Short communication

Volatile profile of Malbec wine from Buenos Aires province (Argentina)

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Abstract

This work presents the characterization of the volatile composition of Malbec wines from the southwestern of Buenos Aires Province. Volatiles were studied by HS-SPME associated to GC and Mass Spectrum (MS), using DVB-CAR-PDMS and PDMS fibers. This is the first contribution to the characterization of wines from this new and non-traditional production area in Argentina. Ethyl octanoate (28-45%) and ethyl acetate (14-29%) were the aroma volatiles that showed the highest relative percentages, followed by diethyl succinate (9-14%) and ethyl hexanoate (11-13%). Principal components analysis proved to be useful in understanding relationship between aroma attributes and samples examined. Moreover, the results were compared with those observed in Malbec wines from others viticulture regions of the country. Similarities were observed between wines produced in different geographical regions, in term of major contributors of volatile compounds from this emblematic Argentine wine.

Introduction

Argentina is the eighth largest producer of wines in the world according to statistical reports of the International Organization of Vine and Wine (2012). Malbec (*Vitis vinifera* L.) variety, of French origin, has nowadays become the emblematic cultivar of Argentinean fine red wines (Rodriguez *et al.*, 1999). Malbec is cultivated in most wine regions along the Andes foothills between 800 and 1600 m elevation. Thus, the province of Mendoza is the main wine producer with over 80% of the country's production (INV, 2013). However, during the last few years, wine production has been growing in non-traditional wine producing areas as the Buenos Aires Province (GAIN report 2012). Although in the early 20th century wine makers tried to establish viticulture at different sites of this province, the soil extremely suitable for growing grain and livestock caused that this activity tended to disappear (Ospital, 2003). Nevertheless during the first decade of the 21st century, vineyards located at the southern of Buenos Aires province become premium wines producers, the only Argentinean terroir with oceanic influence (between 30 and 450 m elevation). While currently it represents only 0.006% of the national production (INV, 2013), vineyards make the entire region of the southwest of the province of Buenos Aires - between green low mountain landscapes and pampas- even more attractive as a touristic destination. Wine route extends along 150 kilometers between the mountain Ventania System and the south of Bahia Blanca city, one of the main entrances to the Patagonia.

The wine industry plays an important role in the country's regional economies. The commercial competitiveness, the development of an image, and the search for typicity contributed to recognition of the importance of having a representative grape variety of a region (Corino and Calo, 2001). The term "typicity" is used to convey those wine qualities and flavour characteristics that can be expected from a region, which is defined as a broad geographic area distinguished by similar features (Lund *et al.*, 2009). Aroma is one of the most important characteristics influencing wine quality and the consumer acceptance. The aroma profile of a wine is produced by a combination of chemical compounds that influence its organoleptic characteristics (Sagratini *et al.*, 2012). Wine aroma is represented by several classes of compounds, such as hydrocarbons, alcohols, terpene alcohols, esters, aldehydes, ketones, acids, ethers, lactones, sulphur and nitrogen compounds (Bonino *et al.*, 2003).

Solid-phase microextraction (SPME) is now widely used for analysis of aroma compounds in many food and beverage matrices (Ebeler, 2001). Respect to conventional solvent extraction, SPME is a fast, easy to use, inexpensive and solvent-free procedure for aroma and flavor studies (Zhang *et al.*, 1994). The technique has been successfully applied

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to analyze volatile compounds of grapes and wines (Jiang *et al*., 2013).

Numerous studies characterizing regional sensory differences in wines (Garcia Carpintero *et al.*, 2011; Cadot *et al.*, 2012; Robinson *et al.*, 2012) have been carried out. Concerning the regionality of Malbec wines, the fenolic composition (Gonzalez *et al*., 2009; Fanzone *et al*., 2010; Fanzone *et al.*, 2012) and elemental composition from soil (Fabani *et al*., 2010; Di Paola Naranjo *et al*., 2011) have been studied to determine wine provenance in Argentina. Only two studies have investigated regional sensory differences of Malbec wines (King *et al*., 2014): Goldner and Zamora (2007) and Aruani *et al*. (2012) who analyzed Malbec wines from seven and eight viticultural regions in Argentina respectively. None of them have studied the Malbec wines from Buenos Aires Province region. Moreover, only two studies have related the chemical composition of Malbec wines to their sensory properties (Goldner *et al*., 2009; King *et al*., 2014). To our knowledge, this is the first time that the aroma profile of Malbec wines from Buenos Aires Province has been characterized.

The aim of this work was the characterization of the volatile composition of Malbec wines from a non-traditional producing area, such as the southwestern of Buenos Aires Province. For this, HS-SPME associated to GC and Mass Spectrum (MS) Detector is used as analysis method, and the experimental conditions were established taking into account previous studies (Torrens *et al*., 2004; Welke *et al*., 2012) and specific criteria that will be duly observed. This is the first contribution to the characterization of wines from this new production area in Argentina. In addition, results were subjected to a descriptive multivariate analysis in order to complete the characterization. Moreover the results are compared with those observed in Malbec wines from others viticulture regions of the country.

Materials and Methods

Wine samples

Analyses were made with the four commercial Malbec wines (vintages 2008-2009) produced at southwest of Buenos Aires province. Two from a vitivinicultural site of Médanos (Villarino Departament) identified as A and B, and two from Tornquist Department, from Villa Ventana and Saldungaray, identified as C and D respectively.

HS-SPME conditions

To perform our study we used a SPME manual holder. The choice of the coating microfiber 50/30 μm divinylbenzenecarboxen-polydimethylsiloxane (DVB-CAR-PDMS) Stable Flex was made taking into account studies conducted by Torrens *et al.* (2004) and Welke *et al.* (2012), while 100 μm Polydimethylsiloxane (PDMS) coating was used for an additional analysis according to Goldner (2008). The fibers were preconditioned according to manufacture's instruction. Holder and SPME fibers were purchased from Supelco (Bellefonte, PA, USA).

For each extraction, 12.5 mL of wine, 3.7 g of NaCl and 10x3 mm stir bar were placed in a vial of 15 mL capped with a PTFE-silicon septum. NaCl addition was made in order to increase the concentration of volatile compounds in the HS (Torrens *et al*., 2004). Thus, to achieve the equilibrium state, the sample was stirred for 15 minutes before extraction. Then, the fiber was exposed to the HS under these conditions for additional 30 minutes. The working temperature (25ºC) was selected to be an intermediate value between the recommended for wine consumption and the perception of the human nose. Each HS-SPME experiment was performed in triplicate.

GC–MS analysis

The chromatographic determinations were carried out using a Hewlett-Packard (HP6890 GC system) equipped with a HP5 column (30m x 0.25mm, 0.25 μm), and coupled to HP5972 Mass Spectrometer Detector. The gas carrier was Helium at a flow rate of 2.3 mL.min-1. The injector port temperature was 250 °C, and split less injection mode was used. The oven temperature program was: initial 50°C, increased to 70°C at 4°C.min^{-1}, then programmed from 70 to 150°C at 6°C.min^{-1}, then increased to 270°C at 40°C.min^{-1} and then held isothermal (3 min). The mass spectrometer was operated in the scan mode (mass range m/z 35-500). Peaks were identified by comparison with the mass spectra library of Hewlett-Packard (NBS7K). Only the volatile compounds with a match value higher than 90% comparing its mass spectra with those present in the MS library databases were reported. Furthermore the results of volatile constituents in Malbec wines are expressed as relative percentages of identified compounds. Thus, the relative amounts of volatiles (per cent) were obtained by dividing the area of each component by the total area of all isolated and identified components. Finally the values reported and analyzed were the mean of three replicates for each sample.

PCA analysis

In order to obtain an overview of correlations of the dates obtained, a principal component analysis was performed. As an exploratory technique, PCA

Table 1. Volatile constituents identified in Malbec wine samples (Buenos Aires Province) obtained by SPME followed by GC-MS, the corresponding retention times (RT), aroma descriptors and relative percentages calculates as media on three replicates

RT (min)	Volatile component	Aroma descriptor [a]	Wine samples							
			A		B		C		D	
			mean	SD	mean	SD	mean	SD	mean	SD
1.72	Ethyl acetate	*Fruity, Swseety*	27.0	2.4E-01	14.4	4.2E-01	28.7	5,9E-01	16.3	9.2E-02
1.78	2-methyl-1-propanol	*Glue, Alchohol, Leek, Licorice*	2.9	8.3E-01	2.2	4.8E-01	2.9	5,9E-02	0.7	1.4E-02
2.68	2-methyl ethyl propanoate	*Fruity, Strawberry*	0.3	1.3E-02	0.2	1.4E-02	0.3	8,4E-02	2.5	3.9E-01
3.19	ethyl butanoate	*Fruity, Banana, Strawberry, Bubblegum*	0.6	4.0E-02	0.4	2.6E-02	0.4	4,8E-03	0.5	8.6E-03
3.39	2-hydroxy ethyl propanoate	*Ethereal-buttery*	6.6	6.2E-01	3.7	4.1E-01	3.9	4,4E-01	1.7	8.4E-02
3.97	ethyl-d-methyl butanoate	*Fruity, Strawberry, Green apple*	n.d.		0.08	1.4E-02	0.1	3,6E-02	0.5	6.9E-03
4.05	ethyl-3-methyl butanoate	*Fruity, Strawberry, Green apple*	0.3	3.3E-04	0.1	5.2E-04	0.2	3,0E-02	0.7	2.1E-02
4.45	isoamylacetate	*Banana, Fruity, Pear*	4.8	3.7E-01	2.1	7.0E-02	1.9	7,7E-02	1.8	6.9E-02
4.89	1,2-dimethyl benzene	*Geranium*	n.d.		n.d.		0.6	2,5E-02	0.3	2.5E-02
7.37	ethyl hexanoate	*Fruity, Strawberry, Anise, Wine Gum*	13.3	9.4E-01	11.7	3.5E-01	11.7	1.3E+00	10.5	8.1E-01
7.71	hexyl acetate	*Frutal*	0.5	3.8E-03	0.2	3.0E-02	n.d.		n.d.	
8.1	limoneno	*Lemon*	n.d.		0.2	2.6E-02	n.d.		n.d.	
10.29	phenylethanol	*Honey-like, Yeast-like, Floral, Spicy*	3.1	5.2E-02	3.7	6.0E-02	3.9	1.9E-01	5.8	4.9E-01
11.94	diethyl succinate	*Fruity, Watermelon, Flower*	8.7	6.1E-01	8.9	5.0E-02	11.3	6.2E-02	14.0	1.4E+00
12.34	ethyl octanoate	*Fruity, Floral, Green leafy, Menthol, Anise*	28.0	6.7E-01	44.9	5.9E-01	27.7	8.7E-01	39.6	2.4E+00
16.89	ethyl decanoate	*Grape, Fruity*	4.0	4.5E-02	7.3	2.2E-02	6.3	1.0E-01	5.1	3.4E-01

[a]Comuzzo, 2006; Monson, 2011; Jiang *et al.*, 2013.

allows to study of main sources of variablity present in the data sets, to detect clustering formation, and to establish relationships between samples (objets) and compounds (variables) (Jolliffe, 1986). Statistical analysis was implemented with Matlab software (Version 7.0 The Math Works Inc. Natick, USA). Dates were mean-centered before the application of PCA. The results of this multivariate analysis are presented as biplot graphic.

Results and Discussion

Around 60 compounds per sample were detected, of which about 20 could be identified according to the experimental conditions detailed above. The volatile constituents identified in Malbec wines are shown in Table 1. This table shows also the descriptors for each aroma compound studied.

About 60% of the compounds were esters. Ethyl octanoate and ethyl acetate were the aroma volatiles that showed the highest relative percentages, followed by diethyl succinate and ethyl hexanoate. These volatile ethyl esters are responsible for the floral and fruity characters giving a winey and fresh aroma profile (Sagratini *et al.*, 2012). Thus, taking into account the corresponding descriptors flavorings, these volatiles found in Malbec wines produced at southwest of Buenos Aires province could be the mainly responsible for its fruit aromatic base.

Furthermore, the compounds ethyl acetate, 2-methyl-1-propanol, ethyl isovalerate, 1-butanol-3-methylacetate, ethyl hexanoate, diethyl succinate, ethyl octanoate and ethyl decanoate were selected to make a comparison of the profile of volatiles found in the present study with those reported by Goldner (2008) in wines from the major viticultural regions of the country. Since that Goldner (2008) used PDMS fiber, a previous study of the comparative extraction efficiency of the covering DVB-CAR-PDMS vs PDMS was conducted. A statistic t calculated (t= 0.288) by applying a student´s paired test, was lower than the tabulated (0.78) at 95 % confidence level, so no significant differences were found in the use of either coating. Finally, a graphic comparing data from Goldner (2008) and the results obtained in this study is showed at Figure 1. Although there is an apparent higher concentration of volatiles of wines compared to other regions of the country, this cannot be taken into account since the concentrations are given in relative percentages and based on different numbers of constituents. However, it can be seen that the profile of these selected volatile compounds from different regions of Argentina are very similar, coinciding the trend of major contributions of volatile components compared between all Malbec wines.

With regard to PCA analysis, wine samples were located in all quadrants of the biplot graphic (Figure 2). Results showed that the two first principal components
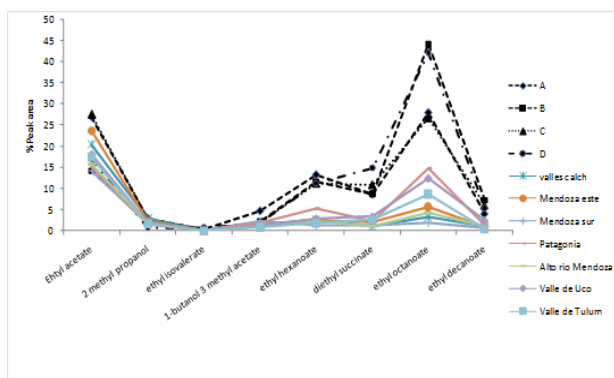
Figure 1. Comparison of the volatile profiles from A, B, C and D Malbec wines analyzed in our laboratory and those obtained by Goldner (2008) from others viticulture regions of Argentina
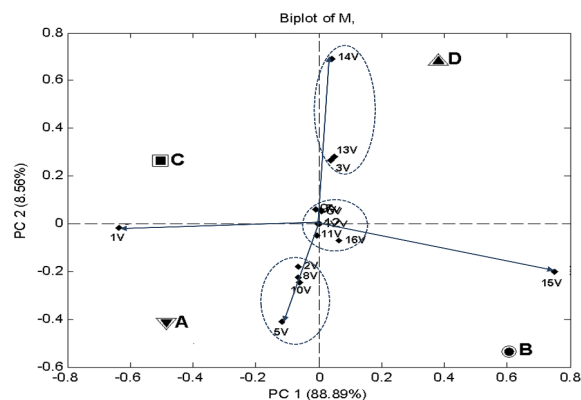

Figure 2. Principal component analysis of mean relative percentages of volatile compounds for the Malbec wines produced in the southwest of Buenos Aires Province

1v: ehtyl acetate; 2v: 2-methyl-1-propanol; 3v: 2-methyl ethyl propanoate; 4v: ethyl butanoate; 5v: 2-hydroxy ethyl propanoate; 6v: ethyl-2-methyl butanoate; 7v: ethyl-3-methyl butanoate; 8v: isoamylacetate; 9v: 1,2-dimethyl benzene; 10v: ethyl hexanoate; 11v: hexyl acetate; 12v: limoneno; 13v: phenylethanol; 14v diethyl succinate; 15v: ethyl octanoate; 16v: ethyl decanoate.

explained 97.45% of the total variability present in the data set. From this plot one can see that the four wine samples can be separated. This could indicate a diversity of style between the wines produced in southwest region of Buenos Aires Province. On the one hand, PC1, which explains 88.89% of the variability, characterizes the separation between B + D and A + C wines. On the other hand, the PC2 axis, which explains 8.56% of the total variability, is related to the distinction between C + D (scored negatively) and A + B (scored positively) samples wines. Figure 2 also reveals the relationship between aroma components and wine samples. The variability is mainly related to the content of ethyl acetate (1v) and ethyl octanoate (15v) on PC1, and diethyl succinate (14v) and 2-hydroxy ethyl propanoate (5v) on PC2. While A is linked to ethyl acetate (fruity and sweety aroma descriptor) and 2-hydroxy ethyl propanoate (ethereal and buttery aroma descriptor), B is mainly linked to ethyl octanoate (fruit, floral, green leafy, menthol and anise aroma descriptor), C to ethyl acetate and D is mainly characterized with diethyl succinate (fruity, watermelon and flower aroma descriptor). Meanwhile diethyl succinate (14v), phenyl ethanol (13v) and 2-methyl ethyl propanoate (3v) are clustered positively on PC2 and linked to C and D wines, and anti-correlated to 2-methyl-1-propanol (2v),   2-hydroxy ethyl propanoate (5v), isoamyl acetate (8v) and ethyl hexanoate (10v). Thus, these last volatiles (clustered negatively on PC2) are linked to A and B. Moreover, the content of ethyl butanoate (4v), ethyl-2-methyl butanoate (6v), ethyl-3-methyl butanoate (7v), 1,2-dimethyl benzene (9v), hexyl acetate (11v) and limoneno (12v) do not present a significant contribution to differentiate the samples studied.

On the other hand, other substances not directly related to the wine aroma also were found in this study. Thus, toluene, xylenes (1,2-dimethyl benzene and 1,3-dimethyl benzene), hexamethyl cyclotrisiloxane, and 4-methoxy-1,1-biphenyl were detectable in some of the samples analyzed, probably as result of some process contamination. Toluene also was detected in studies of wine volatiles from other viticulture regions of Argentina by Goldner (2008), and considered its origin as a contaminant (Baldock and Hayasaka, 2004). Xylenes are used an inert ingredient in agricultural crop products, in post- harvest grains storage products, and residential pesticide products used in and around the home (Wagner, 2005), nevertheless 1,2-dimethylbenzene (o-xylene) also is considered geranium aroma descriptor (Comuzzo *et al.*, 2006) and therefore was also included in Table 1. Furthermore, the 4-methoxy-1,1-biphenyl has been presented as a probable metabolite (degradation product) from the potent acaricide known by bifenazate (Hamilton, 2006). Moreover hexamethylcyclotrisiloxane was found at all samples. Some siloxane derivatives may be caused by using PDMS-coated microfibers (Bryant and McClung, 2011), but in particular it has been recognized as a natural antibacterial agent in olive leave extracts obtained by a conventional methods (Keskin *et al.*, 2012), so it also can be considered as probable natural origin.

Conclusions

Wine volatiles were satisfactorily studied by HS-SPME-GC-MS, using DVB-CAR-PDMS and PDMS fibers. Ethyl octanoate and ethyl acetate were the aroma volatiles that showed the highest relative percentages (28-45% and 14-29% respectively.

Furthermore multivariate analysis allowed to observe that the former of these compounds has been associated with wine B (fruit, floral, green leafy, menthol and anise aroma descriptor) and the former has been related with wines A and C (fruity and sweety aroma descriptor). Thus, the data were successfully implemented for multivariate data analysis and showed that this technique is suitable for differentiating between different wine samples. Similarities were observed between wines produced in different geographical regions, in term of major contributors of volatile compounds from this emblematic Argentine wine.

This work presents the first characterization of aroma profile of Malbec wines from the Southwest of Buenos Aires province in Argentina. Sensory evaluation is suggested to further confirm the impact of aroma compounds already identified. New information generated are expected to be a reference to future studies that allow evaluating if such aroma characteristics are consolidated over time.

Acknowledgements

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