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A survey on the composition of wines made with grapes produced by an organic system

Avaliação da composição de vinhos elaborados com uvas produzidas pelo sistema orgânico

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Summary

There is concern about the health problems caused by pesticides in humans, which has led some grape producers to adopt organic procedures in their vineyards, and a certain amount of these grapes are directed to winemaking. Despite the approval awarded to this organic grape production by the certified organizations, there has been a demand to carry out a survey to determine the physicochemical composition of the wine derived from these products. Some of these wines were made from a single grape variety and others from more than one. For this survey, the samples consisted of five bottles of each type of wine, acquired from wineries and supermarkets in the Serra Gaúcha region, RS, Brazil. The analyses were carried out by physicochemical methods: volatile compounds by gas chromatography; minerals and trace elements by inductively coupled plasma optical emission spectrometry; and pesticide residues by liquid chromatography-mass spectrometry. The results showed that in general the physicochemical composition of these wines was within the limits established by Brazilian legislation. The mineral and trace element concentrations were very low and pesticide residues were not detected (MRL = 10 $\mu g.kg^{-1}$) in any of the wines.

Keywords: *Minerals; Heavy metals; Pesticide residues; Vitis* spp.

Resumo

Há preocupação em relação a problemas causados por pesticidas no ser humano, o que levou uma parcela de viticultores a adotar procedimentos de agricultura orgânica em seus vinhedos. Assim, devido a essa preocupação, eles estão produzindo uva pelo sistema orgânico, sendo que uma parte dessa produção é direcionada à elaboração de vinho. Apesar de essas uvas terem sido aprovadas por entidades certificadoras, houve demanda para a realização de um levantamento para determinar a composição dos vinhos delas derivados. Portanto, cinco garrafas de cada tipo de vinho foram coletadas em vinícolas e supermercados da Serra Gaúcha, Rio Grande do Sul, sendo uma parte de vinhos varietais e outra, de cortes de diferentes variedades. As análises foram feitas por métodos físico-químicos: compostos voláteis, por cromatografia gasosa; minerais e elementos-traço, por espectrometria de emissão ótica com plasma acoplado indutivamente, e resíduos de pesticidas, por cromatografia líquida-espectrometria de massa. Os resultados mostram que a composição físico-química desses vinhos e dos minerais situou-se, em geral, dentro dos limites da legislação brasileira. As concentrações de minerais e de elementos-traço foram muito baixas, e não foram detectados resíduos de pesticidas (LMR = 10 $\mu g.kg^{-1}$) em nenhum vinho.

Palavras-chave: *Minerais; Metais pesados; Resíduos de pesticidas; Vitis* spp.

1 Introduction

Currently, there is an increasing demand for grapes produced by organic viticulture in many countries. Following this trend, some grape producers in the Serra Gaúcha, RS, Brazil, are using organic viticulture. However, in this location it rains and the temperature is high during the vegetative cycle of the grapevine, which are ideal conditions for the development of some diseases, which should be controlled by fungicides, but these products, and other pesticides applied in the vineyards, may leave residues on the grapes and be transferred to the wines. In addition, they may cause problems in the environment and to the human beings. On the other hand, wines made from organic viticulture may have some other contaminants due to the alternative products applied to the vineyards.

The literature about the composition of wines made with grapes produced around the world according to organic procedures is scarce. In fact, there are papers evaluating this type of wine where the authors considered the physicochemical composition of one thousand wines made in different regions of Europe and determined the presence of ochratoxin A (COMUZZO et al., 2011; GENTILE et al., 2016), biogenic amines (GARCÍA-MARINO et al., 2010; COMUZZO et al., 2011), phenolic compounds and their antioxidant activity (YILDIRIM et al., 2005; MULERO et al., 2009, 2011; GARAGUSO; NARDINI, 2015), the evolution of volatile compounds during the alcoholic fermentation (LORENZO et al., 2015), the yeast population during the alcoholic fermentation (TOFALO et al., 2011) and the copper content (PROVENZANO et al., 2010). However, there are many papers related to the market and marketing of organic wine, such as the production of environmentally safe wine (CHRIST; BURRITT, 2013), the evaluation of the local wine market to assure profit (BRUGAROLAS et al., 2009), consumer attitudes towards organic wine (ROJAS-MÉNDEZ et al., 2015) and an investigation of consumer perception (WIEDMANN et al., 2014), but to the authors' knowledge, there are no Brazilian studies related to this issue.

Thus the objective of the present work was to carry out a survey on wines made from organic grapes in the Serra Gaúcha viticultural region, RS, Brazil, to determine their physicochemical composition and to detect the presence of heavy metals and any pesticide residues.

2 Material and methods

The wines surveyed were produced in the Serra Gaúcha region, RS, the southernmost and most important Brazilian viticultural region. The samples consisted of five bottles of each wine which were acquired in wineries and supermarkets in the region. Some of them were made from a single grape variety and others from more than one.

The physicochemical variables were determined according to Ribéreau-Gayon et al. (1982); anthocyanins by pH difference; tannins by acid hydrolysis; absorbance at 420 and 520 nm by UV/VIS spectrophotometry using a 1-mm cell path and at 620 nm using a 10-mm cell path (RIBÉREAU-GAYON; STONESTREET, 1965, 1966).

The volatile compounds were determined using a Perkin Elmer GS AutoSystem XL gas chromatograph with flame ionization detection, equipped with a 60 m length capillary column and polyethylene glycol WAX stationary phase (N9316406). The wine samples (3 µL) were injected directly into the chromatograph and the internal standard was a 10% solution of 4-methyl-2-pentanol at 1 $g.L^{-1}$ (BERTRAND, 1975).

The minerals and trace elements were determined by a nitric acid-perchloric digestion of the samples using a specific POP developed by the Soils Laboratory of the Agronomy Faculty of the Federal University of *Rio Grande do Sul* (Universidade Federal do Rio Grande do Sul), Brazil, and analyzed by inductively coupled plasma optical emission spectrometry (FRANSON, 1995).

The pesticides were analyzed by the QuEChERS method (ANASTASSIADES et al., 2003) using a Varian 1200L LC-MS/MS (triplequadruple) equipped with an ESI source. The column was a Phenomenex RP 80 one, 4.6 mm × 150 mm and 4 µm, the injection volume 20 µL and the flow rate 0.4 $mL.min^{-1}$. Detection and quantification of the pesticides were carried out by mass spectrometry using two transitions. The pesticides were analyzed in the Residues and Contaminants Laboratory of *Embrapa Meio Ambiente* in Jaguariúna, SP, Brazil. The following pesticides were analyzed: a) fungicides – azoxystrobin, cyproconazole, difenoconazole, fenarimol, myclobutanil, pyraclostrobin, tebuconazole, thyophanate-methyl and triadimefon; b) insecticides – fenthion, carbaryl and fenitrothion; c) herbicides – simazine and diuron.

3 Results and discussion

As expected, there was a considerable difference between the maximum and minimum values of certain variables (Tables 1 and 2), which was largely due to the type of wine, red or white, and to the winemaking process used, so some variables showed high standard deviations. In general, this was observed for those variables related to phenolic compounds, where white wines had lower values for absorbance at 420, 520 and 620 nm. Nevertheless the mean values for the wines showed concentrations within the limits of the Brazilian legislation, although one had an alcohol content (9.87% v/v) below that specified by the legislation.

Most of the wines were dry, with reducing sugar concentrations below 5 $g.L^{-1}$. Indeed, only one was sweet, a red one containing 111.5 $g.L^{-1}$ of sugar. Variables related to color, such as absorbance at 420, 520 and 620 nm,

Table 1. Physicochemical composition and volatile compounds of the wines made from organic grapes.

Variable	Wine			Standard deviation
	Maximum	Minimum	Mean	
Density at 20 °C (g.mL^{-1})	1.0381	0.9927	0.9989	0.0131
Titratable acidity (meq.L^{-1})	102	62	81	14
Volatile acidity (meq.L^{-1})	34	5	15	8
Fixed acidity (meq.L^{-1})	84	48	66	11
pH	3.83	3.12	3.36	0.22
Alcohol (% v/v)	13.25	9.87	10.84	0.91
Reducing sugars (g.L^{-1})	111.5	0.8	12.5	32.9
Dry extract (g.L^{-1})	140.23	13.9	32.8	35.9
Reducing dry extract (g.L^{-1})	29.7	14.1	21.4	4.7
Alcohol/Reducing dry extract	5.79	2.77	4.23	0.91
Ash (g.L^{-1})	4.54	1.84	2.53	0.73
Ash alkalinity (meq.L^{-1})	45.5	20.0	25.0	7.1
Absorbance at 420 nm	0.578	0.013	0.252	0.210
Absorbance at 520 nm	1.042	0.005	0.378	0.354
Absorbance at 620 nm	0.201	0.001	0.081	0.077
Colour intensity	1.555	0.018	0.630	0.552
Hue	2.60	0.55	0.67	0.59
Total polyphenols index (I 280)	83.7	5.1	41.5	26.8
Anthocyanins (mg.L^{-1})	967.7	1.2	352.5	368.4
Tannins (g.L^{-1})	6.53	0.06	2.22	2.13
Acetaldehyde (mg.L^{-1})	104.6	17.9	37.9	26.6
Ethyl acetate (mg.L^{-1})	271.6	46.4	124.0	57.5
Methanol (mg.L^{-1})	488.8	90.1	276.1	123.5
1-Propanol (mg.L^{-1})	40.7	18.7	29.8	6.9
2-Methyl-1-propanol (mg.L^{-1})	93.4	22.1	59.2	22.1
2-Methyl-1-butanol (mg.L^{-1})	68.6	22.1	45.7	15.5
3-Methyl-1-butanol (mg.L^{-1})	256.8	97.4	162.2	46.2
Sum of higher alcohols (mg.L^{-1})	453.9	193.2	296.9	80.0
3-Methyl-1-butanol/2-Methyl-1-butanol	6.55	3.27	3.81	0.93
3-Methyl-1-butanol/2-Methyl-1-propanol	6.57	1.87	3.05	1.30

and the anthocyanin contents were much higher in red wines, as were the values for the total polyphenols index and tannins. However, white wines showed higher values for hue and slightly higher values for the alcohol/reduced dry extract ratio.

One red wine showed a very high volatile acidity (34 meq.L^{-1}) which exceeds the limits of the Brazilian legislation and two wines showed values for the alcohol/reduced dry extract ratio greater than 4.80, the maximum permitted value. In general, high values were observed for the dry extract, ash content, ash alkalinity, absorbance, total polyphenols index and tannins content. The anthocyanin concentrations were much higher in the three Bordô (local name of Ives grapes) wines and another one made using a blend of Cynthiana and Isabella grapes.

Red wines produced in the Serra Gaúcha region, RS, using labrusca varieties presented tannin concentrations between 1.0 and 2.0 g.L^{-1} (RIZZON et al., 2000). However, the red wines evaluated in this study showed a mean value of 3.29 g.L^{-1} for tannins, but one reached 6.53 g.L^{-1}, which means that these wines were probably submitted to some enological procedure that increased their tannin contents.

The composition of European wines made from organic grapes is generally the same as that of conventionally produced wines (COMUZZO et al., 2011). However, besides the physicochemical variables evaluated, there are many other variables that should be considered in both kinds of wine, conventionally or organically made, including some biological compounds, such as ochratoxin A and biogenic amines. Ochratoxin A was found in 31% of Brazilian wines as against 52.9% of the imported ones sold in supermarkets in the city of São Paulo (SHUNDO et al., 2006).

The concentrations of volatile substances may vary due to a diversity of factors, such as variety, cultural practices used in the vineyards, climatic conditions, maceration time, fermentation temperature, yeast and

Table 2. Minerals and trace elements in the wines made from organic grapes.

Variable (mg.L^{-1})	Wine		
	Maximum	Minimum	Mean
Phosphorus (P)	224.6	45.5	107.2
Potassium (K)	1033	313	671
Calcium (Ca)	106.4	37.2	72.0
Magnesium (Mg)	102.8	47.3	75.5
Sulphur (S)	151.5	41.0	96.5
Copper (Cu)	2.27	nd	0.27
Zinc (Z)	0.61	0.06	0.34
Iron (Fe)	2.80	0.85	1.55
Manganese (Mn)	2.47	0.52	1.37
Sodium (Na)	35.33	2.03	11.61
Aluminium (Al)	0.88	0.07	0.32
Cadmium (Cd)	0.007	<0.002	0.003
Chromium (Cr)	0.049	0.004	0.021
Nickel (Ni)	0.023	<0.004	0.011
Lead (Pb)	0.016	<0.002	0.019
Molybdenum (Mo)	0.012	0.001	0.004
Cobalt (Co)	0.012	0.002	0.005
Arsenic (As)	0.028	0.006	0.020
Selenium (Se)	0.028	<0.020	0.023
Tin (Sn)	nd	nd	nd
Barium (Ba)	nd	nd	nd
Vanadium (V)	0.115	0.001	0.021

nd = not detected.

the amount of sulphur dioxide used during winemaking. It should be pointed out that these compounds could have an effect on the quality of the wine.

Of the volatile compounds, methanol, 3-methyl-1-butanol and ethyl acetate showed the highest mean concentrations, and were responsible for 75.8% of the volatile compounds analyzed (Table 1). In general there was a considerable difference between the maximum and minimum values, which was probably due to some factors already mentioned above.

Two wines were made with vinifera varieties, Malbec and Muscat, and both had lower methanol concentrations. Indeed, the mean methanol concentration of these two wines was 139.8 mg.L^{-1} whereas that of the labrusca ones was 393.9 mg.L^{-1}. This parameter is greater than that specified by the Brazilian legislation (350 mg.L^{-1}), which implies that the difference could be mediated primarily by the genetic background. In fact labrusca grapes have more pectin and consequently produce more methanol in the wines. In addition, red labrusca wines are macerated for a shorter period, releasing smaller amounts of this alcohol into the medium.

The mean concentrations of the macroelements (Table 2) decreased in the following sequence K, P, S, Mg and Ca. With respect to the microelements, Na was present in the highest concentration. It was shown that the K content was higher in the vinifera wines, with a mean of 967 mg.L^{-1}, whereas in the labrusca wines the mean was 605 mg.L^{-1}.

Most of the wines had mineral concentrations within the limits of the Brazilian legislation, but P, Na and Al showed higher mean levels than those generally found in Brazilian wines (RIZZON et al., 2008). Phosphorus could be liberated from the peel and seeds during maceration, because these have relatively high contents of this element. The low K concentration was due to the lower content of this cation in labrusca varieties as compared to vinifera ones. Copper precipitates during winemaking, so its concentration is very low in wines. For this reason it does not raise a direct concern with respect to human health, although it should be regarded as potentially harmful to the environment because it may be present in some fungicidal sprays.

The Brazilian legislation (BRASIL, 1965) specifies the MRL for 11 trace elements, but not all the trace elements evaluated in the present work were included in this publication. However they were present in very low concentrations, vanadium (V) showing the highest value (0.115 mg.L^{-1}). Two trace elements evaluated, barium (Ba) and strontium (Sn), were not detected (Table 2), and in a previous work, D'Agostini and Daudt (1997) detected small amounts of cadmium (Cd) in Cabernet Sauvignon

(0.70 and 0.88 $\mu g.L^{-1}$, depending on the vineyard) and Saint Émilion (0.76 $\mu g.L^{-1}$) wines.

No residues of the pesticides evaluated (MRL= 10 $\mu g.kg^{-1}$) were detected in any of the wines.

4 Conclusion

The results show that the compositions of the wines made from organic grapes in the Serra Gaúcha region, RS, were generally within the limits established by the Brazilian legislation. The concentrations of trace elements were very low and pesticide residues were not detected.

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