Fraction volatile de jeunes vins de Cabernet Sauvignon de l'État de Santa Catarina, un nouveau terroir du Brésil

Volatile fraction of young Cabernet Sauvignon from Santa Catarina state, a new terroir in Brazil

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Abstract

A total of 52 volatile compounds were measured in varietal Cabernet Sauvignon wines from four sites in Santa Catarina State (Brazil), over two consecutive vintages (2004 and 2005). Concentrations were measured by gas chromatography using FID, FPD and mass spectrometry as detectors. Principal Component Analysis of the concentrations of the varietal compounds showed a strong dependence on the characteristics of the soil in the vineyards ($p<0.05$). In contrast, little differentiation of the fermentative aromatic compounds was found in each vintage at all the sites. The levels of α- ionone (violet note) and β-ionone (violet, berry notes) were inversely related. ß-ionone was found above its threshold concentration (90 ng/l) in all samples except Bom Retiro 2004 vintage. α-Ionone was found to be well below its threshold concentration (400 ng/l) in all the samples. Only the Bom Retiro wines have higher concentrations of α- ionone than β-ionone, in both vintages. This indicates that these compounds can be markers for differentiating these Cabernet Sauvignon wines. The vineyard soils were classified as Inceptisols (for São Joaquim A, São Joaquim B, Bom Retiro vineyards) and as Oxisols (for Videira vineyard), according to U.S.D.A. classification of soil taxonomy.

Keywords: Cabernet Sauvignon wine; aromatic composition; GC/FID/FPD/MS analysis; principal component analysis, soil type.

Introduction

Unlike other agricultural commodities, wine is marketed by the geographical location of production, and quality is associated with minimal vineyard inputs or manipulation (Bisson et al., 2002). Aroma is one of the most important factors in determining wine character and quality. Over 800 different compounds are found in the volatile fraction of a wine but only some tens are odour-active and must be considered for differentiation purposes (Ebeler, 2001).

Because the location of the vineyard is frequently associated with a wine's characteristics and quality, the practice of certifying the geographic origin of wines has increased considerately in the few last years. Identification of wine aroma components and the relationships between relative content may be a useful tool in differentiating the wines from different regions and varieties and it may verify their authenticity. The aims of the current study are to characterize the volatile fraction of Cabernet Sauvignon wines from four different sites in Santa Catarina State, Brazil, and to report the soil description of this new grape growing region. Volatile fractions were evaluated by GC-FID, GC-FPD and GC-MS and chemometric analysis (PCA), in to order to characterize their aromatic profiles.

Material and Methods

Experimental area and soil analyses

Soil and wine samples from Cabernet Sauvignon plantings taken from four commercial vineyards in Santa Catarina State, Brazil, were studied. The following sample codes were used: SJA (coordinates:

28º16' 41” lat. and 49º55' 96” long.) and SJB (coordinates: 28°19’0’’ lat. and 49°34’51’’ long.) correspond to São Joaquim vineyards, at 1415 and 1160 m altitude above sea level (asl), respectively; BR corresponds to Bom Retiro vineyard (coordinates: 27°51’80’’lat. and 49°35’43’’ long.) at 960 m asl and VID corresponds to Videira vineyard (27°0’14’’lat. and 51°9’0’’long.) at 774 m asl. These vineyards were selected all had the same rootstock (paulsen 1103), clone (R-5), age (4-5 years) and conduction vineyard system (V System). The only exception was the clone (A) in São Joaquim, which is unknown. At each site, two adjacent rows of 30 plants each were examined. Soil profile observations were fully described according to the FAO guidelines (2006). Soil colors were described according to the Munsell code (Munsell, 1990). Soil sampling followed the procedure in the *National Soil Survey Handbook* published by the U.S. Department of Agriculture (U.S. Department of Agriculture, Natural Resources Conservation Service, 2005) and soil classifications followed the procedure in the U.S. soil taxonomy (Soil Survey Staff, 1998).

Wines sample

Replicated wine fermentations were prepared for each sample. The wines were produced prepared at EPAGRI, in Videira, SC, Brazil, using a previously reported microvinification procedure (Falcão et al., 2007).

Reagents

Internal standards employed were all from Sigma-Aldrich-chemie (Germany) and the solvents from SDS (France).

Analysis by GC-FID

The assay of higher alcohols, acetaldehyde and methanol and the assay of C4-C12 fatty acids, ethyl esters, alcohols acetates, C6-aldehydes and C6-alcohols were carried out according to the protocols of the Laboratory of Analytical Chemistry, at Bordeaux University.

Analysis by GC-MS. Assay of α- and β-ionones

The isomers were analysed according to Falcão et al. (2007). *The assay of free monoterpenols and the assay of volatile phenols* were carried out according to the protocols of the Laboratory of Analytical Chemistry, at Bordeaux University.*Assay of furaneol.* The method used by Guedes de Pinho and Bertrand (1995), was modified by Falcão et al. (2008).

GC-FPD Analysis. Determination of volatile sulphur compounds

The method of Beloqui and Bertrand (1995) was followed. *Determination of low boiling point volatile sulphur compounds* was carried out according to the headspace method used in the Laboratory of Analytical Chemistry, at Bordeaux University.

Data analysis

The software used for ANOVA and Principal Component Analysis (PCA) was Statistica 6 (2001) (StatSoft Inc., Tulsa, OK, USA).

Results and Discussion

Soil chemical composition, surface and specific characteristic

According to U.S.D.A. classification (Soil Taxonomy, 1998) the soils are classified as Inceptisols for all the vineyards, except for Videira, which was Oxisols. All the vineyards have well-drained soils without stones (Table 1). The clay-siltey texture of the inceptisols and the clayey texture of oxisols contribute to a high water-retention capacity. Under natural conditions these soils have low nutrient availability, high acidity and medium to high aluminum character. However, after corrections, these soils become epitrophic, and this makes them suitable for vine growing (Table 1). The pH analyses show slight acidity in the epipedons and acidity in the subsurface of the soils for all de sites. Organic matter and potassium levels in the epipedons section were very high for all vineyards, increasing soil fertility; consequently, vine nutrition may be improved. Potassium exchange has a positive influence on yield, plant vigor, and drought resistance (Chone et al., 2001). This was notably higher for São Joaquim (B) and Bom Retiro soils.

Soils description							Chemical analysis											
vineyards	USDA soil classification	asl (m)	horizon	Color	texture	consistence	depth (cm)	clay (%)	organic matter (%)	pH	P availability (mg/kg)	K exchange (mg/kg)	Mg exchange (mg/kg)	Al availability (mg/kg)	Ca availability (mg/kg)	sum of bases*	saturation of bases*	capacity of exchange ionic
SJA	Inceptisols	1415	Ap1	10YR/3/2	clay-siltey	soft, friable, and 'plastic', with high water retention capacity	0-20	31.0	7.0	5.9	3.2	165.0	5.5	0.0	10.5	16.4	64.0	25.5
							20-40	33.0	5.8	5.3	1.8	77.0	3.5	1.4	5.5	9.2	51.0	18.1
SJB		1160	Ap1	10YR/3/2		friable, with high water retention capacity	0-20	48.0	5.2	6.1	3.7	209.0	4.2	0.0	9.9	14.6	68.0	21.4
							20-40	70.0	3.3	5.2	1.0	63.0	1.6	0.8	3.6	5.4	51.0	10.5
BR		960	Ap1	10YR/2/1		friable, with high water retention capacity	0-20	31.0	5.6	6.1	10.1	247.0	4.1	0.0	13.2	17.9	71.0	25.1
							20-40	33.0	4.7	5.2	4.6	116.0	2.0	2.5	5.0	7.3	46.0	15.9
VID	Oxisols	774	Ap1	2.5YR4/6		friable, with high water retention capacity	0-20	70.0	4.1	5.4	2.8	142.0	3.6	0.0	5.6	9.7	56.0	16.5
							20-40	72.0	4.1	5.1	20.0	98.0	2.5	1.2	4.1	6.8	36.0	19.1

Table 1 Soils description and chemical analyses.

The percentage of organic matter, a measure closely related to fertility, was 1.3 - 1.7 times higher in the Inceptsoils than in the Oxisols. As shown in Table 1, a further difference was the percentage of clay, which was considerably higher in Oxisols. In general, very argillaceous soils have been shown to be associated to tannic characteristics in excess in wines (Fregoni et al., 1980).

Gas chromatography analyses

In general, significant differences between the concentrations of most of the varietal compounds were observed between the sites in each vintage analyzed ($p<0.05$). In contrast, independent of the site, the fermentative aromatic compounds in the wines generally have similar concentrations in each vintage (data not shown).

Multivariate analysis.

Application of principal components analysis (PCA) was carried out on correlation matrix (Figure 1 and Table 1). Figure 1 gives the results of PCA on the aroma profile of Cabernet Sauvignon wines for 2004 and 2005 vintages. Figure 1A shows Factor 1 *x* Factor 2 axes, that explain 65,8 % of the total variance among the data; the first axis represents 43.02 % and the second axis, 22.78 % of the total dispersion. Factor 1 axis shows mainly the opposition between the isomers α- and β-ionone that were, respectively, strongly positively and negatively correlated to Factor 1 axis.

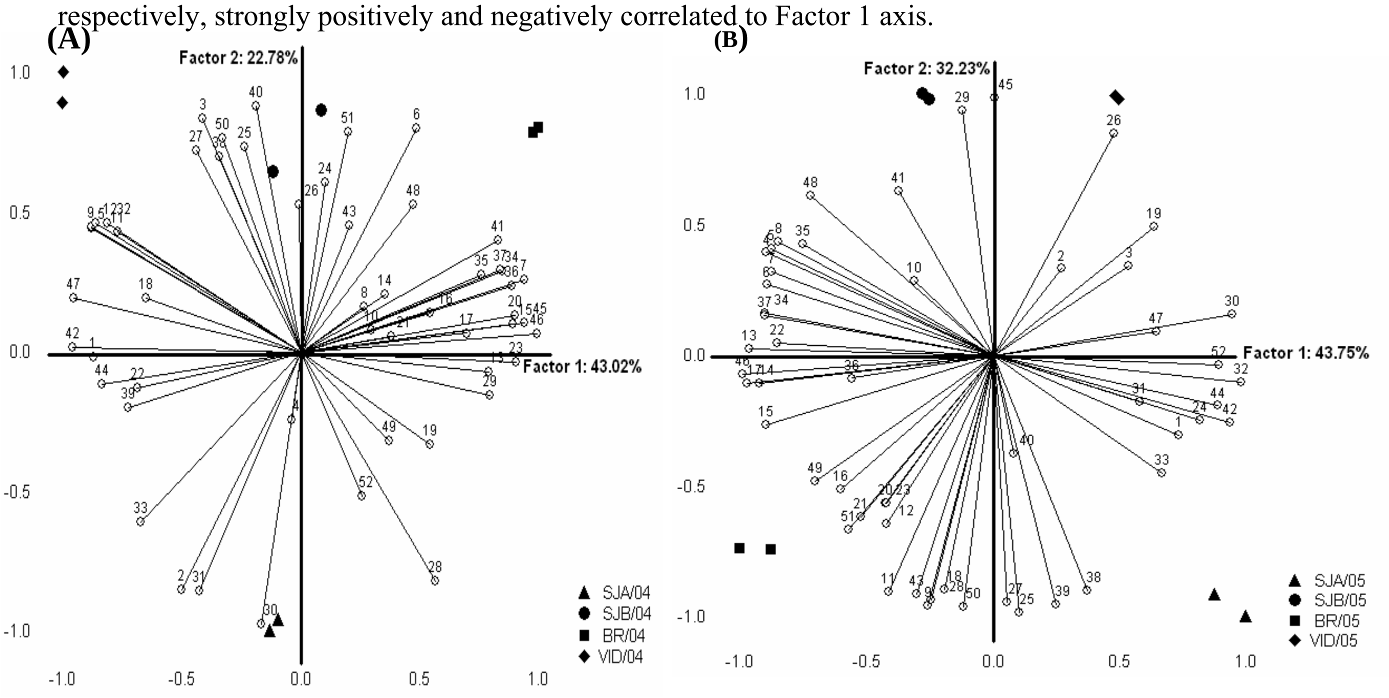

Figure 1 PCA on the volatile compounds content in Cabernet Sauvignon wines from 2004 (A) and 2005 (B) vintages. Where: SJA = São Joaquim (A) wines; SJB = São Joaquim (B) wines; BR= Bom Retiro wines; VID = Videira wines. 1= acetaldehyde; 2= methanol; 3= 1-propanol; 4= 2-methyl-1-propanol; 5= 1-butanol; 6= 2-methyl-1-butanol; 7= 3-methyl-1-butanol; 8= Σ major alcohols; 9= butyric acid; 10= isobutyric acid; 11= isovaleric acid; 12= Σ C_4-C_5 acids; 13= hexanoic acid; 14= octanoic acid; 15=decanoic acid; 16= dodecanoid acid; 17-Σ C_6-C_{12} acids; 18= ethyl butyrate; 19= ethyl hexanoate; 20= ethyl octanoate; 21= ethyl decanoate; 22= ethyl dodecanoate; 23= Σ C_6-C_{12} fatty acids ethyl esters; 24= Σ free monoterpenols; 25= 2-linalool; 26= α-terpineol; 27= β-citronellol; 28= nerol; 29= geraniol; 30= 4-ethyl-guaiacol; 31= 4-ethyl-phenol; 32= 4-vinyl-guaïacol; 33= 4-vinyl-phenol; 34= isoamyl acetate; 35= hexyl acetate; 36= 2-phenylethyl acetate; 37= Σ alcohols acetate; 38= ethyl lactate; 39= diethyl succinate ; 40= furaneol; 41= α-ionone; 42= β-ionone; 43= 2-phenylethanol; 44= 1-hexanol; 45= 2-mercaptoethanol; 46= 2-methyl tetrahydro thiophen-3-one; 47= ethyl-3(methylthio)propanoate; 48= 3(methyltio) propyl acetate; 49= methionol; 50= 3-(methylthio)propanoic acid; 51= hydrogen sulfide; 52= methanthiol.

Projection of the cases onto these two axes showed that in 2004 vintage (Figure 1 A), wines from São Joaquim A (SJA/04) are better correlated with the secondary fermentative compounds volatile phenols, and to 2-methylpropan-1-ol. São Joaquim B wines (SJB/04) were more correlated to varietal compounds furaneol, Σ free monoterpenols, 2-linalool, α- terpineol, and to fermentative compounds such as 2-phenylethanol, and ethyl lactate. Bom Retiro wines (BR/04) were more correlated to α-ionone and to 3-(methylthio)propyl acetate. Videira wines (VID/04) were more correlated to β-citronellol, and to the Σ C_4-C_5 acids, butyric acid, and isovaleric acid.

Compounds	2004 vintage		2005 vintage	
	Factor 1 axis	Factor 2 axis	Factor 1 axis	Factor 2 axis
Acetaldehyde	-0.871165		0.735066	
Methanol	-0.500361	-0.851708		
Propan-1ol		0.834204	0.536627	
2-Methylpropan-1-Ol			-0.89553	
Butan-1-Ol	-0.878785		-0.87737	
2-Methylbutan-1-Ol	0.488051	0.799520	-0.89441	
3-Methylbutan-1-Ol	0.940218		-0.87462	
Σ Major Alcohols			-0.84748	
Butyric Acid	-0.880723			-0.96057
Isovalerianic Acid	-0.771432			-0.90683
Σ C4-C5 Acids	-0.811540	0.460569	-0.4228	-0.64683
Hexanoic Acid	0.792502		-0.96158	
Octanoic Acid			-0.92524	
Decanoic Acid	0.892634		-0.89839	
Dodecanoic Acid	0.545037		-0.60229	-0.51204
Σ C6-C12 Acids	0.698772		-0.97266	
Ethyl Butyrate	-0.649848			-0.8964
Ethyl Hexanoate	0.544530		0.635593	0.492681
Ethyl Octanoate	0.899459		-0.42497	-0.56814
Ethyl Decanoate			-0.5216	-0.61925
Ethyl Dodecanoate	-0.687704		-0.85091	
Σ C6-C12 Fatty Acid Ethyl Esters	0.905053			-0.56788
Σ Free Monoterpenols		0.607144	0.816166	
2-Linalol		0.733528		-0.98553
3-Terpineol		0.525316	0.479772	0.848443
4-B-Citronellol		0.722957		-0.94435
5-Nerol	0.567869	-0.820785		-0.93716
6-Geraniol	0.797347			0.937341
4-Ethylgaiacol		-0.976589	0.944367	
4-Ethylphenol		-0.858012	0.58142	
4-Vinylgaiacol	-0.864045		0.982446	
4-Vinylphenol	-0.672129	-0.611746	0.668159	
Isoamyl Acetate	0.849866		-0.90209	
Hexyl Acetate	0.758794		-0.75165	
Phenyl Ethyl Acetate	0.889340		-0.55684	
Σ Alcohols Acetates	0.842089		-0.90367	
Ethyl Lactate		0.699166		-0.89986
Diethyl Succinate	-0.723813			-0.95615
Furaneol		0.880221		
A-Ionone	0.832886			0.630297
B-Ionone	-0.958500		0.938629	
2-Phenylethanol		0.451002		-0.91313
1-Hexanol	-0.834712		0.890424	
2-Mercaptoethanol	0.940570			0.986168
2-Methyl Tetrahydro Thiophen-3-One	0.993979		-0.98779	
Ethyl-3(Methyl Thio) Propanoate	-0.954592		0.646754	
3(Methylthio)Propyl Acetate	0.474904	0.526141	-0.72239	0.611522
Methionol			-0.70533	-0.48159
3-(Methylthio)Propanoic Acid		0.764598		-0.963
Hydrogen Sulfide (H_2S)		0.786482	-0.56916	-0.66938
Methanthiol (MetSH)		-0.519269	0.89233	

Table 2 Summary of correlations from PCA analyses.

As in 2004, Factor 1 axis showed again in 2005 vintages the opposition between the isomers α- and β-ionone, with β-ionone strongly positively correlated to this axis. In 2005 vintage, projection of the cases onto these two axes showed that in 2005 vintage, wines from São Joaquim A (SJA/05) appear

more correlated to the free monoterpenols 2-linalool and β-citronellol, as well as to the secondary fermentative compounds ethyl lactate and diethyl succinate. São Joaquim B (SJB/05) was more correlated to varietal compounds α- terpineol, geraniol and α- ionone while Bom Retiro wines (BR/05) were more correlated to secondary fermentative compounds dodecanoic acid, methionol and ethyl decanoate. Videira wines (VID/05) was more correlated to α- terpineol.
In both vintages, furaneol and geraniol were strongly negatively correlated. Also, interestingly, geraniol has a strong positive correlation with α-ionone and negative strong negative correlation with the isomer β-ionone. These findings indicate that these molecules can be used as possible marker for these terroir. In conclusion, Cabernet Sauvignon wines were well separated by PCA. It was clear that the localization of the vineyard have a strong influence on the aroma wine. The isomers α- and β-ionones have a strong negative correlation between themselves and an interesting inverse ratio of these compounds was observed for Bom Retiro wines, indicating that these compounds can have a role as marker of these wines. Also, α-ionone presented an important negative correlation with geraniol while furaneol was inversely correlated to geraniol content in Cabernet Sauvignon wines, in both vintages.

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