MALBEC WINES FROM ARGENTINA: INFLUENCE OF CLIMATE ON AROMATIC COMPONENTS AND ORGANOLEPTIC PROFILE. IS IT POSSIBLE TO STABLISH REGIONAL IDENTITIES?

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Abstract
Malbec grapes have been cultivated for 150 years in Argentina. In the last 20 years Argentinian Malbec wines have emerged as a commercial boom worldwide. Today Malbec is the most planted variety in Argentina, representing 17% of 226.400 ha, and stands for 54% of bottled exported wine in volume. Producers are afraid that the growth of this wine will be limited in the future if the consumers think of Malbec as one homogeneous product. The aim of this study is to determine if there are arguments to think that we can offer to the world different Malbec wines depending on the region in which they are produced.
Fanzone found differences on Malbec no volatile compounds (Fanzone *et al.*, 2012) according to the origin of the grapes.
During the season 2015 Malbec wines were obtained using a standard protocol from grapes cultivated at latitudes ranging from 23° to 39° south, average seasonal temperatures from 18,1°C to 21°C (Winkler-Amerine classification III to V), and elevations over sea level from 220 to 1850 meters. Grapes were picked with 24 to 24.5°Brix and elaborated in plastic bins. Corrections of SO2 and acidity, addition of yeasts and lactic-bacteria for malolactic fermentation were also standard. After natural clarification of lees, wines were bottled. Wines were characterized by a professional tasting panel (following ISO 8586 norms), aromatic compounds were measured by GCMS (Flash profile) and tiols were extracted (SPME) and measured (GCMS). Correlations between growing season average temperature (GST), flavors (measured by the tasting panel) and volatile chemical compounds were done.
As in previews studies (Jofré, V. 2011, Goldner *et al.*, 2008), Malbec did not present a distinctive family of flavors. By contrast aromatic profile of wines results from the interaction of many families of volatile compounds. The concentration of some of them increased with GST (norisoprenoids $R2=0,947$, other decreased with GST (alcohols $R2=0,873$), while acids, terpenes, aldehydes, C6 compounds, esters did not present clear relation with GST. Molecules like 2-Phenyl ethanol (rose) and ethyl-isovalerate (apple) increases with decreasing GST ($R2=0,976$ and $R=0,920$ respectively). GST, Winkler and Huglin explained better the variations of volatile compounds than altitude, average minimum and maximum temperatures.
In the tasting Malbec's fruity and flower flavors taken as a whole increased with decreasing GST ($R2=0,79$). There was a tendency on spices and wild herbs flavors to increase with GST ($R2=0,69$). Some differences of flavors could be related with the concentration of some compounds.
Finally Argentinian Malbec wines presented difference on taste and volatile compounds that can be explained by temperature (GST). This will permit in the future promote a pallet of Malbec wines, creating a more interesting category of wine.
Keywords: terroir, Argentina, climate, aromatic compounds, aromatic profile, flavor, Malbec, wine, grapevine

1 INTRODUCTION

Malbec grapes have been cultivated in the last 150 years in Argentina. And, in the last 20 years, Argentinian Malbec wines have emerged as a commercial boom worldwide. In 2015 Malbec was the most planted variety in Argentina and represented 17% of 226.400 ha, and stood for 54% of bottled exported wine in volume.
The flavour of a wine presents an extremely complex chemical pattern in both qualitative and quantitative terms. Over 1000 aroma compounds have been identified, with a wide concentration range varying from hundreds of mg/l to ng/l level (Rapp, 1988). Moreover, several classes of compounds, such as hydrocarbons, alcohols, terpenes, alcohols, esters, aldehydes, ketones, acids, ethers, lactones, sulfurs and nitrogen compounds are responsible for wine aroma. All aroma compounds may play a role in the characterization of the specific flavour pattern of each wine type. In some cases it has been possible to isolate a few key compounds mostly representing the typical flavour of a wine (Versini et al., 1994; Williams, Strauss, & Wilson, 1980; Wilson, Strauss & Williams,1986), while in the majority of wines several compounds seem to cooperate, with specific ratios between them (Bayonove et al., 1971, Strauss et al., 1988). A better understanding of the key aroma compounds helps to control quality and may have an impact on the viticultural and wine technological processes.
The evaluation of the profile of phenolic compounds seems to be a very suitable method of defining the authenticity of the individual varieties (Lampir *et al.*, 2013). Several works have been carried out to classify different wine varieties for their geographic origin, vintage and wine state by sensory and/or compositional analysis. In this way, Chardonnay wine has been extensively investigated (Moio *et al.*, 1993; Arrhenius *et al.*,

1996; Cliff and Dever, 1996; Zamora and Guirao 2002, 2004; Schlosser *et al.*, 2005). Guinard and Cliff (1987) have studied pinot Noir and Riesling wines was characterized by Fischer *et al.*, (1999) and by Douglas *et al.*, (2001). For Malbec wine, there are evidence that the most common aromatic descriptors are plum, red fruit and spice. It sometimes shows herbal notes. Viticultural management should try to avoid strong herbal flavors that tend to produce bitterness and undesired rapid evolution of the wine (Boidron *et al.*, 1988). Fanzone (2002) commenced to identified the chemical components and its source of origin (varietal, prefermentative or fermentative) of Malbec wine from grapes cultivated in an experimental plot in Luján de Cuyo (part of Alto Río Mendoza region). Another previous studies (Jofré, V. 2011, Goldner, M.C., 2008), demonstrated that Malbec did not present a distinctive family of flavors. By contrast aromatic profile of wines results from the interaction of many families of volatile compounds. Fanzone (2012), found differences on volatile compounds on Malbec wines with different origins. Golder *et al.*, 2009, did not observe correlation between aromatic components and sensory attributes; probably, the sensory attributes that characterized these samples were not correctly identified or not defined. Quini of Instituto Nacional de Vitivinicultura (INV) differenciated Malbec wines of Mendoza by its visual and aromatic characteristics. Their concluded what Malbec wine of warmer regions have more herbaceous and fruit aromas than cooler regions. These differences was explained for Schermer (2014) and concluded that the altitude seems to be the most crucial terroir factor in Mendoza. I also made a short analysis to explain the observed differences in terroir. The altitude in Mendoza has a great influence on the main terroir-drivers: temperature, the temperature amplitude and light. In addition, they found that the highest altitude subzones (Alto Valle de Uco) produce Malbec wines with good structure and ageing potential, intense colour, red fruit aromas and flavours, complexity and specific floral aromas, like violets. The Malbec wines of average altitude, especially from the Classic zone near Luján excelled in fruit, body and were very homogenous. The Malbec wines from the warm and relative low zone Mendoza Este are easier to drink and have more typical stewed fruit aromas and flavors.
Understanding the regional difference of Malbec wines will increase the interest of journalist and consumers on this variety. The aim of this study is to determine that differences, especially in aromatic profile and volatile compounds, and the relation between this two.

2 MATERIALS AND METHODS

In 2015, Malbec grapes of 7 different wine growing regions were elaborated (see table nº1). All these regions are desertic or semidesertic, with Monzonic regime of precipitation, been winters very dry, and with most of the scarce rain occurring in the months of January to March. Vineyards used in the trial complied with the following characteristics: vertical trellising system, 8 to 15 years old, north-south orientated rows, 7 to 8 feet of distance between rows. Soil: 4 feet of depth or more, sandy-loam. The scion of Malbec were mass selection, own rooted in all cases except sample 107 and 120 that were grafted on Paulsen 1103.

Table 1: regions under study and their main geographical and climatic characteristics.

Sample	Region	Soil type	Latitude	Altitude (m)	GST (ºC)	Winkler Index	Winkler Category	Av. Max. Tº March	Av. Min. Tº March	Max-Min ºT March	Huglin Index	Huglin Category
E 107	Gualtallary, Tupungato, Mza	Deep sandy-loam	33,37	1300	18,1	1707	III	23,9	12,1	11,8	2452	Warm
E 120	El Cepillo, San Carlos, Mza	Deep sandy-loam	33,84	1100	19,0	1910	III	26,3	12,3	14,0	2751	Warm
E 138	Luján de Cuyo, Mendoza	Deep sandy-loam	33,25	1015	20,1	2157	IV	26,5	14,0	12,5	2916	Warm
E 146	San Patricio del Ch., Neuquén	Deep sandy-loam	38,60	350	19,2	1952	IV	29,4	9,5	19,9	2638	Warm
E 144	Mainque, Rio Negro	Deep sandy-loam	39,07	220	19,3	1965	III	27,3	8,0	19,3	2700	Warm
E 147	Cafayate, Salta	Deep sandy-loam	26,02	1660	21,0	2345	V	28,3	15,6	12,7	2878	Warm
E 148	Santa María, Catamarca	Deep sandy-loam	26,62	1850	19,9	2133	IV	26,0	14,5	11,5	2692	Warm

Elaboration: 500 kg of grapes were harvested for each vineyard in 20 kg plastic boxes. The picking point was determined by the sugar content (between 24,5º and 25,5ºBrix). Grapes were crushed and added with 80 mg of metabisulfite per kg of grape. Acidity was corrected when necessary to 6g/l of acidity expressed as tartaric acid. Primary fermentation was done by added L1118 yeast (50 g/hl). Fermentation was made in 730 lts of capacity plastic bins with 14 days of maceration at a temperature of 20 to 25ºC. After maloláctica fermentation wines were bottled. Studies of flavors and aromatic compounds were performed after 6 month of aging in bottle.
Flavors were determined by a 8-tasters panel trained with ISO 8586 standards. Before tasting the wines, the panelist went through a process of calibration of olfactory and gustatory attributes, with standard flavor samples and basic tastes solutions. Wines were served at 19ºC, and in a first round of tasting the main flavors and tastes (perceived by more than 50% of the panelists) were determined and described in a 0 to 9 points scale. In a second round wines were evaluated using the flavor descriptor selected in the first round with the 0 to 9 point

scale. For the analysis of the figures for each wine the intensity of the flavors were related with the sum of all the flavors, so that we obtained the relative weight of each flavor for that wine, expressed as a percentage.
Aromatic compounds were extracted with solvent at low temperature in nitrogen medium and then concentrated and injected in a gas-chromatograph (GC 7890A/MSD 5975C) with a mass detector (GCMS). Compounds were determined by comparison with NIST-EPA-NIH database. Volatile compounds of different families were determined: acids, alcohols, aldehydes, C6 compounds, furans, sulfurs, esters, terpens and norisoprenoids. Five thiols: FFT (2-Furfuril tiol), BMT (Benceno metanotiol), 4MMP (4-Metil-4 mercaptopentanone), 3MH (3-Mercaptohexanol), Ac3MH (3-mercaptohexanol acetate) were determined separately by metoximation and derivatization, and later microextraction on solid fase (SPME) and direct desortion to a GCMS.
Total Polyphenols Index (TPI, absorbance at 280 nm), color summation (absorbance at 480+580+680 nm) and the concentration of anthocians (Glorie Method) were also determined in the wines with and spectrophotometer.
Different climate index were used to correlate with flavors and volatile compounds: average growing season temperature (GST), Winkler-Amerine index (Winkler), average maximum temperature of March (Av. Max. Tº March), average minimum temperature of March (Av. Mim ºT March); diurnal amplitude of temperature in March (Max-Min ºT March) and Huglin Index (Huglin). All of them are expressed in Celcius degrees.
Principal component analysis and coefficient of correlation (over -/+60% were considered valid) were calculated for statistical analysis. Coefficient of variation (CV) is also used to express the dispersion of the figures.

3 RESULTS AND DISCUSSION

The tasting panel identified 9 flavors, all with significant differences (P<0,05) in the wines (Figure 1A). In occasions we have separate the flavors in two big families: Floral & Fruity (includes Red berries, Plums, Jam, Violet flowers, Blackberry) and Spicy & Herbal (includes Eucalyptus, Clove-cinnamon, White pepper, Rosemary-thyme).

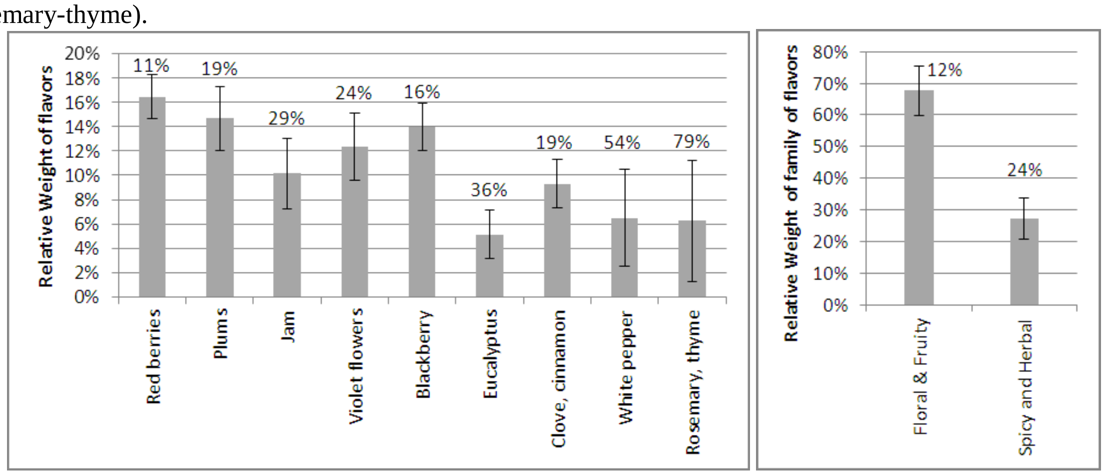

Figure 1 A. (left): Average weight of flavors and CV (on top) for all regions. B. (right): Average weight of families of flavors and CV (on top) for all regions.

Fruity &Floral flavors are in general more important in Argentinian Malbec representing on average 68% of the aromatic profile, whilst Spicy & Herbal notes represent 27% (see figure 1 B), the rest is represented by some secondary flavors (for ex. butter). Coefficient of variation (CV) of each flavor varies from 11% to 79%, so that some flavors (red berries, plums, clove-cinnamon, blackberry) could be considered basic descriptors for Argentinian Malbec, while others present a bigger variation from region to region (Jam, Violet flowers, Eucalyptus, White pepper and Rosemary-thyme). The weight of the primary flavors for each wine is shown in **table 2**. It's important to note that in no case a single flavor represented more than 19% of the aromatic profile.

Table 2: relative weight of flavors for each region

Region	Red berries	Plums	Jam	Violet flowers	Blackberry	Eucalyptus	Clove, cinnamon	White pepper	Rosemary, thyme
Gualtallary, Tupungato, Mza	16%	16%	11%	16%	17%	5,5%	8%	4%	2%
El Cepillo, San Carlos, Mendoza	17%	17%	13%	12%	15%	4,3%	10%	5%	4%
Luján de Cuyo, Mendoza	14%	10%	5%	17%	16%	8,5%	8%	9%	9%
San Patricio del Chañar, Neuquén	17%	15%	11%	11%	13%	4,2%	11%	11%	3%
Mainque, Rio Negro	18%	18%	12%	12%	14%	4,2%	12%	2%	3%
Cafayate, Salta	14%	12%	7%	9%	10%	5,4%	7%	10%	16%
Santa María, Catamarca	19%	15%	12%	10%	13%	3,8%	9%	4%	7%

The correlation of flavors with latitude, altitude and the climate indexes is resumed on **table 3**: GST and Winkler were the indexes that correlated with more flavors (4 out of 9) followed by Av. Min ºT March and Huglin (3 flavors); then Latitude, Av. Max ºT March (2 flavors) and Max-Min ºT March and Altitude showed correlation only with one flavor.

Table 3: Correlation of flavors and family of flavors (below) with geographic and climatic characteristics.

Flavor	Latitude	Altitude (m)	GST (ºC)	Winkler Index	Av. Max. Tº March	Av. Min. Tº March	Max-Min ºT March	Huglin Index
Red berries*	0,222	-0,160	-0,403	-0,376	-0,087	-0,472	0,320	-0,496
Plums*	0,460	-0,363	**-0,673**	**-0,676**	-0,181	**-0,683**	0,436	**-0,659**
Jam*	0,301	-0,186	**-0,628**	**-0,616**	-0,172	-0,525	0,318	**-0,654**
Violet flowers*	0,335	-0,179	-0,461	-0,463	-0,589	-0,076	-0,233	-0,152
Blackberry*	0,437	-0,213	**-0,751**	**-0,742**	**-0,720**	-0,258	-0,158	-0,421
Eucalyptus**	-0,120	0,111	0,298	0,296	-0,173	0,415	-0,405	0,503
Clove-cinnamon**	**0,787**	**-0,803**	-0,394	-0,402	0,335	**-0,899**	**0,857**	-0,259
White pepper**	-0,113	-0,004	0,492	0,482	**0,646**	0,305	0,086	0,447
Rosemary-thyme**	**-0,743**	0,562	**0,921**	**0,915**	0,316	**0,767**	-0,433	**0,751**
***Floral & Fruity**	0,352	-0,162	**-0,795**	**-0,781**	-0,247	-0,436	0,069	-0,484
****Spicy & Herbal**	-0,176	0,054	**0,691**	**0,674**	0,303	0,314	0,025	0,560

TPI, color and anthocians did not present correlation with any geographic and climatic characteristic (data not shown). **Floral & fruity** flavors and **Spicy & Herbal** flavors showed correlation with **GST.** In warmer climates Malbec wines showed more Spicy & Herbal flavors, while in cooler climates Floral & Fruity flavors were enhanced (see figure 1 A and B).

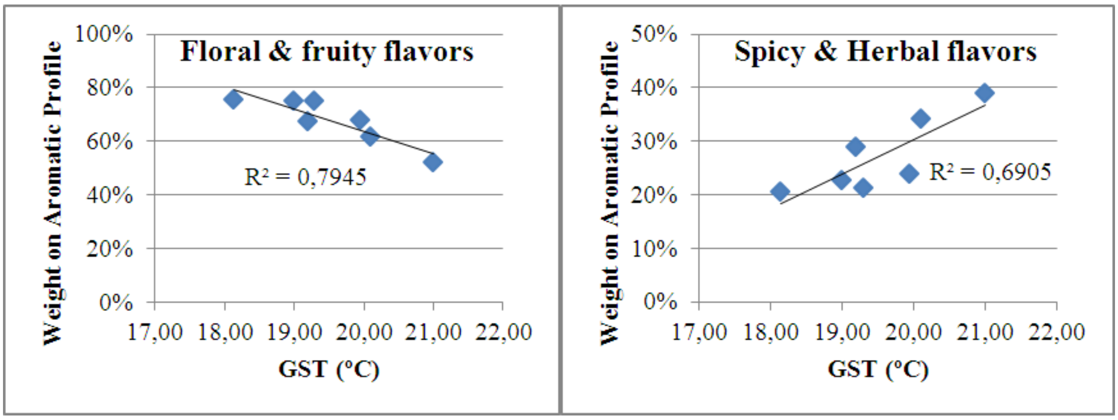

Figure 2: Correlation among families of flavors (Floral & Fruity and Spicy & Herbal) and GST.

Three families of aromatic compounds showed correlation with **Huglin,** 2 with **Av. Min.ºT March**, **Latitude, GST** and **Winkler,** while **Altitude, Av. Max. Tº March** and **Max-Min ºT March** only correlated with 1 family of flavor (table 4).

Table 4: Correlation among families of aromatic compounds and single aromatic compounds (*) with the main geographical and climatic characteristics.

Aromatic compound	Latitude	Altitude	GST	Winkler Index	Av. Max. Tº March	Av. Min. Tº March	Max-Min ºT March	Huglin Index
Acids	0,412	-0,562	0,327	0,310	**0,683**	-0,260	0,539	0,362
Alcohols	0,547	-0,329	**-0,873**	**-0,876**	-0,336	-0,410	0,149	**-0,638**
Aldehydes	0,367	-0,343	-0,177	-0,189	-0,072	-0,315	0,207	0,248
C6 compounds	0,127	0,018	-0,398	-0,412	-0,588	0,025	-0,311	-0,007
Furans	-0,493	0,430	0,337	0,372	0,093	0,229	-0,130	0,056
Sulfurs	0,365	-0,354	0,035	0,028	-0,029	-0,061	0,032	0,521
Esters	**0,739**	**-0,761**	-0,457	-0,480	0,189	**-0,914**	**0,797**	-0,523
Terpenes	-0,023	-0,064	0,497	0,500	0,157	0,281	-0,139	**0,735**
Norisoprenoids	**-0,612**	0,417	**0,947**	**0,957**	0,372	**0,630**	-0,300	**0,792**
FFT*	**-0,820**	**0,735**	0,564	0,595	0,065	**0,607**	-0,435	0,162
BTM*	-0,328	0,220	0,486	0,506	**0,651**	0,295	0,096	0,273
4MMP*	**-0,877**	**0,768**	**0,659**	**0,682**	0,095	**0,676**	-0,473	0,262
3MH*	0,344	-0,183	-0,525	-0,528	-0,159	-0,137	0,027	-0,150
Ac3MH*	0,524	**-0,619**	-0,096	-0,121	0,162	**-0,705**	**0,623**	-0,072
P-1-Menthen-7.8-diol*	-0,157	0,108	0,463	0,466	-0,019	0,448	-0,354	**0,735**
g-Butyrolactone*	**0,737**	**-0,829**	-0,162	-0,175	0,489	**-0,841**	**0,890**	-0,189
Ethyl isobutyrate*	**0,637**	-0,452	**-0,915**	**-0,928**	-0,446	**-0,660**	0,287	**-0,696**
Ethyl isovalerate*	0,590	-0,386	**-0,920**	**-0,928**	-0,493	-0,587	0,208	**-0,667**
2-Phenyl ethanol*	**0,613**	-0,388	**-0,976**	**-0,978**	-0,438	-0,551	0,207	**-0,802**

Alcohols in general and 2-Phenyl ethanol in particular (rose flower flavor) increase concentration in cooler climates. Esters in general, Ethyl isobutyrate and Ethyl isovalerate in particular (related with floral and fruity flavors) are also more important in cooler conditions.
Terpens in general and P-1-Menthen-7.8-diol in particular (mainly related with herbal flavors) and Norisoprenoids (related with herbal and fruity flavors) are more concentrated in warm climates.
Some thiols like FFT (coffe flavor), BTM (powder flavor); and 4MMP (rue, tomato leaf) show a tendency to increase concentration in warmer climates, while other thiols like 3MH (grape fruit, passion fruit) show the opposite behavior in relation with temperature.
Aldehids, sulfurs, furans and C6 compounds did not show correlation with the geographic and climatic factors considered in this trial.

Table 5: Correlation among families of aromatic compounds and aromatic compounds (*) with flavors.

	Red berries	Plums	Jam	Violet flowers	Blackberry	Eucalyptus	Clove, cinnamon	White pepper	Rosemary, thyme
Acids	-0,35	-0,50	-0,56	0,12	-0,17	0,42	0,18	**0,67**	0,14
Alcohols	0,09	0,41	0,41	0,47	**0,68**	-0,13	0,23	-0,08	-0,75
Aldehydes	0,17	0,42	0,33	0,09	0,27	-0,11	0,46	-0,43	-0,26
C6 compounds	-0,25	0,19	0,07	0,53	**0,61**	0,22	-0,12	-0,39	-0,20
Furans	**0,66**	0,20	0,39	-0,69	-0,50	-0,51	0,12	-0,29	0,16
Ketones	0,26	0,27	0,42	-0,05	0,13	-0,41	-0,09	0,06	-0,40
Sulfurs	-0,39	-0,35	-0,43	**0,64**	0,50	**0,70**	0,07	0,13	-0,05
Esters	0,48	**0,66**	0,48	-0,06	0,07	-0,48	**0,77**	-0,37	-0,61
Terpenes	-0,51	-0,77	-0,78	0,44	0,13	**0,87**	-0,24	0,41	0,38
Norisoprenoides	-0,35	-0,76	-0,69	-0,28	-0,58	0,44	-0,45	0,43	**0,85**
FFT*	0,24	-0,19	0,00	-0,64	-0,63	-0,24	-0,36	0,01	0,53
BTM*	0,11	-0,28	-0,03	-0,66	-0,67	-0,24	-0,04	**0,63**	0,35
4MMP*	0,09	-0,27	-0,10	-0,66	-0,70	-0,18	-0,46	0,07	**0,67**
3MH*	-0,08	0,21	0,27	0,31	0,48	-0,03	0,12	0,09	-0,42
Ac3MH*	0,39	0,53	0,30	-0,11	-0,05	-0,30	**0,68**	-0,54	-0,29
P-1-Menthen-7.8-diol*	-0,65	-0,81	-0,82	0,52	0,21	**0,93**	-0,43	0,38	0,45
g-Butyrolactone*	0,44	0,37	0,25	-0,11	-0,06	-0,28	**0,82**	-0,09	-0,46
Ethyl isobutyrate*	0,37	**0,79**	**0,67**	0,35	**0,64**	-0,38	0,50	-0,60	-0,84
Ethyl isovalerate*	0,37	**0,76**	**0,67**	0,37	**0,69**	-0,35	0,45	-0,59	-0,84
2-Phenyl ethanol*	0,25	0,56	0,52	0,49	**0,73**	-0,22	0,33	-0,30	-0,87

Relations between volatile compounds and flavors were studied (**table 5**). Alcohols in general show a tendency to be related with fruity and floral flavors (plums, jam, violet flowers). In particular 2-Phenyl ethanol correlated with Blackberry. C6 compounds even if they related to Blackberry it is not likely responsible of this flavor because their concentration is below the detecting threshold (data not shown). The same situation occurs between sulfurs (far under detecting threshold) and Violet flower and Eucalyptus. Acids seem to be related with white pepper. Furans show correlation with red berry flavor. Esters in general are related with Plums and Clove-cinnamon, and in particular, Ethyl isobutyrate and Ethyl isovalerate are related with Plums, Jam and Blackberry. Terpens in general are related with Eucalyptus, and P-1-Menthen-7.8-diol in particular shows a very high correlation with this flavor.

4 CONCLUSIONS

Average temperature of the season (GST) and Winkler Index seem to be a major factor determining aromatic profile on Argentinian Malbec wines, more important than latitude, altitude and minimal, maximal or diurnal variation of temperature of march (month previous to harvests). Malbec wines from Argentina are mainly characterized by their predominant fruity flavors. Spicy and herbal notes also are present, but they become more relevant in warm climates, this could explain the aromatic profile of some northern regions of Argentina (for example Cafayate, Salta) and warmer areas of Mendoza (not included in this study). Cooler climates show stronger flavors of violet flowers and blackberry, and this would explain the aromatic profile of wines of the highest parts of Uco Valley (San Carlos and Gualtallary, Mendoza) and Rio Negro in Patagonia. These differences could be partially explained by the variation of concentration of some compounds according to the climate (in particular temperature). Some of this aromatic compounds are more concentrated in warmer regions (norisoprenoids, acids and terpens), while others are more concentrated in cooler regions (alcohols, esters). The herbal notes of Eucalyptus in some Malbec wines could be explained by a higher concentration of P-1-Menthen-7.8-diol (for example Malbecs of Luján de Cuyo). Further studies need to be performed to complete and affirm these preliminary results. The present trial looks forward to be used as a reference for farther studies that should be performed in the future to deepen our knowledge on Malbec and the identity of Argentinian wines in other varieties too.

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