VOLATILE PROFILE CHARACTERIZATION OF YOUNG CABERNET-SAUVIGNON WINES FROM A NEW GRAPE GROWING REGION IN BRAZIL

Leila Denise FALCÃO[1], G. de REVEL[2]*, Marie-Claire PERELLO[2], L. RIQUIER[2], J.-P. ROSIER[3], A. AYRTON AUZANI UBERTI[4] and Marilde T. BORDIGNON-LUIZ[1]

1: Departamento de Ciência e Tecnologia de Alimentos CAL/CCA/UFSC, Rodovia Admar Gonzaga, 1346, Itacorubi, 88034-001, Florianópolis-SC - Brazil
2: UMR 1219 Œnologie, Université de Bordeaux, INRA, ISVV, Faculté d'Œnologie, 351 cours de la Libération, 33405 Talence, France
3: Empresa de Pesquisa e Extensão Agropecuária de Santa Catarina (EPAGRI-SC) Estação Experimental de Videira, Brazil
4: Departamento de Engenharia Rural, CCA/UFSC. Rodovia Admar Gonzaga, 1346, Itacorubi, 88034-001, Florianópolis-SC, Brazil

Abstract

Aims: Volatile fractions were characterized for Cabernet Sauvignon wines from four different sites in Santa Catarina State, Brazil, a new grape growing region. Soil characteristics of the different sites were also assessed.

Methods and results: A total of 49 volatile compounds were determined in these wines by gas chromatography coupled to FID, FPD detectors and to mass spectroscopy. Principal component analysis correctly classified the wines for 2004 vintage according to their origin. α-Ionone and β-ionone were present in concentrations inversely proportional in the wines; in both vintages, furaneol® and geraniol were strongly negatively correlated.

Conclusion: Vineyard location had a strong influence on the volatile wine fraction. The varietal volatile compounds were a key factor in differentiating wines according to the sites.

Significance and impact of study: The importance of the volatile compounds to the overall quality of wines it's already known. Santa Catarina State is a new grape growing region in Brazil that has a varied orography and its climate strongly depends on elevation. Grapes harvested from climatically different regions produce very different wine characteristics. Therefore the need for volatile profiles of Cabernet-Sauvignon wines recently produced at Santa Catarina State had significant enological and economic importance.

Keywords: wine, Cabernet-Sauvignon, volatiles, gas chromatography, principal component analysis

Résumé

Objectif : L'objectif de ce travail est de caractériser le profil des composés volatils des vins de Cabernet-Sauvignon de différents sites dans l'État de Santa Catarina (Brésil), d'une nouvelle région viticole. Les caractéristiques du sol des différents sites sont aussi évaluées.

Méthodes et résultats : La concentration des 49 composés volatils dans les vins est déterminée grâce à la chromatographie en phase gazeuse reliée aux détecteurs FID, FPD et la spectroscopie de masse. L'analyse en composantes principales classifie correctement les vins des millésimes 2004 et 2005 selon leur origine. L'α-ionone et la β-ionone dans les vins sont présentes dans des concentrations inversement proportionnelles; et ce pour les deux millésimes ; le furanéol® et le géraniol sont fortement négativement corrélés.

Conclusion : Les données montrent que la localisation du vignoble a eu une forte influence sur la fraction volatile des vins. Les composés volatils variétaux sont apparus en tant que facteur clef dans la différentiation des vins selon leur origine.

Signification et impact de l'étude : L'importance des composés volatils sur la qualité globale des vins est déjà connue. L'État de Santa Catarina est une nouvelle région viticole au Brésil qui présente une orographie très variée et le climat de ces localités varie fortement selon l'altitude. Des raisins provenant de régions climatiquement différentes résultaient dans des vins aussi diverses. Ainsi, la connaissance du profil des vins de Cabernet-Sauvignon récemment produits dans l'État de Santa Catarina se justifie œnologiquement et économiquement.

Mots-clés : vins, Cabernet-Sauvignon, composés volatils, chromatographie en phase gazeuse, analyse en composants principales

manuscript received: 12th of March 2008 - revised manuscript received: 25th of August 2008

*Corresponding author: revel@oenologie.u-bordeaux2.fr

J. Int. Sci. Vigne Vin, 2008, **42**, n°3, 133-145

INTRODUCTION

Unlike most agricultural commodities, wine is marketed by its geographical location of production, and quality is associated with minimal crop intervention or winemaking manipulation (BISSON *et al.*, 2002).

Aroma is one of the most important factors in determining wine character and quality. Over 800 different compounds constitute the volatile fraction of a wine but only some tens are odour-active and must be considered for differentiation purposes (EBELER, 2001). These compounds belong to very heterogeneous groups such as monoterpenes, higher alcohols, ethyl esters or fatty acids, norisoprenoids and pyrazines, among others. However, chemical composition data is insufficient for predicting human preference; efforts of flavor chemists have focused on linking chemical data to sensory measurements of flavor (BISSON *et al*., 2002, CHAPMAN *et al*., 2004) and to « terroir » (VAN LEEUWEN *et al*., 2004, CHAPMAN *et al*., 2005, PEREIRA *et al.*, 2007). Geographic certification of controlled origin of wines has drawn considerable recent interest because it is strongly associated with wine quality. Identification of wine aroma components and their quantitative relationships may be useful tools in differentiating wines by region and by variety. These data may also establish criteria for authenticity. Multivariate methods and chemometrics have been used to interpret and extract information from complex data obtained by instrumental techniques in wine analysis (BURATI *et al*., 2004 and SPERKOVÁ and SUCHANEK, 2005).

The wine producing nations of South America are making great strides to fully understand their products and the means to improve its quality (MC DONALD *et al*., 1998, MARTINELLI *et al*., 1998, BOIDO *et al*., 2003, SCHUARZ *et al*., 2003, MEDINA *et al*., 2005, BELANCIC and AGOSIN 2007).We have recently shown that in the regions we studied, there is a positive correlation between a vineyard's altitude (which has a colder growing season) and the amount of 2-methoxy-3-isobutylpyrazine in the wine it produces (FALCÃO *et al*., 2007). But because Brazil is an emerging country in wine production, a complete aroma profile of these wines is not yet known. This paper reports two critical aspects of wine from four different sites in Santa Catarina State, Brazil: characterization of the volatile fraction of its Cabernet-Sauvignon wines and the soil description data of this new grape growing region. Volatile fractions were evaluated using GC-FID, GC-FPD and GC-MS and chemometric analysis (PCA).

MATERIAL AND METHODS

1. Experimental area and soil analyses

Samples of Cabernet-Sauvignon wine from four commercial vineyards in Santa Catarina State (SC), Brazil, were analyzed: codes 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 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 (Figure 1). These vineyards have uniform rootstock (paulsen 1103), clone (R-5), age of vines (4-5 years) and conduction vineyard system (Y System). However, in São Joaquim (A), the clone is unknown. Inside each parcel 30 vines distributed in two rows were selected for winemaking tests. Soil profile measurements closely followed the FAO guidelines (FAO, 2006). In addition, all color descriptions listed in this study correspond to those used in the Munsell code (MUNSELL, 1990). Soil sampling was conducted according to the National Soil Survey Handbook published by the U.S. Department of Agriculture (U.S. Department of Agriculture, 2005) and soil classification was carried out according to parameters of the U.S. soil taxonomy (SOIL TAXONOMY, 1998).

2. Wine samples

Two replicated wine fermentations were prepared for each sample. The wines were produced under the same conditions of microvinification at EPAGRI (Empresa de Pesquisa e Extensão Agropecuária de Santa Catarina), in Videira town, SC, Brazil: The grapes were separated from the stalks, crushed and maintained in a 20 L capacity stainless steel vat. The maceration period was 10 days, with two daily pumpings over at 22 °C. The must was separated from the solid parts and transferred to 13 L capacity stainless steel vats. Prior to initiating alcohol fermentation, a commercial sulfiting agent (20 g 100 kg^{-1} of must, corresponding to 10 mg L^{-1} of free SO_2) (Noxitan, Pascal Biotech, Paris), *Saccharomyces cerevisae* strain (20g 100 kg^{-1}) (Fermol rouge, Pascal Biotech, Paris) and commercial enzymes with pectinolytic activity (2-4 g hL^{-1}) (Pectinex SPL/Ultra, Pascal Biotech, Paris) were added to the musts. Malic acid consumption by lactic bacteria occurred spontaneously within 20-25 days. Once alcohol fermentation had finished, the wines were chilled to 4 °C for 10 days, Noxitan (35 mg L^{-1} of free SO_2, on average) was added, before bottling. All the samples were between 14 and 20 months old, at the time of analysis. The 2004 and 2005 wine samples were stored at 5 °C prior to analysis and were analyzed at Bordeaux University.

3. Classical wines and grape analyses

Total soluble solids (TSS), pH, titratable acidity (TA) levels were carried out in grape samples at the moment of harvest (OIV, 1990). Maturation indices were calculated in grapes at maturity (TSS AT^{-1} and TSS x pH^2). Titratable acidity, volatile acidity, ethanol and pH in the wines were also carried out according to protocols established by the OIV (1990); malic acid was quantified using an enzymatic kit (Boehringer, Mannheim, Germany/R-Biopharm).

4. Volatile compound analyses

Higher alcohols, methanol, C4-C12 fatty acids, free fatty acids ethyl esters, alcohols acetates esters, C6-alcohols and C6-aldehydes were determined by GC-FID. Volatile phenols, free monoterpenols, α- and β-ionones and dimethyl-4-hydroxy-furan-3-one (furaneol®) were determined by GC/MS/SIM.

5. Reagents

Internal standards used were: 4-methylpentan-2-ol (Sigma-Aldrich-chemie GmbH, Germany) octan-3-ol (Sigma, USA), 4-methylsulfanylphenol (Sigma, USA), thiophen (Sigma-Aldrich-chemie GmbH, Germany), 2-methoxy-3-methyl pyrazine (Aldrich Chemicals Co., Millwaukee, WI, EUA), octan-2-one (Sigma, USA). The solvents employed were dichloromethane (ultra-high-purity, Merck, Darmstadt, Germany) and ether (99.7 % min, SDS, France), isohexane (99.7 %, SDS, France) and ethanol (99.9 % minimum, Merck, Germany).

6. Sample extraction procedure

Liquid-liquid extractions were performed for all the samples. Wine samples (50 mL) were extracted by stirring for 5 min with 4 then 2 then 2 mL of ether:isohexane (1:1, v:v) (esters, acids and aldehydes) or dichloromethane (other volatile compounds). The decanted organic phases were collected and any stable emulsions were broken by stirring. Determination of the different compounds was made in two repetitions.

7. Analysis by GC-FID

a- Assay of higher alcohols and methanol

An Agilent Tech. 5890 series II gas chromatograph, equipped with a FID detector, an automatic injector (5890 Series II Injector) and a CP-WAX 57 CB (50 m x 0.25 mm, film thickness 0.20 µm; Varian, Les Ullys, France) capillary column were used. Sample (0.4 µL) was injected in split mode (split: 1/ 60). The carrier gas pressure (Hydrogen 5.0) was 18 psi with a linear velocity of 1.5 mL min^{-1}. Temperature program: held 5 min at 40 °C, raised at 4 °C/min to 100 °C and held in this temperature for 0 min. The injector and detector were 200 °C and 240 °C, respectively. Fifty millilitres of wine were distilled (Gibertini apparatus, BT 10D, Italy) and to the initial 5 mL of distillate was added 50 µL of 4-methyl pentan-2-ol (10 g L^{-1}, in an ethanol 50 % solution) as internal standard. The GC-FID analysis was identical with that for the extracted samples.

b- Assay of C4-C12 fatty acids, ethyl esters, alcohols acetates, C6-aldehydes and C6-alcohols

A Carlo Erba HRGC 5300 gas chromatograph (Thermo Separation Products, Courtabœuf, France), equipped with a FID detector and a FFAP capillary column (BP 21: 50 m x 0.32 mm, film thickness 0.25 µm; SGE, Courtabœuf, France) was used. Two microliter extract sample were injected in split/splitless mode (division: 30 mL min^{-1} and split time: 0.5 min). The carrier gas pressure (Hydrogen 5.0) was 8 psi with a linear velocity of 1.5 mL min^{-1}. Temperature program: held 5 min at 40 °C, raised at 2 °C min-1 to 220 °C and held 25 min. The injector and detector temperature were 200 and 250 °C, respectively. Two hundred µL of octan-3-ol solution (400 mg L^{-1} in 50 % ethanol) and 300 µL of an orthophosphoric acid solution (1/3) were added to 50 mL of wine sample. This mixture was extracted with ether:isohexane (1:1, v:v).

8. Analysis by GC-MS

An Agilent Tech. 6890 series system gas chromatograph, with a mass spectrometer detector and equipped with a FFAP capillary column (BP 21: 50 m x 0.32 mm, film thickness 0.25 µm, SGE, Courtabœuf, France) and an automatic injector (HP 6890 Series Injector) was used to analyse free monoterpenols, furaneol and volatile phenols. Mass spectra were acquired in the electron impact mode at 70 eV. The mass range was 50-600 *m/z*, and the electron multiplier was set in the relative mode autotune procedures. The identification of the volatiles compounds in GC-MS was confirmed by comparing both their mass spectra in SCAN mode (NBS75K library) and their retention times in relation to the standards.

a- Assay of free monoterpenols

Two hundred µL of octan-3-ol (400 mg L^{-1} in 50 % ethanol solution) was added to 50 mL of wine sample. The sample was extracted with ether:isohexane (1:1, v:v). Two microliters of the extract was injected using an automatic sampler in splitless mode. The injector was heated to 250 °C with a division of 30 mL min^{-1} and a split time of 0.5 min. The detector temperature was 280 °C. The carrier gas pressure (Helium 5.6 Alphagaz) was 20 psi with a linear velocity of 4.1 mL min^{-1}. The oven temperature program was held 1 min at 40 °C, increased at 3 °C min^{-1} to 200 °C and held at this

temperature for an additional 30 min. Quantification was carried out in SIM mode, selecting the ions as follows: *m/z* = 41, 55, 59, 61, 67, 69, 71, 79, 82, 83, 93, 106, 121 and 135 for linalool, α-terpineol, β-citronellol and nerol. Peak integrations were made using all ions except for geraniol, that quantification was carried out using only ion *m/z* = 93 and in this case, the octan-3-ol was quantified using only ion *m/z* = 83.

b- Assay of furaneol

The method used was adapted from GUEDES DE PINHO and BERTRAND (1995). Ten µL of octan-2-one internal standard solution (2.0 g L^{-1} in 50 % ethanol solution) was added to 50 mL of wine sample. The mixture was extracted with dichloromethane as described above. Two microliters of the extract were injected using an automatic sampler in splitless mode with pressure, flow and temperature programs as reported above for the monoterpenols except that the initial oven temperature was held for 5 min at 60 °C and increased at 3 °C min^{-1} from 60 to 200 °C and held at this temperature for 15 min. Quantification was carried out in SIM mode following the ions at *m/z* = 57, 85 and 128 for quantification and *m/z* = 128 for quantification.

c- Volatile phenols

Two thousand µL of dodecanol solution (674 mg L^{-1} 50 % of ethanol) was added to 50 mL of wine sample. These samples were extracted with dichloromethane. Two microliters of the extract were injected using the same temperature, flow and pressure program as for the monoterpenols except that the final temperature, 200 °C, was held for 15 min. Quantification was carried out in SIM mode, following ions m/z = 91, 137 and 152 to 4-ethylgaïacol; *m/z* =107 and 122 for 4-ethylphenol; *m/z* = 107, 135 and 150 for 4-vinylgaïacol, *m/z* = 91 and 120 for 4-vinylphenol and *m/z* = 83 for dodecanol (internal standard).

9. GC-FPD analysis

a- Determination of volatile sulphur compounds

The method used was adapted from BELOQUI and BERTRAND (1995). Fifty mL of wine samples were treated with 50 µL of 4-(methylsulfanyl)phenol at 702 mg L^{-1} (hydroalcoholic solution, 50 % of ethanol), internal standard and 200 µL of di-tertbutyl-para-cresol and 1.1 mg L^{-1} and 300 µL of H_3PO_4 1/3 (v/v with water). These mixtures were extracted twice with 5 mL dichloromethane by stirring 5 min. The combined organic solutions were dried with 5.0 g anhydrous sodium sulphate and concentrated under nitrogen to one-fourth their initial volumes. Two µL of extract were injected in an Agilent Tech., HP 6890 gas chromatograph Series II fitted with a flame photometric detector (FPD). The column was a FFAP capillary column (BP 21: 50 m x 0.32 mm, film thickness 0.25 µm, SGE, Courtabœuf, France). The oven temperature program was held 1 min at 40 °C, increased at 3 °C min^{-1} of 40 °C to 220 °C, the final step for 20 min. The carrier gas was hydrogen 5.0 (1.5 mL min^{-1}). The injector was a splitless system: the splitless time was 20 s and the split vent 30 mL min^{-1}. The injector and detector temperature were 250 and 220 °C, respectively.

b- Determination of low boiling point volatile sulphur compounds

Identification (using authentic samples) and quantification was carried out on 50 mL samples mixed with 100 µL of thiophene internal standard at 309 mg L^{-1} in a 125 mL bottle. The bottle was hermetically closed by a stopper and was tightened with a metal capsule. After 24 hours in the dark at a temperature of 22 °C, one mL of the gas phase was injected according to the headspace method. The gas chromatograph (Agilent Tech. 5890) was coupled with FPD detector. The column was HP 5 (30 m x 5 µm x 0.53 mm). The oven temperature was kept at 32 °C for one min and programmed at a rate of 10 °C min^{-1} to 100 °C and a final rate of 20 °C min^{-1} to 180 °C. The carrier gas was hydrogen at 5.0 (1.5 mL min^{-1}). The flow rate in the flame was 65 mL/min and a mixture of nitrogen:oxygen (80:20) at 80 mL min^{-1} was used. The make-up gas was Nitrogen 4.6 at 45 mL min^{-1}. The injector and detector were 70 and 150 °C, respectively.

10. Repeatability study of GC- methods

The statistical study is based on six consecutive determinations by six extractions of the same wine. The repeatability results of the chromatographic methods were good; variation analyses and coefficients are presented in table 4.

11. Data analysis

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

RESULTS AND DISCUSSION

1. Soil chemical composition, surface and specific characteristics

According to U.S.D.A. classification (SOIL TAXONOMY, 1998), the soils used in our study are classified as Inceptisols for all the vineyards, except Videira, where was Oxisols (table 1). All the vineyards have well drained soils without stones (table 1).

The untreated soils we evaluated had little availability of nutrients, with high acidity and aluminium character.

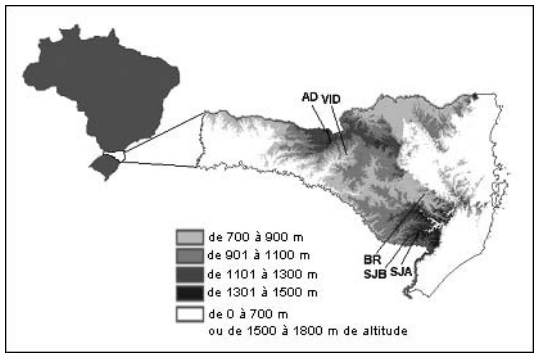

Figure 1 - Map of the Santa Catarina State, Brazil, showing location of the viticultural sites of this study.
SJA = São Joaquim (A) wines; SJB = São Joaquim (B) wines; BR= Bom Retiro wines; VID = Videira wines. Acknowledgement: EPAGRI/CIRAM.

Table 2 gives the soil chemical profile of the different sites studied. Once treated however, these soils became epitrophic, making them suitable for vine growth (table 2). The pH data gave slightly acidic values in the epipedons and acidic in the subsurface of the soils for all de sites. Organic matter and potassium levels in the epipedons section were considerably higher for all vineyards, increasing soil fertility and probably vine nutrition. Organic matter percentage, a measure closely related to fertility, was generally higher in the Inceptsols (from 1.3 to 1.7 times) than the Oxisols. Also shown in table 2, the percentage of clay, which was significantly higher in the Oxisols; very argillaceous soils are generally associated with excessive tannic characteristics in wines (FREGONI, 1980).

According to SABON *et al.* (2002), excessive quantities of water can be detrimental for grape composition; vine vigor and production is greater, but rot development is promoted, reducing harvest quality. The clay-siltey texture of inceptisols and the clayey texture of oxisols contribute to water-retention capacity. In a recent work, ANDRÉS-DE PRADO *et al.* (2007) compared two vineyards; the more fertile one also had a greater water-holding capacity, but produced wines with significantly lower color intensity and shade, a lower total phenolic composition and lower amounts of hydroxycinnamic compounds.

2. Classical analyses in grapes and wines

Table 3 gives the results of some classical analyses in grapes at the moment of harvest and in the wines. The TSS results (more than 20 °Brix) indicated that Cabernet-Sauvignon grapes reached a good maturation stage, and this is confirmed by the maturation commercial indices. L-malic acid dominates the organic acids present. Table 3 also shows a drop in titratable acidity and an increase of pH in the wines as a result of malolatic fermentation. In general, the wines analyzed had completed this fermentation except for Videira wines of 2004 vintage. The predominant non-volatile organic acids are tartaric acid and malic acid, accounting for 90 % of the titratable acidity of grape juice; levels between 4.8-5.1 g L^{-1} are considered as good total acidity. The volatile acidity of wines is usually between 0.5 and 1.0 mg L^{-1} (10 - 15 % of the total acid content) of which acetic acid usually constitutes about 90 % (FOWLES, 1992). According to DUBOIS (1994), the optimal volatile acidity concentration in wines ranges between 0.2 and 0.7 g L^{-1}. In São Joaquim (A) and Videira wines from 2004 vintage, or São Joaquim (A) from 2005 vintage values of 0.7 g L^{-1} or higher it were observed.

Table 1 - Soils description

Vineyards	Soils description					
	USDA soil classification	Altitude asl (m)	Color	Structure	Texture	Consistence
SJA	Inceptisols	1415	10YR/3/2 (very dark grayish brown)	moderated	clay-siltey	soft, friable, and «plastic», with high water retention capacity
SJB		1160				
BR		960	10YR/2/1 (black)			
VID	Oxisols	774	2.5YR4/6 (red)	strong		

SJA = São Joaquim A ; SJB- São Joaquim B, BR = Bom Retiro, VID = Videira. Asl = above sea level.

Table 2 - Soil chemical analyses.

			Chemical Analyses										
Vineyards	Horizon	Depth (cm)	Clay (%)	Organic matter (%)	pH	P availability (mg kg^{-1})	K exchange (mg kg^{-1})	Mg exchange (mg kg^{-1})	Al availability (mg kg^{-1})	Ca availability (mg kg^{-1})	Sum of bases*	Saturation of bases*	Capacity of exchange ionic
SJA	A1	0-20	31.0	7.0	5.9	3.2	165.0	5.5	0.0	10.5	16.4	64.0	25.5
	A2	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	A1	0-20	48.0	5.2	6.1	3.7	209.0	4.2	0.0	9.9	14.6	68.0	21.4
	A2	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	A1	0-20	31.0	5.6	6.1	10.1	247.0	4.1	0.0	13.2	17.9	71.0	25.1
	A2	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	A1	0-20	70.0	4.1	5.4	2.8	142.0	3.6	0.0	5.6	9.7	56.0	16.5
	A2	20-40	72.0	4.1	5.1	20.0	98.0	2.5	1.2	4.1	6.8	36.0	19.1

SJA = São Joaquim A ; SJB- São Joaquim B, BR = Bom Retiro, VID = Videira. *(Ca + K +H).

Table 3 - Composition of the Cabernet-Sauvignon grapes and wines assayed (2004 and 2005 vintages).

Samples	Grape analyses*					Wine analyses				
	pH	TA (g L^{-1})	TSS (°Brix)	TSS x TA^{-1}	TSS x pH^2	pH	TA (g L^{-1})	VA (g L^{-1})	MA (g L^{-1})	A (% vol.)
2004 vintage										
São Joaquim (A)	3.68	5.7	21.7	38	294	3.7	4.8	0.7	0.11	13.0
São Joaquim (B)	3.69	6.5	20.3	31	276	3.8	5.0	0.5	0.09	13.0
Bom Retiro	3.66	6.5	22.0	34	295	3.8	4.8	0.5	0.08	12.5
Videira	3.50	7.0	21.0	26	257	3.8	5.4	0.5	0.48	12.3
2005 vintage										
São Joaquim (A)	3.53	7.1	22.0	31	277	3.7	5.1	0.9	0.04	13.0
São Joaquim (B)	3.80	6.7	23.5	35	332	4.0	4.6	0.5	0.08	13.5
Bom Retiro	3.79	8.2	21.0	26	313	3.7	5.1	0.5	0.14	13.0
Videira	3.57	8.5	21.5	25	279	3.8	4.8	0.7	0.06	12.8

* Analyses made in the harvest. TA = total acidity expressed in g L-1 of tartaric acid; TSS= Total soluble solids; VA = volatile acidity expressed in g L-1 of acetic acid; MA = malic acid content; A = alcohol content (%).

3. Gas chromatographic analyses

The volatile profiles of Cabernet-Sauvignon wines are presented in table 4.

In general, significant differences appeared between the most of the varietal compounds from the various sites in each vintage analysed ($p<0.05$). On the other hand, concentrations of compounds derived from fermentation were similar in each vintage (table 4).

It is interesting to note that flavour development during fermentation may be influenced by compounds in the grape berry that do not contribute directly to aroma and flavour, but instead change yeast metabolism leading to altered levels of aroma compounds. Furthermore, the influence of yeast type, malolactic fermentation and wood and bottle aging add to the complexity of wine flavour. Yeast-derived flavour compounds may be produced from grape berry precursors or from yeast metabolism alone.

At this point, we know that certain odorants common to all wines constitute a set of aromas which have a curious « buffer capacity » effect on wine aroma that has a somewhat indefinite odour. This buffer capacity can be overcome by groups of compounds having related odours;

Table 4a - Volatile composition of Cabernet-Sauvignon wines from Santa Catarina State Brazil (vintage 2004)

	2004 Vintage								
	SJ (A)		SJ (B)		BR		VID		VC (%)
Compound	χ	SD	χ	SD	χ	SD	χ	SD	
mg L $^{-1}$									
Methanol	207 a	11.10	174 b	4.40	158 c	1.70	181 b	14.60	9
2-Butanol	nd		nd		nd		nd		
1-Propanol	21.50 a	2.00	24.40 a,b	5.00	24.60 a,b	4.80	27.50 c	1.10	3
2-Methylpropan-1-ol	75.20 a	18.00	68.30 b	24.30	76.30 a	5.20	75.60 a	4.30	5
1-Butanol	1.60 a,b	0.50	1.70 a	0.00	1.50 b	0.00	2.10 c	0.30	6
2-Methylbutan-1-ol	80.30 a	6.90	82.10 a,b	6.50	82.70 b	11.20	81.30 a,b	2.60	5
3-Methylbutan-1-ol	266 a	79	284 b	18	293 c	90	258 d	25	4
Σ Higher major alcohols	**444.60 a**	**100.38**	**460.50 a**	**107.07**	**478.10 a**	**110.47**	**444.50 a**	**96.66**	
2-Phenylethanol	42.73 a	8.14	57.01 a	17.67	90.16 a	63.81	78.95 a	5.60	8
1-Hexanol	1.88 a	0.09	2.23 a	0.23	0.62 b	0.12	2.29 a	0.70	3
Trans-2-hexenal	τ		τ		τ		τ		2
Cis-3-hexen-1-ol	τ		τ		τ		τ		6
Trans-2-hexen-1-ol	τ		τ		τ		τ		5
Isoamyl acetate	0.47 a	0.03	0.48 a	0.02	2.97 b	0.33	0.41 a	0.26	3
Hexyl acetate	nd		nd		0.06	0.03	nd		11
Phenyl ethyl acetate	0.03 a	0.00	0.03 a	0.00	0.26 b	0.02	nd		28
Σ Higher alcohols acetates	**0.50 a**	**0.26**	**0.51 a**	**0.27**	**3.29 b**	**1.63**	**0.41a**	**0.23**	
Ethyl butyrate	6.22 a	0.16	4.58 a	5.39	5.88 a	0.15	11.75 b	1.05	9
Ethyl lactate	105.02 a	32.88	183.66 b	11.12	130.83 a,b	5.22	165.70 a,b	13.10	6
Diethyl succinate	10.74 a	2.15	13.67 a	1.14	1.01 b	0.28	10.74 a	3.40	4
Ethyl hexanoate	0.32 a	0.04	0.42 a	0.01	0.34 a	0.02	0.18 b	0.02	2
Ethyl octanoate	0.37 a,b	0.01	0.45 b,c	0.06	0.52 c	0.06	0.22 a	0.06	6
Ethyl decanoate	0.13 a	0.02	0.08 a	0.12	0.17 a	0.03	0.14 a	0.00	27
Ethyl dodecanoate	0.01 a	0.01	nd		nd		0.02 a	0.01	48
Σ C6 - C12 fatty acid ethyl esters	**0.83 a**	**0.17**	**0.95 a**	**0.23**	**1.03 a**	**0.22**	**0.56 b**	**0.09**	
Isobutyric acid	13.46 a	2.66	15.63 a	6.10	13.87 a	1.20	12.09 a	0.40	31
Butyric acid	11.43 a	0.6	18.44 b	0.62	8.16 c	0.22	33.67 d	9.24	7
Isovalerianic acid	9.33 a	0.99	10.60 a	0.78	8.83 a	2.90	20.83 b	7.25	5
Σ C4-C5 acids	**34.22 a**	**2.26**	**44.67 a,b**	**4.81**	**30.86 a**	**3.13**	**66.59 b**	**10.16**	
Hexanoic acid	2.66 a,b	0.08	3.55 b	0.00	3.42 b	0.88	1.22 a	0.52	3
Octanoic acid	3.56 a	0.65	5.18 a	0.71	3.89 a	0.34	3.24 a	0.61	1
Decanoic acid	0.98 a	0.01	1.41 b	0.03	1.55 b	0.20	0.53 c	0.45	5
Dodecanoic acid	0.03 a	nd	0.04 a	nd	0.03 a	0.01	0.02 a	0.01	29
Σ C6-C12 acids	**7.23 a,b**	**1.60**	**10.18 a**	**2.28**	**8.89 b**	**1.78**	**5.01 a**	**1.41**	
µg L $^{-1}$									
4-Ethylgaiacol	3.09 a	0.31	0.29 b	0.13	nd		0.37 b	0.07	4
4-Ethylphenol	1.90 a	0.29	0.25 b	0.07	0.13 b	0.01	0.88 c	0.06	3
4-Vinylphenol	23.08 a	7.89	2.66 b,c	0.34	0.50 c	0.06	18.69 a,b	1.01	6
4-Vinylgaiacol	3.17 a,b	1.04	6.18 b	0.81	2.06 a	0.36	10.28 c	0.89	4
2-Mercaptoethanol	17.92 a	3.16	17.81 a	0.27	29.88 b	2.55	12.98 a	0.03	16
2-Methyl tetra hydro thiophen-3-one	47.88 a	0.70	59.93 b	0.10	124.52 c	4.01	nd		6
3-(Methylthiol) ethyl propanoate	20.67 a	1.40	20.79 a	0.30	17.85 a	0.67	25.91 b	0.13	10
3-(Methylthiol) propyl acetate	nd		nd		16.67 a	1.19	8.06 b	0.09	14
Methionol	1866 a	391.37	1687 a	18.11	1878 a	20.63	1688 a	16.87	2
3-(Methylthio) propionic acid	98.64 a	1.21	125.18 b	0.25	161.02 c	6.06	202.74 d	3.88	8
Hydrogen sulfide (H2S)	nd		0.44 a	0.62	1.03 a	0.04	0.88 a	0.02	16
Methanthiol (MetSH)	0.92 a	0.03	nd		0.79 a	0.12	0.45 a	0.30	11
Furaneol	*111.47 a*	*2.1*	*334.52 b*	*20.5*	*252.61a,b*	*3.9*	*314.85 b*	*91.7*	*7*
Linalool	*5.05 a*	*1.23*	*8.44 b*	*2.31*	*6.04 c*	*2.10*	*6.97 d*	*2.30*	*4*
α-Terpineol	*4.02 a*	*1.65*	*34.68 b*	*1.32*	*11.05 c*	*3.40*	*12.01 d*	*3.30*	*4*
β-Citronellol	*4.18 a*	*1.98*	*4.97 b*	*2.01*	*5.94 c*	*2.10*	*7.88 d*	*2.60*	*4*
Nerol	*4.20 a*	*2.10*	*1.97 b*	*1.12*	*2.94 c*	*1.90*	*0.85 d*	*0.21*	*4*
Geraniol	*3.21 a*	*0.56*	*0.42 b*	*0.12*	*5.80 c*	*0.40*	*0.97 d*	*0.30*	*4*
Σ Free monoterpenols	***20.66 a***	***0.6***	***50.48 b***	***14.1***	***31.77 c***	***2.9***	***28.68 a,c***	***4.8***	
ng L $^{-1}$									
α-Ionone	*66.34 a*	*8.09*	*68.20 a*	*15.70*	*162.16 b*	*5.99*	*75.12 a*	*2.57*	*12*
β-Ionone	*144.11 a*	*4.65*	*174.42 a*	*21.66*	*83.22 b*	*8.03*	*195.33 a*	*9.37*	*6*

SJ (A) = São Joaquim (A) wines (vineyard at 1415 m asl); SJ (B) = São Joaquim (B) wines (vineyard at 1160 m asl); BR = Bom Retiro wines (vineyard at 960 m asl) ; VID = Videira wines (vineyard at 774 m asl). χ = mean value; SD = standard deviation ; τ = traces; nd = not detected, VC (%) = variation coefficient of the method (n = 6). Different letters in the same line indicate significant difference (for each vintage) (Tukey Test HSD, $p<0.05$). In italics: varietal compounds.

Table 4b - Volatile composition of Cabernet-Sauvignon wines from Santa Catarina State Brazil (vintage 2005)

	Vintage 2005								
	SJ (A)		SJ (B)		BR		VID		VC (%)
Compound	χ	SD	χ	SD	χ	SD	χ	SD	
mg L $^{-1}$									
Methanol	226 a	9.78	214 b	5.10	179 c	3.60	162 d	12.10	9
2-Butanol	nd		nd		nd		nd		
1-Propanol	42.30 a	3.10	33.80 b	5.60	22.20 c	3.90	22.30 c	0.90	3
2-Methylpropan-1-ol	61.00 a	13.80	69.20 b	28.40	80.10 c	6.10	54.80 d	3.50	5
1-Butanol	1.40 a	0.80	1.50 b	0.20	1.90 c	0.10	1.40 a,b	0.20	6
2-Methylbutan-1-ol	61.30 a	8.10	68.90 b	5.80	90.30 c	10.00	67.60 b	1.50	5
3-Methylbutan-1-ol	204 a	68	234 b	16	355 c	80	228 b	19	4
Σ Higher major alcohols	**370.00 a**	**74.93**	**407.40 a**	**86.92**	**549.50 b**	**134.73**	**374..10 a**	**85.72**	
2-Phenylethanol	24.70 a	8.90	129.00 b	23.30	55.20 c	2.80	86.84 d	4.90	8
1-Hexanol	1.74 a	0.30	1.32 a	0.40	0.54 b	0.10	1.34 a	0.30	3
Trans-2-hexenal	τ		τ		τ		τ		2
Cis-3-hexen-1-ol	τ		τ		τ		τ		6
Trans-2-hexen-1-ol	τ		τ		τ		τ		5
Isoamyl acetate	0.32 a	0.07	0.78 b	0.10	1.79 c	0.20	0.77 b	0.21	3
Hexyl acetate	nd		nd		0.04	0.01	nd		11
Phenyl ethyl acetate	0.02 a	0.01	0.10 a	0.01	0.20 a	0.02	0.11 a	0.03	28
Σ Higher alcohols acetates	**0.34 a**	**0.18**	**0.88 b**	**0.42**	**2.03 c**	**0.94**	**0.88 b**	**0.42**	
Ethyl butyrate	3.98 a	1.00	6.37 b	1.01	5.49 c	0.50	7.44 d	1.75	9
Ethyl lactate	71.02 a	19.90	114.00 b	31.50	52.38 c	20.40	152.90 d	35.90	6
Diethyl succinate	1.46 a	0.60	4.17 b	1.50	0.62 c	0.20	3.87 b	1.60	4
Ethyl hexanoate	0.24 a	0.05	0.19 a	0.09	0.20 a	0.07	0.19 a	0.05	2
Ethyl octanoate	0.26 a	0.03	0.68 b	0.10	0.33 c	0.15	0.27 a,c	0.04	6
Ethyl decanoate	0.09 a	0.06	0.27 b	0.02	0.16 c	0.04	0.14 a,c	0.01	27
Ethyl dodecanoate	0.01 a	0.01	0.01a	0.00	0.02 a	0.00	0.01 a	0.01	48
Σ C6 - C12 fatty acid ethyl esters	**0.60 a**	**0.12**	**1.15 b**	**0.28**	**0.71 a**	**0.13**	**0.61 a**	**0.11**	
Isobutyric acid	8.00 a	3.10	5.55 b	2.29	13.26 c	0.72	11.52 d	0.60	31
Butyric acid	5.18 a	2.97	15.33 b	2.53	9.44 c	3.50	14.70 b	6.23	7
Isovalerianic acid	3.51 a	2.64	11.50 b	1.31	7.99 c	1.92	10.57 b	5.25	5
Σ C4-C5 acids	**16.69** a	**2.27**	**32.38** b	**4.93**	**30.69** b,c	**2.72**	**36.79** d	**2.16**	
Hexanoic acid	1.83 a	0.35	2.55 b,c	0.35	3.22 c	0.33	2.08 a,b	0.50	3
Octanoic acid	2.37 a	0.79	4.30 b	0.45	4.31 b	0.51	2.51 a	0.52	1
Decanoic acid	0.70 a	0.14	2.47 b	0.17	2.12 b	0.42	1.17 a	0.39	5
Dodecanoic acid	0.03 a	0.02	0.08 b	0.01	0.05 c	0.02	0.03 a	0.00	29
Σ C6-C12 acids	**4.93 a**	**1.06**	**9.40 b**	**1.73**	**9.70** b	**1.82**	**5.79** c	**1.10**	
µg L $^{-1}$									
4-Ethylgaiacol	1.37 a	0.10	nd		nd		1.15 a	0.07	4
4-Ethylphenol	0.87 a	0.11	0.13 b	0.05	0.56 a,b	0.03	1.76 c	0.20	3
4-Vinylphenol	10.35 a	2.69	5.64 a	0.20	2.91 a	0.03	22.70 b	3.39	6
4-Vinylgaiacol	5.23 a	0.39	2.56 b	0.36	0.29 c	0.05	4.37 a	0.55	4
2-Mercaptoethanol	22.61a	3.38	nd		19.57 a	4.19	nd		16
2-Methyl tetra hydro thiophen-3-one	40.03 a	4.55	94.94 b	0.08	111.42 c	0.31	55.86 d	0.20	6
3-(Methylthiol) ethyl propanoate	19.59 a	5.65	15.68 a	0.45	16.04 a	0.25	19.57 a	0.60	10
3-(Methylthiol) propyl acetate	8.60 a	0.99	9.69 a	0.43	16.69 b	0.48	nd		14
Methionol	1448 a	231.83	1821 a	30.25	1904 a	7.48	1849 a	1.80	2
3-(Methylthio) propionic acid	121.14 a	5.29	163.09 b	2.70	136.69 c	3.20	170.65 b	0.50	8
Hydrogen sulfide (H2S)	0.64 a	0.06	0.96 b	0.08	0.95 b	0.08	1.01 b	0.01	16
Methanthiol (MetSH)	0.52 a	0.03	nd		nd		0.63 b	0.04	11
Furaneol	*189.73 a*	*5.39*	*184.56 a*	*6.62*	*250.70 b*	*8.99*	*346.95 c*	*4.31*	*7*
Linalool	*5.08 a*	*2.31*	*10.61 b*	*2.34*	*5.13 a*	*1.34*	*11.30 b*	*1.41*	*4*
α-Terpineol	*14.23 a*	*3.32*	*4.70 b*	*1.81*	*7.76 c*	*0.81*	*4.85 b*	*0.98*	*4*
β-Citronellol	*4.15 a*	*1.90*	*7.21 b*	*2.10*	*4.08 a*	*1.10*	*6.60 b*	*1.00*	*4*
Nerol	*3.74 a*	*1.12*	*5.15 b*	*1.85*	*4.09 a,c*	*0.85*	*4.85 b,c*	*1.20*	*4*
Geraniol	*3.28 a*	*0.31*	*2.00 b,c*	*0.24*	*3.04 a,b*	*0.12*	*1.72 c*	*0.10*	*4*
Σ Free monoterpenols	***30.48 a***	***4.60***	***29.67 a***	***3.20***	***24.10 a***	***1.82***	***29.32 a***	***3.51***	
ng L $^{-1}$									
α-Ionone	*89.36 a*	*0.91*	*13.17 b*	*1.74*	*180.12 c*	*7.33*	*89.11 a*	*7.48*	*12*
β-Ionone	*139.31 a*	*0.97*	*114.03 b*	*4.21*	*98.16 c*	*1.47*	*142.18 a*	*5.97*	*6*

SJ (A) = São Joaquim (A) wines (vineyard at 1415 m asl); SJ (B) = São Joaquim (B) wines (vineyard at 1160 m asl); BR = Bom Retiro wines (vineyard at 960 m asl) ; VID = Videira wines (vineyard at 774 m asl). χ = mean value; SD = standard deviation ; τ = traces; nd = not detected, VC (%) = variation coefficient of the method (n = 6). Different letters in the same line indicate significant difference (for each vintage) (Tukey Test HSD, $p<0.05$). In italics: varietal compounds.

these groups give subtle odoriferous notes to wine. A single odorant compound can also overcome this « buffer capacity » if it is in sufficient concentration. Aroma compounds such as these are known as « aroma impact compounds » (CACHO, 2007). Some of these compounds are present in grapes and can reveal aromatic notes and express the varietals characteristic of a variety. On the other hand, wine fermentation also creates aroma compounds that can predominate and impart particular aromatic notes to wine. The buffer capacity effect attributed to aroma groups or to components such as ethanol can explain aspects aroma perception but this concept is still in its empirical form (CACHO, 2007).

Methanol is present in wine samples in acceptable amounts, about 200 mg L^{-1}; it arises from the enzyme methyl pectin esterase action during the mashing stage. Higher alcohols (also known as fusel alcohols) are present in wines and are formed in small amounts by yeast metabolism during alcoholic fermentation process. The total concentration of methanol ranges in wine is between 100-500 mg L^{-1} (BOULTON *et al*., 1996). The variation ranges in the wines was between 370-550 mg L^{-1}. These concentrations can have positive impact in the wines (fruity, floral characters) but higher levels confer negative impacts on the aroma and flavour of wine (pungent smell and taste).

2-Phenylethanol, compounds that contributes to fine rose odour in the wines, was detected in every wine in concentration relatively high (24.7-90.16 mg L^{-1}) compared to its threshold detection in hydroalcoholic solution (10 mg L^{-1}) (ETIEVANT, 2001). 1-Hexanol and hexenols, in higher amounts can provide herbaceous aromas, but they were detected at insignificant amount negatively influence the wines analyzed. Higher alcohol acetates were found to vary in the range 0.34-3.29 mg L^{-1}. The presence of these molecules in the wine has a strict relation with fermentation conditions.

Ethyl butyrate concentrations in Videira wines presented the highest amounts in both vintages. Its odour threshold detection in hydroalcoholic solution is 0.020 mg L^{-1} (ETIEVANT, 2001), indicating that the concentration of this molecule in the wines (3.98 - 9.59 mg L^{-1}), can be participating actively of wines aromas as fruity notes. Among the C6-C12 ethyl fatty acid esters, ethyl octanoate and ethyl hexanoate have higher concentrations (table 4). The total of C6-C12 ethyl fatty acid esters, in both vintages of Bom Retiro wines were the ones that presented the highest concentrations. The majority of wine esters are produced by yeast during alcoholic fermentation. However, esters can also be derived from the grape, from the alcohols and acids chemical esterification during wine ageing (GUTH, 1997).

Videira wines presented the highest total concentrations of C4-C5 fatty acids. However, the levels found are very far from the threshold values of these molecules reported in previous studies (FERREIRA *et al*., 2000). Fatty acids are formed during the first two phases of the alcoholic fermentation (unpleasant odours described as cheese, dirty socks among others).

The presence of C6-C10 fatty acids is usually related with negative odours, but it occurs when they are present in amounts above 20 mg L^{-1} (RIBÉREAU-GAYON *et al*., 2004), which did not occurred in the wines. In low quantities, they can be important for the wine aromatic equilibrium because they are opposed to the hydrolysis of the corresponding esters.

The amounts found of total volatile phenols were not significant to affect the wine aroma. Volatile phenols (formed from the hydroxycinnamic acid precursors in the grape must) have a relatively low detection threshold. They are better known for their contribution to off-flavors such as « band-aid », « barnyard » or « stable », which results from high concentrations of ethylphenols (DUBOIS, 1983).

Hydrogen sulphide (H_2S) is a highly volatile compound, which imparts a « rotten egg » with a low olfactory threshold (50 - 80 µg L^{-1}). It was found in amounts much lower than their odours threshold in the wines (table 5). Sulphur-containing flavor compounds typically occur in wine at very low concentrations, which has very low detection thresholds and generally confer a negative sensory contribution to wine. Other important sulphur compounds are methionol or 3-methylthio-1-propanol, which has « cauliflower » and « cabbage » odours and that are formed by the metabolism of methionine by the yeast (MESTRES *et al*., 2000). Methionine can also be further converted to 3-methylthiopropyl acetate, which has a « mushroom » or « garlic » odour. It has also been proposed that 4-methylthio-1-butanol with an onion/garlic odour and 2-mercapto-1-ethanol with a « poultry » or « farmyard » odour can be biosynthesised by yeast in the same way by using the amino acids homocysteine and cysteine, respectively (MESTRES *et al*., 2000).

Furaneol (caramel, candy cotton, jam notes) was found in higher concentration in our wines than those findings of KOTSERIDIS *et al.* (2000) for Merlot (71-156 µg L^{-1}) and Cabernet-Sauvignon wines (20-63 µg L^{-1}) from Bordeaux region; moreover its was very higher than its odour threshold in wine model solution (37 µg L^{-1}, KOTSERIDIS and BAUMES, 2000).

With the exception of off-flavor compounds, most aroma impact compounds are of varietal origin and belong to a few groups. Terpenes are one of these groups. The role terpenes play in wine aroma has been the subject of many studies intended to classify varieties. MATEO and JIMÉNEZ (2000) proposed three categories: 1)

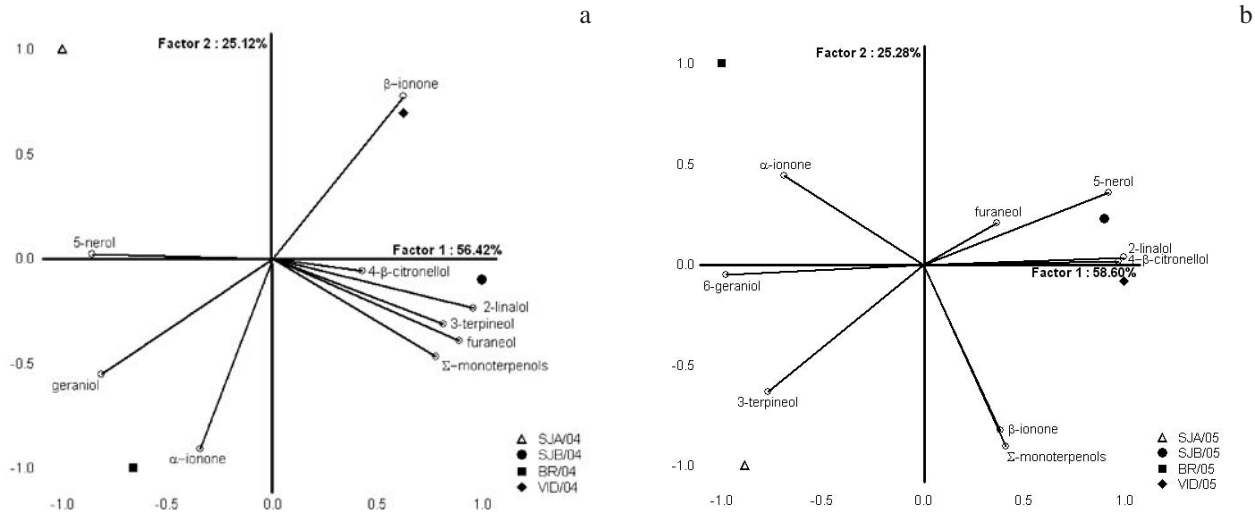

Figure 2 - PCA on the volatile compounds content in Cabernet-Sauvignon wines from 2004 (/04, A) and 2005 (/05, B) vintages.
Where: SJA = São Joaquim (A) wines; SJB = São Joaquim (B) wines; BR= Bom Retiro wines; VID = Videira wines.

Intensely aromatic Muscat, in which the concentration of free monoterpenols reaches ~ 6 mg/L. 2) Aromatic non-Muscat varieties, in which the concentration of monoterpenols varies between 1 and 4 mg/L and 3) neutral varieties whose aroma does not depend on the monoterpenols. Cabernet-Sauvignon is a neutral type of vine, as are Grenache, Carignan, Syrah, Cinsault (SABON *et al*., 2002). In our work, total free monoterpenols were found in amounts between 20.66-50.48 µg L^{-1}, similar to the results of SABON *et al.* (2002) for Grenache wines. These concentrations were much lower than the sensory thresholds in white wine (130 µg L^{-1} for geraniol, 100 µg L^{-1} for linalool, 400 µg L^{-1} for α-terpineol) (RIBÉREAU-GAYON, 1975).

Carotenoids and nonaromatic intermediates are also known to be precursors of aroma-active C13-norisoprenoids, such as β- and α-ionones or β-damascenone, which are responsible for the typical aroma of some grape varieties. Carotenoid levels emerge at véraison chlorophylls begin to metabolize to carotenoid compounds, and at maturation, carotenoid levels decrease (RAZUNGLES *et al*., 1996). A number of mechanisms for the reaction and decomposition of carotenoids into norisoprenoids with nine to 13 carbon atoms are given in the literature for various foodstuffs. These include enzymatic processes, auto-oxidation, and thermal decomposition (GUEDES DE PINHO *et al*., 2001). Despite it is well known that the formation of ionones results from the thermal decomposition of β-carotene (LAROE and SHIPLEY, 1970), the biochemical pathway to formation of the ionone isomers in grapes it until now not completely established.

The C13-norisoprenoid results show that the isomers α- ionone (violet note) and β-ionone (violet, berry notes) were present in inversely proportional concentrations in the wines studied; this result agrees with the work of KOTSERIDIS *et al.* (1998). ß-Ionone was found above its threshold concentration in wines (90 ng L^{-1}, KOTSERIDIS *et al*., 1999) except to Bom Retiro wines in 2004 vintage. α-Ionone was found to be much below its threshold concentration in all the wines (400 ng L^{-1}) (FAZZALARI, 1978). Interestingly, Bom Retiro wines are the only ones that have α-ionone in higher concentration that β-ionone, in both vintages. The same can be observed in both vintages for ester acetates, especially isoamyl acetate, that which was found in high concentration in this wine in relation to the other wine samples. Interesting, the soil profile of Bom Retiro showed an important higher content of minerals, particularly in Potassium concentration if compared to the other soil sites (table 2). Potassium exchange, which has a positive influence on yield, plant vigor, and drought resistance (CHONE *et al*., 2001), was notably higher for São Joaquim (B) and Bom Retiro soils. We can speculate that in our study, a soil profile richer in minerals could product wines richer in some aroma compounds. OLIVEIRA *et al.* (2003) have showed a relationship between soil characterisitics and some C13-norisoprenoid precursors; in their research, vineyards not irrigated produced higher levels of berry-derived carotenoids (β-carotene, neoxanthin, violoxhantin and luteoxanthin), but only when the soil had a low water-holding capacity. This phenomenon indicates the potential for a physiological response elicited within the root system that necessitates sufficient drying of the soil. C13-norisoprenoids are also

Table 5 - Correlation coefficients of some varietal volatile compounds in Cabernet-Sauvignon wines (2004 and 2005 vintages).

	Σ Free monoterpenols	2-Linalool	α-Terpineol	4-β-Citronellol	Nerol	Geraniol	Furaneol	α-Ionone
2004 vintage								
2-Linalool	0.92							
α-Terpineol	0.98	0.93						
4-β-Citronellol	-0.014	0.29	-0.07					
Nerol	-0.46	-0.75	-0.46	-0.83				
Geraniol	-0.45	-0.68	-0.58	-0.15	0.60			
Furaneol	0.79	0.92	0.74	0.61	-0.89	**-0.47**		
α-Ionone	0.05	-0.15	-0.12	0.12	0.16	**0.83**	0.10	
β-Ionone	0.07	0.39	0.21	0.32	-0.58	**-0.91**	0.28	**-0.89**
2005 vintage								
Σ Free monoterpenols								
2-Linalool	0.38							
α-Terpineol	0.25	-0.80						
4-β-Citronellol	0.36	0.97	-0.75					
Nerol	0.03	0.93	-0.93	0.994				
Geraniol	-0.38	-0.98	0.80	-0.91	-0.89			
Furaneol	0.06	0.37	-0.47	0.14	0.27	**-0.54**		
α-Ionone	-0.63	-0.67	0.22	-0.80	-0.56	**0.54**	0.36	
β-Ionone	0.95	0.35	0.20	0.26	-0.01	**-0.41**	0.34	**-0.56**

closely associated to stress-related plant hormones such as abscisic acid (ANTOLIN *et al*., 2008).

4. Multivariate analysis

Although Cabernet-Sauvignon is classified as a neutral variety, the interaction between C13-norisoprenoids and terpene compounds remains interesting. Then, we have carried out a principal components analysis (PCA) among the varietal compounds from wines from different sites, which is given in figures 2 A and B.

Application of PCA was carried out on correlation matrix. Figure 2 A gives the results of PCA on the varietal aromas of Cabernet-Sauvignon wines for 2004 vintage. Factor 1 *x* Factor 2 axes explain 81.54 % of the total variance among the data; the first axis represents 56.42 % and the second axis, 25.12 % of the total dispersion.

Factor 2 axis shows the inverse relationship between the isomers α- and β-ionones that are negatively and positively correlated, respectively, to the Factor 2 axis. Factor 1 is strongly positively correlated to with β-ionone, furaneol, Σ free monoterpenols, linalool, α-terpineol, and weakly positively correlated with β-citronellol. Projection of the cases onto these two axes showed that in 2004 vintage, wines from São Joaquim B (SJB/04) appear; more correlated to the monoterpene compounds and furaneol. Bom Retiro wines (BR/04) were more correlated to α-ionone while Videira wines (VID/04) were more correlated to β-ionone.

Figure 2 B gives the results of PCA on the aroma profile of Cabernet-Sauvignon wines for 2005 vintage. The first two principal components explain 83.88 % of the variance; the first axis represents 58.60 % and the second axis, 25.28 % of the total dispersion. As in 2004, once again the two first components showed the opposition between the isomers α et β-ionones. β-Ionone was too strongly negatively correlated to Factor 2. Factor 1 was strongly positively correlates with 2-linalool, β-citronellol, nerol; α-terpineol and geraniol are strongly negatively correlated to this axis. Factor 2 axis presents

a strong negative correlation with the Σ free monoterpenols, 3-terpineol , and β-ionone. Projection of the cases onto these two axes shows that in 2005 vintage, wines from São Joaquim A (SJA/05) appear more correlated to the α-terpineol. São Joaquim B (SJB/05) was more correlated to varietal compounds furaneol, β-citronellol, linallol and nerol while Bom Retiro wines (BR/05) to α-ionone.

The correlation matrix of the varietal aroma compounds is showed in table 5. Interesting, in both vintages, furaneol and geraniol are inversely correlated. Also, geraniol has a strong positive correlation with α-ionone and a negative strong negative correlation with the isomer β-ionone. A weaker correlation was observed among compounds in 2005 if compared to 2004 vintage, which may be explained by a more important rainfall in the 2005 season in these sites (especially in the summer), that promote a dilution effect in the grape and wine composition (data not shown).

CONCLUSION

Generally Cabernet-Sauvignon wines from four different vineyards in Santa Catarina State, were well separated by Principal Component Analysis. It was clear that the location of the vineyard has a strong influence on the wine it produces. Soil composition and seasonal weather differences are the principal factors affecting wine aroma in these wines. 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. Bom Retiro soils showed a high content of minerals, particularly Potassium and the wines from this site are richer in ester acetates (mainly isoamyl acetate) and in α-ionone. α-Ionone presented an strong correlation with geraniol while geraniol was inversely correlated to furaneol content. These entire findings have been observed in both two consecutive vintages studied.

Acknowledgements: Special thanks are extended viticulturists for providing the sections of their vineyards and the grape samples and to Empresa de Pesquisa e Extensão Agropecuária de Santa Catarina (EPAGRI) - Brazil for assistance on the wine microvinification. We have also to thanks to John Almy for revision of the English on this manuscript. L.D. Falcão is grateful to Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) and to Conselho Nacional de Pesquisa (CNPq) from Brazilian government, for providing a doctoral scholarship Brazil/France.

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