

Mineral analysis, anthocyanins and phenolic compounds in wine residues flour

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Abstract. This study analyzed the mineral content (N, P, K, S, Ca, Fe, Mg, Mn, Fe and Zn), anthocyanins and phenolic compounds in flours produced from residues of different grape cultivars from the wineries in the Southern region of Brazil. Mineral analysis showed a significant difference for all grape cultivar, with the exception for phosphorus content. Residues from cv. Seibel showed higher levels of N, Cu and Mg. The cultivars Ancelotta, Tanat and Bordô present higher contents of K, Zn, Mn, Fe and Ca. For the concentration of anthocyanins, cultivars Cabernet Sauvignon (114.7 mg / 100g), Tannat (88.5 mg / 100 g) and Ancelotta (33.8 mg/100 g) had the highest concentrations. The cultivars Pinot Noir (7.0 g AGE / 100 g), Tannat (4.3 g AGE / 100 g), and Ancelotta (3.9 g AGE / 100 g) had the highest content of phenolic compounds. Considering these results, it became evident the potential of using the residue of winemaking to produce flour for human consumption, highlighting the grapes 'Tannat' and 'Ancelotta'.

1. Introduction

Brazil is a country with an important wine industry, generating significant quantities of grape pomace. Currently, there is a growing interest in the exploitation of waste generated by the wine industry (Arvanitoyannis et al., 2006) [1]. The wine by-products are characterized as the pomace, which consists mainly of seeds and grape skins (Silva, 2003) [2].

The most part of this pomace are discarded, although having a high content of fiber, antioxidants and other substances that could be important to use as food for human consumption. One of the best applications of the pomace is the elaboration of grape flour, which could be used in the preparation of biscuits, bread, cereal bars, homemade pasta, vitamins and juices. This flour has a high fiber content as well as high amounts of flavonoids, anthocyanins, aromatic substances, acids and tannins and microorganisms, which are responsible for the fermentation of the must (Karakaya et al., 2001) [3].

These flours can be used in cooking practice (Perin, 2011) [4] and have considerable nutritional values, highlighting the significant amount of fiber, minerals, phenolic compounds and anthocyanins, and therefore exhibits a significant antioxidant potential, as the processing of this drink does not remove all the bioactive compounds.

In this context, this trial aimed to verify the differences in the content of the flour obtained from pomace generated by the winery industry of different grape cultivars, considering their potential for human consumption.

2. Material and methods

2.1. Preparation of flour

Flours were produced from pomace of nine grape cultivars (Bordô, Seibel, Malbec, Merlot, Ancelotta, Pinot Noir, Tannat, Cabernet Sauvignon and Cabernet Franc) obtained in two wineries, one located in Bituruna (Paraná State, Brazil) and other in Água Doce (Santa Catarina State, Brazil). Samples were collected soon after opening the fermentation tanks. They were dried in an oven with circulation and air exchange (Solab Co., Brazil) at 55 °C until the moisture of 14% w/w suited for the production of grape waste flour. After, the samples remained at room temperature (22 °C) to full cooling. Then, the peels and seeds were ground in a mill rotor (Marconi Co., Brazil) until obtaining grapes residues flour. This material was subjected to sieving in sieves type Tyler mesh with openings of 28 Tyler (Tamis[®], Brazil).

2.2. Mineral content analysis

Mineral content analysis (N, P, K, S, Ca, Fe, Mg, Mn, Fe and Zn) were performed according to the methodology described by Silva (2009) [5]. The N concentrations in flour were determined by digestion using sulfuric acid and semimicro – Kjeldahl method. After digestion in nitric perchloric acid, phosphorus (P) was determined by molecular absorption spectrophotometry, sulfur (S) by turbidimetry barium sulfate, potassium (K) by photometry flame emission and calcium (Ca) and magnesium (Mg), by atomic absorption spectrophotometry.

2.3. Content of anthocyanins

The analysis of the total content of anthocyanins was carried by the pH difference method (Giusti and Wrolstad 2001) [6], by means of potassium chloride buffer, pH 1.0 and sodium acetate buffer, pH 4.5.

2.4. Polyphenol contents

The total polyphenol content of each extract was valued spectrophotometrically according to the Folin-Ciocalteu method (Rossi & Singleton, 1965) [7], with the reading of the absorbances at 764 nm and the results expressed as equivalent grams of the gallic acid (GAE) per 100 g of dry extract.

2.5. Statistical analysis

The data were submitted to analysis of variance, and when significant, the means were compared by SNK test at 5% probability by SISVAR statistical program. All analyzes were performed in triplicate and the results presented as mean \pm standard deviation.

3. Results and discussion

3.1. Mineral content in the samples evaluated

Table 1 shows the mineral content in the analyzed flours, and there was no significant difference for phosphorus content between grape cultivars. The grapes 'Tannat', 'Ancellotta' and 'Bordô', stand out for the higher content of P, Zn, Mn and Fe Potassium. For N content, cultivars Seibel and Bordô showed the highest values. For Mg a higher content was verified in the grapes 'Ancellotta', 'Bordô', 'Pinot Noir', 'Seibel' and 'Cabernet Franc', significant superior to the cultivars Malbec, Seibel and Cabernet Sauvignon. Significantly higher levels of Ca were identified in the varieties Pinot Noir, Tannat, Ancellotta and Seibel. Souza et al (2014) [8], in a study of grape pomace flour of 'Benitaka' grapes grown in Pernambuco, semi-arid region of the Brazilian Northeast, identified lower rates of assessed minerals when compared to those obtained in the present study (Calcium 0.44 mg / 100 g, Magnesium 0.13 mg / 100 g, Potassium 1.40 mg / 100 g, Iron 18.08 mg / 100 g, Manganese 0.817 mg / 100 g, Phosphorus 0.183 mg / 100 g, Sulfur 0.089 mg / 100g, Zinc 0.98 mg / 100 g).

A justification for this difference between the mineral content would be the difference in the composition of the soil and climate of the growing regions. Elements such as the soil and weather factors, especially temperature, humidity and solar radiation, exert great influence on the development, production and grape quality. The climatic characteristics of the Brazilian wine industry are very specific and different from those found in most wine countries. This situation gives the product a set of features and its own typicality. This typicality is due largely to the climate effect follows also the wide range of cultivars used.

Grape wines have typical characteristics that vary from region to region in the Brazilian conditions. The state of Santa Catarina is characterized by a set of vineyards for the production of fine wines, which altitude vineyards are called, and located in cold regions. In the Northeast of Brazil, specially the States of Pernambuco and Bahia, is the

wine region of the San Francisco's Sub-Middle Valley. It is situated in an area of semi-arid tropical climate, between 09° and 10° South latitude. The viticultural climate of the region has intra-annual variability, which enables the production of grapes and wines throughout every month of the year.

The world viticulture destined for agribusiness is mainly concentrated between the latitudes 30 and 50° north and 30 and 45° South. The main occurring climates are temperate type of climate, Mediterranean type climates and with different levels of aridity. In Brazil types occurring climate in producing wine regions of fine wines with an annual harvest are temperate and subtropical (Embrapa Grape and Wine, 2003) [9]. Our results are similar to those obtained in the study of Rizzon and Miele (2012) [10] for Copper, Manganese and Magnesium. These authors evaluated grape juice samples from Bento Gonçalves – RS, Brazil, climate region and soil similar to those grown samples of this study, and which would justify a minor loss of these minerals in the products.

An adult has an average daily requirement of 8 to 18 mg Fe, 31 to 400 mg Mg, 700 mg P, Calcium 2500 mg, 4700 mg K. The data obtained in this study show that all cultivars have higher Fe content than the daily requirement for intake in 100 g of pomace flour (155 mg and 250 mg / 100 g). The contribution of minerals, copper, calcium, potassium, manganese and magnesium, also proved important in the composition of flours. Calcium, potassium and magnesium are present in the composition of muscles and bones, and are important for forming processes, contraction and energy metabolism. Copper is a cofactor in the formation of melanin, which plays a role in skin pigmentation, hair and eyes. Some copper dependent enzymes are responsible for many reactions essential for normal function of the brain and nervous system (Colli 2005) [12].

3.2. Phenolic compounds content

The analysis of phenolic compounds highlights significantly higher concentrations in the flour pomace of 'Pinot Noir' (AGE 7.0g / 100g), 'Tannat' (AGE 4.3 g /100 g) and 'Ancelotta' (AGE 3.9 g/100 g) grapes (Table 2). Rockenbach et al (2009) verified phenolic compounds concentrations of GAE.100 7.56 g g⁻¹ dry weight for grapes cv. Ancellotta GAE.100 and 6.59 g g⁻¹ dry for cv. Tannat. Regarding the difference obtained from several studies, Antolovich (2000) concluded that it is not an easy task to find a single method that is suitable for the analysis of a group of various phenolic compounds due to the diversity of chemical structures and variation in sensitivity of the compounds to the extraction conditions (Antolovich et al., 2000) [13].

3.3. Anthocyanins content

The content of phenolic compounds in grape pomace represents a wide variety of compounds including flavonoids. Among these, there are the anthocyanins (Orak, 2007) [14]. In Table 2 the levels of these compounds in the grape pomace flours are presented. The anthocyanin pigments are present in grape skins, and their levels may vary from 30 to 750 mg / 100 g of fruit, according to Bridle & Timberlake (1997) [15]. Among the cultivars, Cabernet

Table 1. Mineral content in grape pomace flour in southern Brazil.

Variety	Phosphor (mg/100g)	Nitrogen (mg/100g)	Sulfur (mg/100g)	Potassium (mg/100g)	Zinc (mg/100g)
x ± DP					
Cabernet Sauvignon	39.59 ± 1.3	21.83 ± 0.99 ^a	52.27 ± 1, 64 ^{ab}	13.77 ± 2.02 ^a	NS
Tannat	33.05 ± 0.99	22.09 ± 1.31 ^a	38.53 ± 2.5 ^b	23.52 ± 3.14 ^b	16.35 ± 0.44 ^d
Ancelotta	43.88 ± 1.33	22.09 ± 1.06 ^a	85.4 ± 4.32 ^c	25.82 ± 0.01 ^b	33.59 ± 1.66 ^e
Pinot Noir	49.76 ± 9.81	22.45 ± 0.59 ^a	56.49 ± 2.69 ^{ab}	13.44 ± 1.49 ^a	6.7 ± 0.50 ^b
Malbec	42.43 ± 2.01	26.17 ± 0.87 ^b	53.94 ± 3.07 ^{ab}	19 ± 0.94 ^c	9.84 ± 0.81 ^c
Merlot	39.96 ± 3.42	3.92 ± 0.72 ^c	54.92 ± 1.46 ^{ab}	10.84 ± 0.56 ^a	0.08 ± 0.02 ^a
Seibel	44.1 ± 1.77	30.93 ± 1.45 ^e	67.47 ± 0.58 ^{ab}	5.96 ± 1.12 ^d	6.29 ± 0.35 ^b
Bordô	35.65 ± 0.86	25.05 ± 0.91 ^b	87.88 ± 0.98 ^c	25.15 ± 0.69 ^b	17.47 ± 0.24 ^d
Cabernet Franc	45.14 ± 5.3	17.77 ± 0.74 ^d	63.12 ± 1.25 ^{ab}	18.66 ± 0.56 ^c	NS
Variety	Copper (mcg/100g)	Manganese (mg/100g)	Magnesium (mg/100g)	Iron (mg/100g)	Calcium (mg/100g)
x ± DP					
Cabernet Sauvignon	86.52 ± 11.8 ^{ad}	24.87 ± 5.3 ^{abc}	62.21 ± 1.96 ^b	209.78 ± 7.02 ^{ab}	284.22 ± 3.59 ^b
Tanat	63.97 ± 19.18 ^{ac}	36.64 ± 0.26 ^d	104.32 ± 3.03 ^a	286.5 ± 6.05 ^c	429.5 ± 4.74 ^d
Ancelotta	89.94 ± 0.71 ^{ad}	32.27 ± 1.25 ^{bd}	86.93 ± 1.75 ^{ac}	212.89 ± 8.48 ^{ab}	357.02 ± 4.2 ^c
Pinot Noir	52.95 ± 1.44 ^{abc}	25.84 ± 1.37 ^{abc}	105.51 ± 3.62 ^a	164.84 ± 4.71 ^a	362.84 ± 1, 67 ^c
Malbec	125.06 ± 2.57 ^d	19.91 ± 3.15 ^c	75.49 ± 1.95 ^c	250.06 ± 18.54 ^{bc}	312.13 ± 1.21 ^b
Merlot	9.25 ± 0.22 ^b	9.02 ± 1.25 ^e	58.73 ± 2.94 ^b	169.26 ± 11.66 ^a	158.04 ± 4.63 ^a
Seibel	296.42 ± 44.61 ^e	30 ± 6.58 ^{abd}	154.7 ± 20.42 ^d	166.36 ± 10.37 ^a	356.21 ± 13.68 ^c
Bordô	36.38 ± 1.11 ^{bc}	29.26 ± 2.32 ^{abd}	102.87 ± 5.70 ^a	241.54 ± 19.81 ^{bc}	308.8 ± 3.96 ^b
Cabernet Franc	42.64 ± 1.64 ^{abc}	21.09 ± 0.78 ^{ac}	101.36 ± 1.73 ^a	155.3 ± 9.05 ^a	296.21 ± 7.84 ^b

¹ Means followed by different letters on the same column are significantly different according to NSK at *P* < 0.05. NS. Not significant.

Table 2. Anthocyanin content and phenolic compounds in grape pomace flour in southern Brazil.

Varietade	Phenolic compounds (g AGE/100g)	Anthocyanins (mg/100g)
Cabernet Sauvignon	1.7 ± 0.29 ^a	114.7 ± 0.15 ^f
Tanat	4.3 ± 0.18 ^c	88.5 ± 2.02 ^e
Ancelotta	3.8 ± 0.04 ^d	33.8 ± 2.4 ^d
Pinot Noir	7.0 ± 0.17 ^f	3.48 ± 0.35 ^{bc}
Malbec	2.3 ± 0.31 ^b	12.89 ± 0.51 ^{ac}
Merlot	1.7 ± 0.02 ^a	15.78 ± 0.38 ^a
Seibel	5.9 ± 0.39 ^c	18.35 ± 2.1 ^a
Bordô	2.4 ± 0.10 ^b	19.86 ± 6.46 ^a
Cabernet Franc	1.5 ± 0.12 ^a	0.9 ± 0.96 ^b

Sauvignon, Tannat and Ancelotta presented content in this range. The values found for the other varieties are similar to the results found by Pinheiro (2009) [16] in which the values for anthocyanins were 3.56 mg / 100 mL in grape juice in inicial analysis and 1.43 mg / 100 mL after 210 days storage. It is known that anthocyanin levels in grapes can be influenced by factors such method of cultivation, weather aspects and physicochemical factors such as pH and temperature (Souza et al., 2014) [8].

4. Conclusions

Mineral analysis showed a significant difference among cultivars, with the exception of phosphorus. Featured for higher levels of N, Cu and Mg grape cv. Seibel. The cultivars Ancelotta, Tannat and Bordô stood out higher content of K, Zn, Mn, Fe and Ca. When analyzed the concentration of anthocyanins, cultivar Cabernet Sauvignon (114,7 mg / 100 g), Tannat (88.5 mg / 100 g)

and Ancelotta (33.8 mg / 100 g) had the largest and most significant concentrations of these antioxidants. The analysis of phenolic compound showed higher concentrations for the cultivars Pinot Noir (7.0 g AGE / 100 g), Tannat (4.3 g AGE / 100 g), and Ancelotta (3.9 g AGE / 100 g). Based this information there is the potential to use the residue of winemaking to produce flour for human consumption, highlighting the cutlivars Tannat and Ancelotta.

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