017a), to produce coloring additives and to recover dietary fibre, oils and others compounds (Beres et al., 2017; Lavelli et al., 2017b).

However there is still a need for studies that provide more information about the quality of the byproducts produced by wineries, including the sugar, ascorbic acid, pectic compounds and others. These compounds may also be options for biotechnological processes or as natural ingredients in industrialized foods, as well as the use of phenolic compounds maintained in byproducts of winemaking as commonly studied to the grapevine industry. This opportunity should be analyzed focusing differences among varieties, regions and others.

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Such research is justified in Vale do São Francisco, since in addition to producing many different grape varieties it has particular cultivation conditions that could potentiate some compounds. Thus the objective of the present study was to characterize the chemical compounds contents in the different byproducts generated during winemaking using different grape (*Vitis vinifera* L.) varieties cultivated in Vale do São Francisco.

## 2 Materials and methods

### 2.1 Experimental material and treatments

The plant materials used in this study were provided by wineries located in Vale do São Francisco, Brazil. All the companies work with different varieties, including white and red fine grapes for the elaboration of red, white and sparkling wines. The byproducts and fresh grapes were collected in the years 2012 and 2013, during the regular working period of the wineries, separating them by variety, when possible, according to availability throughout the year. So as to preserve their identity, the wineries were denominated as w1, w2, w3 and w4.

The region presented an average annual temperature of 27 °C in 2012/13, with a relative humidity of 56% and rainfall of 227.5 mm (Empresa Brasileira de Pesquisa Agropecuária, 2014).

The study used a completely randomized experimental design with four repetitions formed of ten bunches each for the fresh grapes and 500 g for the byproducts of each variety. The repetitions represented collections made at different moments (hours) of grape processing, so as to better characterize eventual variation that regularly occurs in the winemaking of a determined batch.

Two types of process were evaluated. The first corresponded to the production of red wines, in which the byproduct is generated after the maceration phase, start of alcoholic fermentation, removal from the vat and pressing. For this process the following varieties were studied: Tempranillo, Cabernet Sauvignon, Syrah and Alicante Bouschet, processed by winery w1; Syrah by winery w2; Tempranillo by winery w3; and Cabernet Sauvignon by winery w4. The second type was for the processing of white/sparkling wine, in which the byproduct is removed after pressing of the grapes and before alcoholic fermentation. For this type of process the following varieties were evaluated: Viognier, Chenin Blanc, Moscato Canelli, Italia and Arinto + Fernão Pires (these two varieties were processed together and hence the byproducts were also evaluated together, although the fresh grapes were evaluated separately), processed by winery w1; Tempranillo, Italia, 'Chenin Blanc, Grenache, Mourvèdre, Verdejo and Sauvignon Blanc, by winery w2; and Moscato Canelli and Chenin Blanc, by winery w4. The red grape varieties Tempranillo, Grenache and Mourvèdre were used to elaborate white/sparkling wines by winery w2, as part of its commercial strategy.

### 2.2 Grape characterization

Samples of the fresh grapes used in processing were collected, so as to qualify the raw material as a reference to evaluate the losses or preservation of chemical compounds of interest.

### 2.3 Sample preparation and variables evaluated

Fifty individual grapes were macerated and the musts obtained for the determination of titratable acidity, ascorbic acid content, soluble solids and total soluble sugars. Titratable acidity (g tartaric acid 100 mL<sup>-1</sup>) was determined by titration with 0.1 N NaOH (Association of Official Agricultural Chemists, 2010). The ascorbic acid content (mg ascorbic acid 100 g<sup>-1</sup>) was obtained by titration with 0.02% 2,6 dichloro-phenol indophenol (Strohecker & Henning, 1967). The soluble solids content (°Brix) was obtained by direct reading using a digital refractometer (ATAGO, model PAL-1 Digital Pocket Refractometer, USA) (Association of Official Agricultural Chemists, 2010). The total soluble sugars content (g 100 g<sup>-1</sup>) was determined using the anthrone reagent, reading at 620 nm in a spectrophotometer UV-Vis (Yemn & Willis, 1954).

The pectic compounds and protein contents were evaluated by previously estimating the proportions of skin and pulp of the grape varieties under study, simulating the edible part. This material was homogenized in a Turrax homogenizer.

The pectic compounds (g 100 g<sup>-1</sup>) were extracted according to McReady & MacComb (1952) and determined by colorimetry at 520 nm after the condensation reaction with m-hydroxydiphenyl (Blumenkrantz & Asboe-Hansen, 1973). The protein contents (mg g<sup>-1</sup>) were determined using the reagent Coomassie Brilliant Blue G-250, at 595 nm (Bradford, 1976).

The fresh weight of a bunch of grapes (g) was also determined from the mean value of weighing ten recently-harvested bunches using a semi-analytical balance (Acculab, model VI 2400, USA).

### 2.4 Byproduct characterization

After collecting the byproducts for each specific type of winemaking, they were placed in plastic bags, stored on ice in polystyrene boxes and transported to the laboratory, where the evaluations were carried out. The byproducts were separated into skins and seeds and characterized separately for each variety, with the exception of the 'Arinto' + 'Fernão Pires' grapes that were processed together.

### 2.5 Sample preparation and variables evaluated

The skin samples were homogenized in a Turrax homogenizer, whereas the seeds were macerated with the aid of a pestle and mortar in liquid nitrogen. The material was homogenized in distilled water or in extraction solution depending on the evaluation.

The variables evaluated were: titratable acidity and the contents of ascorbic acid, soluble solids, total soluble sugars, proteins and pectic compounds. The methods employed for each variable were the same as those used in the characterization of the grapes, making any necessary adjustments due to the characteristics of the sample.

The must yields and moisture contents (MC) of the fresh grapes and byproducts were determined in order to characterize and provide information about inferences associated with the variations in concentration of the compounds of interest (Table 1).

**Table 1.** Must yield and moisture content of the fresh grapes (FG) and of the skin (BySk) and seed (BySe) byproducts produced during winemaking in four wineries (w1, w2, w3, w4) in Vale do São Francisco, Brazil\*.

Variety	Must yield	Moisture content		
		FG	BySk	BySe
<i>Processing of red wines</i>				
Alicante Bouschet (w1)	68% ± 1.4	80% ± 0.4	59% ± 6.1	37% ± 1.6
Cabernet Sauvignon (w1)	71% ± 1.5	79% ± 0.6	54% ± 2.5	36% ± 1.1
Cabernet Sauvignon (w4)	70% ± 2.2	82% ± 0.9	66% ± 1.0	37% ± 3.4
Syrah (w1)	65% ± 1.2	81% ± 1.2	65% ± 2.2	22% ± 1.1
Syrah (w2)	71% ± 1.8	79% ± 1.6	51% ± 5.8	33% ± 0.9
Tempranillo (w1)	72% ± 0.6	80% ± 0.2	54% ± 5.6	40% ± 2.5
Tempranillo (w3)	75% ± 1.2	82% ± 0.6	65% ± 2.4	34% ± 1.5
<i>Processing of white/sparkling wines</i>				
Arinto	65% ± 0.7	83% ± 0.3	69% ± 0.4	31% ± 1.3
Fernão Pires (w1)**	72% ± 2.0	80% ± 0.4		
Chenin Blanc (w1)	73% ± 1.2	80% ± 0.2	60% ± 2.4	19% ± 2.5
Chenin Blanc (w2)	73% ± 0.5	83% ± 0.2	61% ± 1.1	22% ± 2.5
Chenin Blanc (w4)	74% ± 2.1	79% ± 1.1	66% ± 1.5	28% ± 2.4
Grenache (w2)	70% ± 0.6	82% ± 0.6	59% ± 3.7	29% ± 2.9
Italia (w1)	74% ± 4.4	81% ± 1.4	70% ± 2.0	38% ± 1.8
Italia (w2)	70% ± 2.7	82% ± 0.3	66% ± 8.4	39% ± 1.6
Moscato Canelli (w1)	70% ± 0.9	83% ± 0.5	61% ± 0.7	27% ± 0.7
Moscato Canelli (w4)	68% ± 2.3	82% ± 0.3	65% ± 0.4	26% ± 2.8
Mourvèdre (w2)	75% ± 1.5	81% ± 0.4	63% ± 9.9	32% ± 2.6
Sauvignon Blanc (w2)	76% ± 1.2	80% ± 0.4	49% ± 3.1	20% ± 2.5
Tempranillo (w2)	75% ± 2.1	79% ± 0.3	52% ± 2.3	26% ± 2.3
Verdejo (w2)	74% ± 2.0	80% ± 1.6	54% ± 2.0	22% ± 2.4
Viognier (w1)	73% ± 1.6	82% ± 1.5	63% ± 0.9	29% ± 1.4

\*Results are expressed as mean values ± standard deviation (n = 4); \*\*The varieties Arinto and Fernão Pires (w1) were processed together; w = winery.

## 2.6 Statistical analysis

The data were submitted to an analysis of variance for each type of sample (fresh grapes and the skin and seed byproducts) and for each type of processing (red wine and white/sparkling wine), the means being compared by Tukey's test ( $p < 0.05$ ), using Sisvar 4.3 software.

## 3 Results and discussion

Although the weight of the bunches of grapes was not of importance in processing, it was determined with the purpose of differentiating the varieties studied. The 'Italia' grapes, that is one of the varieties cultivated in Vale do São Francisco for the elaboration of sparkling muscatels, showed the highest mean values (Table 2). It stands out from the others because of the naturally larger size of the individual berries since it is mainly used as a table grape.

For processing aimed at the elaboration of white/sparkling wines, the titratable acidity (TA) of the skin byproduct varied

from 0.99 g tartaric acid 100 mL<sup>-1</sup> for Italia variety produced by w1 to 2.73 g tartaric acid 100 mL<sup>-1</sup> for Viognier variety (Table 2). There is a loss of liquid mass from the grapes during winemaking which can result in concentration of some compounds in the byproducts obtained. A greater must yield from the grapes can also help explain the concentration of some compounds in the byproducts. For example, skin byproducts of Viognier and Sauvignon Blanc varieties had the highest values for TA and must yields (Table 1). It is proposed the use of those byproducts for tartaric acid manufacturing.

In the elaboration of red wines, the variation in TA was from 1.22 to 4.61 g tartaric acid 100 mL<sup>-1</sup>, these values being registered for the same variety (Syrah), but produced by wineries w1 and w2, respectively (Table 2). The values for TA did not vary between the 'Syrah' skin byproduct processed by winery w3, 'Tempranillo' skin byproducts processed by wineries w1 and w3 and 'Cabernet Sauvignon' skin byproducts processed by w1 and w4. Due to the processing characteristics, the skins removed after maceration and the start of alcoholic fermentation generally presented higher values for acidity. In this type of fermentation, in addition to the predominant acids in the mature grapes, succinic, lactic and acetic acids are also present in the red wines. Others acids as gluconic acid can be found in small quantities resulting from vinification procedures or bacterial attack (Conde et al., 2007). These acids can be present adhered to the skins, increasing the titratable acidity, as observed in the byproducts of the varieties studied.

According to the literature, the values found for TA in the present study were evidence that under semi-arid conditions, the raw material and processing attend the requisites necessary to obtain balanced wines with fine flavor and good taste intensity, as shown by the fresh grapes destined for the production of sparkling wines, whose maximum values for TA were close to 1 g tartaric acid 100 mL<sup>-1</sup> (Gatti et al., 2015; Panceri et al., 2013).

The TA of grape seed byproduct is relatively low, the seed byproduct being considered as a source of other compounds, essentially phenolic such as catechin, epicatechin, epicatechin-3-O-gallate, gallic acid and quercetin (Durante et al., 2017). The highest TA found in the seed byproduct was 2.50 g tartaric acid 100 mL<sup>-1</sup>, found for the 'Syrah' grapes cultivated and used in winemaking by winery w2 (Table 2). This value was also higher than that of the seed byproducts obtained in the production of white/sparkling wines.

The ascorbic acid (AA) content was relatively high in all the grape varieties studied (Table 2) when compared to table grapes as Crimson Seedless, the latter showing contents of about 20 mg ascorbic acid 100 g<sup>-1</sup> (Serrano et al., 2006). The 'Tempranillo' fresh grape showed an AA content of 50.78 mg 100 g<sup>-1</sup> and did not differ statistically from the 'Alicante Bouschet' grapes, both produced by winery w1 and used in the elaboration of red wines. These grapes presented a MC of about 80% (Table 1). Information concerning the relative MC of the fresh grapes used in processing and of the byproducts allows one to estimate the contents of a given compound, so long as it does not undergo degradation or synthesis during winemaking. For the other type of processing, the 'Tempranillo' grapes produced by winery

**Table 2.** Fresh weights of the bunches (FWB), titratable acidity (TA), ascorbic acid (AA) content and soluble solids (SS) content of the fresh grapes (FG) and of the skin (BySk) and seed (BySe) byproducts produced during the making of red and white/sparkling wines in Vale do São Francisco, Brazil, 2012/2013\*.

Variety	FWB	TA (g 100 mL <sup>-1</sup> )			AA (mg 100 g <sup>-1</sup> )			SS (°Brix)		
		FG	BySk	BySe	FG	BySk	BySe	FG	BySk	BySe
<i>Processing of red wines</i>										
Alicante Bouschet (w1)	137.33 <sup>d</sup>	0.61 <sup>b</sup>	3.75 <sup>b</sup>	0.63 <sup>d</sup>	41.67 <sup>ab</sup>	83.23 <sup>a</sup>	46.33 <sup>b</sup>	23.4 <sup>cd</sup>	7.7 <sup>d</sup>	5.3 <sup>cd</sup>
Cabernet Sauvignon (w1)	92.10 <sup>e</sup>	0.45 <sup>c</sup>	4.48 <sup>a</sup>	0.71 <sup>cd</sup>	36.46 <sup>bc</sup>	67.62 <sup>bc</sup>	42.81 <sup>b</sup>	25.8 <sup>a</sup>	7.4 <sup>d</sup>	6.0 <sup>c</sup>
Cabernet Sauvignon (w4)	94.58 <sup>e</sup>	0.94 <sup>a</sup>	2.50 <sup>c</sup>	0.88 <sup>bc</sup>	37.76 <sup>bc</sup>	71.29 <sup>abc</sup>	60.08 <sup>a</sup>	20.4 <sup>f</sup>	8.8 <sup>d</sup>	8.1 <sup>b</sup>
Syrah (w1)	217.14 <sup>ab</sup>	0.38 <sup>c</sup>	1.22 <sup>d</sup>	0.66 <sup>d</sup>	36.46 <sup>bc</sup>	83.19 <sup>a</sup>	44.81 <sup>b</sup>	20.7 <sup>ef</sup>	25.7 <sup>a</sup>	10.7 <sup>a</sup>
Syrah (w2)	169.57 <sup>cd</sup>	0.66 <sup>b</sup>	4.61 <sup>a</sup>	2.50 <sup>a</sup>	28.65 <sup>c</sup>	59.81 <sup>cd</sup>	48.08 <sup>b</sup>	25.5 <sup>ab</sup>	15.8 <sup>b</sup>	7.1 <sup>b</sup>
Tempranillo (w1)	182.36 <sup>bc</sup>	0.98 <sup>a</sup>	4.02 <sup>ab</sup>	0.63 <sup>d</sup>	50.78 <sup>a</sup>	46.79 <sup>d</sup>	51.71 <sup>ab</sup>	23.9 <sup>bc</sup>	7.3 <sup>d</sup>	4.9 <sup>d</sup>
Tempranillo (w3)	232.53 <sup>a</sup>	0.45 <sup>c</sup>	2.52 <sup>c</sup>	0.95 <sup>b</sup>	33.86 <sup>bc</sup>	77.93 <sup>ab</sup>	62.37 <sup>a</sup>	22.1 <sup>ed</sup>	12.2 <sup>c</sup>	10.7 <sup>a</sup>
<i>Processing of white/sparkling wines</i>										
Arinto (w1)	215.33 <sup>c</sup>	1.30 <sup>a</sup>	1.53 <sup>cd</sup>	0.70 <sup>de</sup>	29.95 <sup>cd</sup>	71.25 <sup>ab</sup>	60.17 <sup>a</sup>	20.6 <sup>abc</sup>	16.2 <sup>bc</sup>	10.4 <sup>ef</sup>
Fernão Pires (w1)**	150.0 <sup>def</sup>	0.79 <sup>de</sup>			31.25 <sup>cd</sup>			19.0 <sup>abc</sup>		
Chenin Blanc (w1)	97.64 <sup>f</sup>	0.74 <sup>de</sup>	1.64 <sup>bcd</sup>	0.65 <sup>de</sup>	29.95 <sup>cd</sup>	57.24 <sup>bcd</sup>	48.15 <sup>b</sup>	22.3 <sup>abc</sup>	19.4 <sup>b</sup>	9.4 <sup>f</sup>
Chenin Blanc (w2)	154.06 <sup>de</sup>	1.15 <sup>b</sup>	1.66 <sup>bcd</sup>	0.72 <sup>de</sup>	36.46 <sup>bcd</sup>	51.94 <sup>cd</sup>	57.11 <sup>ab</sup>	19.6 <sup>abc</sup>	16.8 <sup>bc</sup>	10.7 <sup>ef</sup>
Chenin Blanc (w4)	194.69 <sup>cd</sup>	0.82 <sup>cd</sup>	1.46 <sup>d</sup>	0.65 <sup>ef</sup>	29.95 <sup>cd</sup>	71.20 <sup>ab</sup>	53.43 <sup>ab</sup>	21.1 <sup>abc</sup>	24.1 <sup>a</sup>	14.1 <sup>b</sup>
Grenache (w2)	179.21 <sup>cd</sup>	0.60 <sup>fgh</sup>	1.25 <sup>de</sup>	0.83 <sup>abc</sup>	28.65 <sup>d</sup>	51.98 <sup>cd</sup>	55.23 <sup>ab</sup>	21.5 <sup>abc</sup>	18.0 <sup>b</sup>	12.2 <sup>cd</sup>
Italia (w1)	455.82 <sup>a</sup>	0.58 <sup>fgh</sup>	0.99 <sup>e</sup>	0.84 <sup>abc</sup>	31.25 <sup>cd</sup>	60.30 <sup>abc</sup>	48.06 <sup>b</sup>	17.2 <sup>bc</sup>	19.7 <sup>b</sup>	16.3 <sup>a</sup>
Italia (w2)	388.77 <sup>b</sup>	0.70 <sup>ef</sup>	1.23 <sup>de</sup>	0.90 <sup>a</sup>	28.65 <sup>d</sup>	65.99 <sup>abc</sup>	49.86 <sup>ab</sup>	16.2 <sup>c</sup>	13.8 <sup>c</sup>	14.3 <sup>b</sup>
Moscato Canelli (w1)	96.15 <sup>f</sup>	0.73 <sup>de</sup>	1.60 <sup>bcd</sup>	0.81 <sup>abcd</sup>	28.65 <sup>d</sup>	51.98 <sup>cdab</sup>	49.93 <sup>ab</sup>	19.7 <sup>abc</sup>	8.2 <sup>d</sup>	10.5 <sup>ef</sup>
Moscato Canelli (w4)	157.36 <sup>de</sup>	0.75 <sup>de</sup>	1.51 <sup>d</sup>	0.85 <sup>ab</sup>	40.37 <sup>abc</sup>	71.20 <sup>ab</sup>	55.67 <sup>ab</sup>	21.3 <sup>abc</sup>	25.9 <sup>a</sup>	13.3 <sup>bc</sup>
Mourvèdre (w2)	154.30 <sup>de</sup>	0.57 <sup>gh</sup>	1.48 <sup>d</sup>	0.81 <sup>abcd</sup>	28.65 <sup>d</sup>	41.23 <sup>d</sup>	57.02 <sup>ab</sup>	18.7 <sup>abc</sup>	9.0 <sup>d</sup>	13.8 <sup>b</sup>
Sauvignon Blanc (w2)	114.70 <sup>ef</sup>	0.92 <sup>c</sup>	2.62 <sup>a</sup>	0.77 <sup>bcd</sup>	39.07 <sup>abcd</sup>	71.30 <sup>ab</sup>	53.43 <sup>ab</sup>	23.5 <sup>ab</sup>	23.9 <sup>a</sup>	11.2 <sup>de</sup>
Tempranillo (w2)	220.15 <sup>c</sup>	0.54 <sup>h</sup>	1.97 <sup>bc</sup>	0.77 <sup>bcd</sup>	49.48 <sup>a</sup>	75.29 <sup>a</sup>	57.00 <sup>ab</sup>	25.0 <sup>a</sup>	19.0 <sup>b</sup>	10.3 <sup>ef</sup>
Verdejo (w2)	98.17 <sup>f</sup>	0.68 <sup>efg</sup>	2.01 <sup>b</sup>	0.67 <sup>ef</sup>	31.90 <sup>cd</sup>	66.85 <sup>abc</sup>	55.62 <sup>ab</sup>	17.3 <sup>bc</sup>	26.4 <sup>a</sup>	14.0 <sup>b</sup>
Viognier (w1)	143.47 <sup>def</sup>	1.06 <sup>b</sup>	2.73 <sup>a</sup>	0.56 <sup>f</sup>	42.97 <sup>ab</sup>	41.60 <sup>d</sup>	60.14 <sup>a</sup>	17.9 <sup>bc</sup>	7.7 <sup>d</sup>	5.7 <sup>g</sup>

\*Averages followed by the same letter in column do not differ, for each winemaking processes separately, by Tukey's test ( $p \leq 0.05$ ); \*\*The varieties Arinto and Fernão Pires (w1) were processed together; w = winery.

w2 showed a high AA content (49.48 mg 100 g<sup>-1</sup>), which did not differ from the other three varieties (Tables 1 and 2).

The AA contents were relatively high in the byproducts evaluated in the present study, reaching 83.23 mg 100 g<sup>-1</sup>, in the skin byproduct of the 'Alicante Bouschet' grapes, which showed a MC of 59% and came from w1, and 62.37 mg 100 g<sup>-1</sup>, in the seed byproduct of the 'Tempranillo' grapes, characterized by a MC of 34% and coming from winery w3 (Tables 1 and 2). Independent of the type of process, the elaboration of wines did not promote ascorbic acid degradation, which would lead to losses that would depreciate the value of the byproduct obtained. In the present study, the AA contents of the grape skin and seed byproducts suggested association as byproducts with functional properties. In a study carried out with agroindustrial byproducts from acerola (*Malpighia emarginata* DC), jambolan (*Syzygium cumini*), umbu-caja (*Spondias mombin* × *Spondias tuberosa*) and pitanga (*Eugenia uniflora*) cherries, the respective AA contents were 2748.03; 62.21; 24.77 and 17.03 mg 100 g<sup>-1</sup>, justifying their indication as promising natural ingredients for the manufacture of nutraceutical foods (Correia et al., 2012). A comparison of the values informed by these authors with those obtained in the present study, suggests that the skin and seed grape byproducts could be potential vitamin C sources if analyzed in relation to those of jambolan, umbu-caja and pitanga cherries.

Considering the processing, it is known that orange juice has high vitamin C contents. According to a study carried out by Burdurlu et al. (2006), orange juices showed AA contents of 52.4 mg 100 g<sup>-1</sup> after eight weeks of storage at 37 °C, whilst grape juice presented a content of 55.5 mg 100 g<sup>-1</sup> under the same conditions. Even when recognizing that the products and byproducts of processing present distinct characteristics, the AA contents observed in the byproducts studied in this work are relatively high, and should be made better use of. Providing an antioxidant protection for some biological systems could be an example of using AA contents preserved in byproducts.

The majority of the skin byproducts showed low soluble solids (SS) contents, especially those generated during the production of red wines (Table 2). The skin byproducts obtained of winemaking for red wines from Syrah variety were an exception. The processing using the others varieties also generated skin byproducts with the lowest total soluble sugar (TSS) contents, the major constituent of SS (Table 3).

Sugar is the raw material to produce alcohol in the wines (Conde et al., 2007), which justifies the low TSS percentages in the skin byproducts, principally when compared with the corresponding fresh grapes. González-Centeno et al. (2010) highlighted the decrease in TSS contents in the winemaking byproducts of three varieties. The authors registered that TSS content

**Table 3.** Total soluble sugars (TSS), pectic compounds (PEC) and protein (PROT) contents of the fresh grapes (FG) and of the skin (BySk) and seed (BySe) byproducts produced during the making of red and white/sparkling wines in Vale do São Francisco, Brazil, 2012/2013\*.

Variety	TSS (g 100 g <sup>-1</sup> )			PEC (g 100 g <sup>-1</sup> )			PROT (mg g <sup>-1</sup> )		
	FG	BySk	BySe	FG	BySk	BySe	FG	BySk	BySe
<i>Processing of red wines</i>									
Alicante Bouschet (w1)	19.47 <sup>cd</sup>	0.47 <sup>de</sup>	1.94 <sup>d</sup>	0.18 <sup>ab</sup>	1.59 <sup>a</sup>	0.35 <sup>d</sup>	0.30 <sup>a</sup>	0.20 <sup>c</sup>	3.25 <sup>d</sup>
Cabernet Sauvignon (w1)	23.35 <sup>a</sup>	0.29 <sup>e</sup>	1.59 <sup>de</sup>	0.12 <sup>c</sup>	1.31 <sup>b</sup>	0.36 <sup>d</sup>	0.20 <sup>bc</sup>	0.45 <sup>a</sup>	3.47 <sup>cd</sup>
Cabernet Sauvignon (w4)	19.42 <sup>cd</sup>	1.01 <sup>cd</sup>	3.37 <sup>bc</sup>	0.17 <sup>abc</sup>	0.44 <sup>c</sup>	1.05 <sup>a</sup>	0.18 <sup>c</sup>	0.30 <sup>b</sup>	6.38 <sup>a</sup>
Syrah (w1)	17.35 <sup>d</sup>	7.43 <sup>a</sup>	3.91 <sup>b</sup>	0.14 <sup>bc</sup>	1.13 <sup>b</sup>	0.59 <sup>b</sup>	0.18 <sup>c</sup>	0.40 <sup>a</sup>	5.93 <sup>ab</sup>
Syrah (w2)	22.04 <sup>ab</sup>	2.65 <sup>b</sup>	3.11 <sup>c</sup>	0.19 <sup>ab</sup>	1.21 <sup>b</sup>	0.39 <sup>cd</sup>	0.25 <sup>abc</sup>	0.45 <sup>a</sup>	2.95 <sup>d</sup>
Tempranillo (w1)	21.45 <sup>abc</sup>	0.30 <sup>e</sup>	1.26 <sup>e</sup>	0.12 <sup>c</sup>	0.59 <sup>c</sup>	0.26 <sup>d</sup>	0.20 <sup>bc</sup>	0.20 <sup>c</sup>	3.95 <sup>c</sup>
Tempranillo (w3)	20.18 <sup>bc</sup>	1.59 <sup>c</sup>	6.05 <sup>a</sup>	0.21 <sup>a</sup>	0.64 <sup>c</sup>	0.53 <sup>bc</sup>	0.28 <sup>ab</sup>	0.30 <sup>b</sup>	5.48 <sup>b</sup>
<i>Processing of white/sparkling wines</i>									
Arinto (w1)	18.15 <sup>cd</sup>	4.49 <sup>ef</sup>	4.14 <sup>ef</sup>	0.11 <sup>de</sup>	0.94 <sup>c</sup>	0.66 <sup>de</sup>	0.10 <sup>c</sup>	0.30 <sup>cde</sup>	8.58 <sup>abc</sup>
Fernão Pires (w1)**	16.93 <sup>e</sup>			0.11 <sup>de</sup>			0.10 <sup>c</sup>		
Chenin Blanc (w1)	16.93 <sup>e</sup>	5.58 <sup>cde</sup>	3.23 <sup>fg</sup>	0.11 <sup>de</sup>	0.96 <sup>c</sup>	0.66 <sup>de</sup>	0.20 <sup>b</sup>	0.23 <sup>ef</sup>	7.18 <sup>ef</sup>
Chenin Blanc (w2)	17.98 <sup>de</sup>	4.1 <sup>f</sup>	5.28 <sup>de</sup>	0.14 <sup>bcd</sup>	0.97 <sup>c</sup>	0.71 <sup>de</sup>	0.13 <sup>bc</sup>	0.30 <sup>cde</sup>	9.13 <sup>a</sup>
Chenin Blanc (w4)	20.09 <sup>c</sup>	7.47 <sup>ab</sup>	7.01 <sup>b</sup>	0.18 <sup>ab</sup>	0.58 <sup>d</sup>	1.13 <sup>ab</sup>	0.10 <sup>c</sup>	0.30 <sup>cde</sup>	8.95 <sup>ab</sup>
Grenache (w2)	19.57 <sup>cd</sup>	4.87 <sup>def</sup>	3.10 <sup>fg</sup>	0.13 <sup>bcd</sup>	0.88 <sup>c</sup>	0.78 <sup>cde</sup>	0.18 <sup>bc</sup>	0.30 <sup>cde</sup>	8.50 <sup>abc</sup>
Italia (w1)	14.90 <sup>fg</sup>	6.00 <sup>cd</sup>	5.84 <sup>cd</sup>	0.12 <sup>cde</sup>	0.94 <sup>c</sup>	0.86 <sup>cd</sup>	0.10 <sup>c</sup>	0.30 <sup>cde</sup>	6.63 <sup>f</sup>
Italia (w2)	13.61 <sup>g</sup>	4.01 <sup>f</sup>	6.64 <sup>bc</sup>	0.11 <sup>de</sup>	0.89 <sup>c</sup>	0.60 <sup>ef</sup>	0.10 <sup>c</sup>	0.33 <sup>bcd</sup>	8.85 <sup>ab</sup>
Moscato Canelli (w1)	18.48 <sup>cde</sup>	0.86 <sup>g</sup>	3.58 <sup>fg</sup>	0.13 <sup>cde</sup>	1.30 <sup>b</sup>	0.67 <sup>de</sup>	0.13 <sup>bc</sup>	0.25 <sup>def</sup>	8.93 <sup>ab</sup>
Moscato Canelli (w4)	20.15 <sup>bc</sup>	7.97 <sup>a</sup>	6.98 <sup>b</sup>	0.17 <sup>abc</sup>	0.56 <sup>d</sup>	1.35 <sup>a</sup>	0.13 <sup>bc</sup>	0.28 <sup>cdef</sup>	7.95 <sup>cd</sup>
Mourvèdre (w2)	17.82 <sup>cd</sup>	0.73 <sup>g</sup>	8.48 <sup>a</sup>	0.14 <sup>bcd</sup>	0.91 <sup>c</sup>	1.02 <sup>bc</sup>	0.20 <sup>b</sup>	0.30 <sup>cde</sup>	9.08 <sup>ab</sup>
Sauvignon Blanc (w2)	21.90 <sup>ab</sup>	6.51 <sup>bc</sup>	5.25 <sup>de</sup>	0.11 <sup>de</sup>	1.28 <sup>b</sup>	0.72 <sup>de</sup>	0.18 <sup>bc</sup>	0.40 <sup>b</sup>	7.48 <sup>de</sup>
Tempranillo (w2)	22.01 <sup>a</sup>	4.08 <sup>f</sup>	4.46 <sup>d</sup>	0.19 <sup>a</sup>	1.56 <sup>a</sup>	0.67 <sup>de</sup>	0.30 <sup>a</sup>	0.60 <sup>a</sup>	7.60 <sup>de</sup>
Verdejo (w2)	20.16 <sup>bc</sup>	8.13 <sup>a</sup>	5.60 <sup>cd</sup>	0.12 <sup>cde</sup>	1.27 <sup>b</sup>	0.71 <sup>bc</sup>	0.15 <sup>bc</sup>	0.35 <sup>bc</sup>	8.38 <sup>bc</sup>
Viognier (w1)	16.70 <sup>ef</sup>	0.41 <sup>g</sup>	2.53 <sup>g</sup>	0.09 <sup>e</sup>	0.97 <sup>c</sup>	0.39 <sup>f</sup>	0.10 <sup>c</sup>	0.20 <sup>f</sup>	4.10 <sup>g</sup>

\*Averages followed by the same letter in column do not differ, for each winemaking processes separately, by Tukey's test ( $p \leq 0.05$ ); \*\*The varieties Arinto and Fernão Pires (w1) were processed together; w = winery.

of 'Cabernet Sauvignon' grapes was 15.6 g 100 g<sup>-1</sup> and it was reduced to 2.3 g 100 g<sup>-1</sup> in the byproducts. The TSS contents of 'Tempranillo' grapes and byproducts were 15.4 and 2.0 g 100 g<sup>-1</sup>, respectively, whereas the corresponding values for 'Syrah' were 14.4 and 2.1 g 100 g<sup>-1</sup>.

SS contents above 23.0 °Brix in the skin byproducts of some varieties, such as in the 'Verdejo' and 'Sauvignon Blanc' varieties of winery w2, and 'Moscato Canelli' and 'Chenin Blanc' of winery w4, generally correspond to those formed after pressing of the grapes (with reference to the elaboration of white/sparkling wines), as shown in Table 2. Since this byproduct is generated before alcoholic fermentation, the sugars are more easily preserved.

The SS contents of the seed byproducts varied from 5.7 to 16.3 °Brix for the varieties Viognier and Italia produced by winery w1 and processed for white/sparkling wines (Table 2). The SS contents of the seed byproducts of the varieties Tempranillo and Syrah, also produced by winery w1, but destined for red wines, varied from 4.9 to 10.7 °Brix. Since the seeds remained intact after processing, the majority of the chemical contents were maintained.

The highest TSS contents of the seed byproduct of the variety Mourvèdre was 8.48 g 100 g<sup>-1</sup>, and of the variety Tempranillo was 6.05 g 100 g<sup>-1</sup>, for the grapes used by winery w3 for both types of processing (Table 3). There is little information about

the percentages of acids and sugars present in the seeds of winemaking byproducts. Therefore, the present study is inserting these two types of compounds so as to provide subsidies for a more ample analysis aimed at the use of winemaking byproducts as components in human feeding.

At high environmental temperatures, such as those in Vale do São Francisco, Brazil, one can expect a greater accumulation of SS and TSS in the grapes (Gatti et al., 2015). For fresh grapes destined for the production of red wines, the 'Cabernet Sauvignon' produced by winery w1 reached a SS content of 25.8 °Brix, and the 'Syrah' of winery w2 reached 25.4 °Brix (Table 2). For grapes destined for the production of white/sparkling wines, the 'Tempranillo' of winery w2 presented a SS content of 25.0 °Brix.

This information is ratified when one compares the values found in the present study with others carried out under subtropical conditions or in a temperate climate. According to Gris et al. (2010), the SS of fresh grapes from 'Syrah' vines, produced in the state of Paraná, was 20.4 °Brix. The following year the content was 18.4 °Brix. In high altitude regions in the south of the state of Minas Gerais, the 'Cabernet Sauvignon' grapes presented SS contents of 21 °Brix, approximately, during the autumn-winter cycle (Souza et al., 2015).

Processing cultivars with high sugars concentrations can potentiate their contents in winemaking byproducts.

And byproducts with this characteristic could be useful to support fermentative processes supplying the carbohydrates for the growth of microorganisms (Alcântara et al., 2012). In addition, different SS values in byproducts may be required for use as food additives.

Besides large amounts of simple (as fructose and glucose) and storage (sucrose, starch, etc.) carbohydrates, the cell wall structural one (cellulose, hemicellulose and pectins) are potentially useful for human food supplementation and/or bioenergy production (Durante et al., 2017). Particularly, pectin quantification provides information about the physical properties of the tissues that could influence the efficiency of the initial steps of grape processing, when the release of the bagasse and rupture of the grapes are fundamental for the liberation or extraction of the must.

In the red wine processing byproducts, the greatest pectic compound contents were 1.59 g 100 g<sup>-1</sup> for the skin byproduct of 'Alicante Bouschet' and 1.05 g 100 g<sup>-1</sup> for the seed byproduct of 'Cabernet Sauvignon' produced by winery w4 (Table 3). The skin byproducts from the 'Alicante Bouschet' grape had a MC of only 59% and those from 'Cabernet Sauvignon' were 66% (w4), whereas the MC of seed byproducts of both were 37% (Table 1). The fresh grapes of the varieties Alicante Bouschet and Cabernet Sauvignon (w4) showed MC of 80% and 82%, respectively (Table 1). The reduced amount of water in the byproducts justifies the concentration of the chemical compounds. For the skin byproducts obtained during white/sparkling winemaking, the pectic compound contents of the variety Tempranillo, cultivated and processed by winery w2, stood out (Table 3), whereas for the seed byproducts, the largest pectic compound contents were 1.35 and 1.13 g 100 g<sup>-1</sup> for the 'Moscato Canelli' and 'Chenin Blanc' grapes, both processed by winery w4.

Considering the cell wall structural carbohydrates, Lavelli et al. (2017a) proposed the grape skin as a fiber source and its use as ingredient could represent an opportunity to develop value-added products.

In making use of the byproducts, the protein (PROT) contents can also be treated as differential. The PROT contents of the fresh grapes were not high (Table 3), with reports in the literature of 0.5 mg g<sup>-1</sup>, as observed for the fresh consumption variety Crimson Seedless, evaluated for three years in Spain under semi-arid conditions (López-Miranda et al., 2011).

In the elaboration of red wines, the PROT content of the skin byproducts varied from 0.20 to 0.45 mg g<sup>-1</sup> for 'Alicante Bouschet' and 'Cabernet Sauvignon' grapes produced by winery w1 as also 'Syrah' from w2 and 'Cabernet Sauvignon' from w4 (Table 3). Hence, this type of byproduct was more appropriate for use in inserting proteins into another food base, for example.

The skin byproduct of the variety Tempranillo stood out in the other winemaking process (Table 3). However, seven varieties presented higher contents for their seed byproducts, including 'Chenin Blanc' from winery w2, which showed a PROT content of 9.13 mg g<sup>-1</sup> with a MC of only 22%, one of the lowest values observed (Table 1). These values indicate a high potential use, when compared with values obtained from other fruits. For example, studies by Silva et al. (2014) reported PROT

contents in the byproducts (skin + seeds) in the depulping of jaboticaba (*Myrciaria cauliflora*) of only 0.2 mg g<sup>-1</sup>.

During this study the differences found for the same varieties when collected from different wineries can be explained by the cultivation conditions and by the differential definition of the harvesting time, based on the type of processing intended by each winery. These conditions are determinant for the grape quality, and consequently for the product elaborated, as also for the byproducts produced during the process. For their part, these byproducts also suffer the influence of the processing they are submitted to. Knowledge of the characteristics of the fresh grapes allows one to establish more appropriate links with the byproduct samples, preventing the proposition of inferences based only on genetic differences amongst the varieties.

This study represents a characterization to support the following steps. It gives backing to the use of grape byproducts, giving attention to the differences between varieties and types of process, which can result in different potentials for use.

#### 4 Conclusions

The contents of the compounds related to quality were not uniform for the same variety and same type of winemaking, requiring differential ways of using the byproducts in other economic activities for each winery.

In the process of elaborating white/sparkling wines, the skin byproducts from the Tempranillo variety presented relatively high ascorbic acid, pectic compound and protein contents, representing an opportunity for industrial use, especially in foods. Other varieties stood out with respect to their seed byproducts, with high contents of some specific compound. In the elaboration of red wines, the skin byproducts of the Syrah variety, produced and used to winemaking by winery w1, were characterized by large amounts of ascorbic acid, soluble solids and sugars and also of proteins. The seed byproducts resulting from the elaboration of red wines showing greater possibilities for use were those from the Syrah variety processed by winery w1, and from the Tempranillo variety by w3.

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