Sensory profile and contribution of major components of aroma in dry red wine quality

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This study aimed to determine the sensory profile and main volatile compounds of a set of commercial wines from two major wine regions in Brazil. A total of 28 descriptors were selected by quantitative descriptive analysis, and "red", "violet", "pungent aroma", "vinegary aroma" and "softness" were the most important descriptors in sample discrimination ($p \leq 0.05$). 42 volatile aroma compounds were considered relevant for the evaluation of red wine samples. Several acetates and esters that contribute to the pleasant aroma in wines were found in the samples, but other undesirable compounds were also identified: acetic acid and octanoic acid may have contributed to the vinegary and sulphur odors perceived by a trained team.

Key words: Quantitative descriptive analysis. Multivariate Statistics. Quality. Red wine. Volatiles.

Introduction

Although many alternative techniques have been developed, none of them are able to advantageously replace classical descriptive sensory analysis with respect to wine (DAMÁSIO e COSTELL, 1991). Descriptive analysis is a primary tool used in sensory analysis (CAMPO et al., 2010) which provides a complete analysis of complex matrices, such as wine. Cadot et al. (2010) suggested that quantitative descriptive analysis (QDA) is one of the techniques useful for determining the typicality of Cabernet Sauvignon and Cabernet Franc to the French appellation of origin. The same technique has been used to evaluate sensory effects of ethanol levels in the perception of aroma attributes in Malbec wines (GOLDNER et al., 2009).

Among the various sensory attributes of wine, aroma is one of the most important. According to Falcão et al. (2008), aromatic compounds can impact and help steer the development of wines with higher quality. Over 700 compounds have been isolated and identified in the volatile fraction of various wines (JACKSON, 2008) at concentrations ranging from hundreds of mg L^{-1} to ng L^{-1}.

The extraction of volatile compounds by headspace solid phase microextraction (HS-SPME) has been widely used in studies of the aroma of alcoholic beverages, such as

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wine, and it is essential for assessing the quality of such products and for optimization of their production (AUGUSTO; LEITE, 2003). Through this extraction technique, Zhang et al. (2010) identified 11 volatile compounds determining the classification of samples of varietal red wines including Cabernet Sauvignon and Merlot. Câmara et al. (2007) differentiated and classified samples of Madeira wines according to their region of origin based on their aromatic composition.

Currently, there are two main regions producing fine wines (*Vitis vinifera*) in Brazil. One area is located in the region of Serra Gaúcha (Vinhedos Valley, Rio Grande do Sul), and it has geographical indication certification. The principal grape varieties cultivated in this wine region are Cabernet Sauvignon and Merlot. The other area is located in the São Francisco Valley region, on the states of Bahia and Pernambuco border, but it does not have geographical indication certification. The main grape varieties cultivated in this wine region are Cabernet Sauvignon and Shiraz. Thus, the aim of this study was to determine the sensory profile and volatile compounds of fine dry wines from the two major wine regions in Brazil.

Materials and methods

Wine samples

Six brands of commercial fine dry red wines (2006 harvest) produced in Brazil were analyzed. The samples were from the regions of São Francisco Valley (Juazeiro, BA, and Petrolina, PE) and Serra Gaúcha (Bento Gonçalves, RS). These samples were representatives of wines produced in these regions. A total of 11 bottles of each brand (same batch) were sampled randomly from supermarkets and used for sensory analysis. The bottles were stored horizontally in a dark room at 16°C until analysis.

Sensory analysis

QDA, as described by Stone and Sidel (2004), was used to determine the sensory profile of wine samples. The analysis was carried out in the Laboratory of Sensory Analysis in individual booths under white light and in a temperature controlled room (22°C) throughout the day.

The recruitment of judges was done by filling out a questionnaire based on habits of red wine consumption, interest and availability to participate. Candidates with better discriminatory ability were selected in three sessions of a triangular test. Samples were tested in the following pairs: AXD, BXC and EXF. The test result was analysed by a specific table test (minimum number of replies from the triangular test) at 5% significance (MEILGAARD et al., 2007). Only those candidates who correctly discriminated three pairs of sample combinations were selected.

To prevent recruitment of judges with little or no experience in sensory analysis of wines, odor recognition and basic taste tests (MEILGAARD et al., 2007) were also applied only at training level before the QDA. In the odor recognition test, each substance was introduced in porcelain cups covered with perforated aluminum foil to prevent the display of references. To test the basic tastes, aqueous solutions containing different concentrations of substances representing the basic tastes (sweet, sour and bitter) and astringency were prepared as follows: solutions of sucrose (0.4% and 0.8%); solutions of food grade citric acid (0.02%, 0.03% and 0.04%), solutions of food grade caffeine (0.02% and 0.04%) and juice of unripe grape skins.

The descriptive terminology was generated by Repertory Grid Kelly's Method (MOSKOWITZ, 1983). Tests were carried out to select the subjects that would compose the definitive sensory team. The subjects chose the references that indicated the maximum and minimum intensity of each attribute by their own consensus under the supervision of a team leader (Table 1).

Selection of the final sensory panel was performed according to Damásio and Costell (1991) based on discrimination abilities on ($Fp_{sample}<0.50$) and repeatability ($Fp_{repetition}\geq0.05$) of each attribute verified by a two-factor analysis of variance (ANOVA: sample and repetition), and agreement of the averages of each judge with the team for at least 75% of all descriptors collected for samples of red wine.

The sensory panel was composed of 10 judges (seven women and three men, 21 to 55 years old) who were submitted to 9 training sessions. Each judge evaluated three samples per analytical session (about 1 hour long) with three replications on different days. For each repetition, a different bottle of wine was tested. The samples (50 mL) were served at 16ºC in clear glass bowls suitable for red wine, and properly coded. The samples were presented in balanced incomplete blocks, in order to control the contrast effect amongst the samples. Order of presentation of the samples in each session was balanced for the first-order effect. The number of times that each sample appeared in each block (λ) was calculated according to Equation 1 for the experimental design, as follows:

$$\lambda = r(k - 1)/a - 1 \qquad (1)$$

where "r" is the number of repetitions per sample, "k" is the number of samples per analysis session, and "a" is the total number of treatments (samples).

Panelists were asked to rinse their palate with room temperature mineral water and to ingest unsalted roast between samples. References were provided in a separate room during all examination sessions. Thus, if a question was raised, each judge could try the references of the attributes to be analyzed at any time. The quantification of descriptors was performed on 9cm unstructured line scales with the terms of intensity anchored at its left and right extremes.

Table 1. Descriptive terminology and respective references of intensity developed by sensorial team to the red wine samples

Definition	Minimum reference	Maximum reference
1. Red: Intensity of red color typical of red wines.	Weak: 30ml Cabernet Sauvignon wine (Salton Classic, lot 0908916) 2007 + 70ml water	Strong: Cabernet Sauvignon wine (Salton Classic, lot 0908916) 2007 + 15 drops of red food coloring (Arcolor, lot111459)
2. Reddish-orange: Intensity of red with orange tones characteristic of red wines matured. Synonyms: brown, rust.	Weak: 30ml Cabernet Sauvignon wine (Marcus James, lot 001/2007) 2005 + 70ml water	Strong: Cabernet Sauvignon wine (Marcus James, lot 001/2007) 2005
3. Violet: Intensity of violet color characteristic of young red wines. Synonym: purple.	Weak: 30ml Integral grape juice (Aurora, lot 001/2009) + 70ml water	Strong: Integral grape juice (Aurora, lot 001/2009)
4. Amount of tears: Structures formed after shaking that flow through the wall of the cup.	Low: Brandy 40% vol. (Pitu, lot L41203434B) diluted (1:9)	High: 20ml Brandy 40% vol. (Pitu, lot L41203434B)
5. Visual viscosity: Resistance to fluid motion caused by shaking the cup. It can also be perceived by the formation of a film adhered to the wall of the cup to be stirred. Synonym: density.	Low: Brandy 40% vol. (Pitu, lot L41203434B) diluted (1:9)	High: 20ml Brandy 40% vol. (Pitu, lot L41203434B) + 30ml Water
6. Turbidity: Considered "cloudy" strong when you can not read through the cup.	Low: Grape cooler (Keep Cooler Classic, lot 001/2008) without gas	High: 50 mL Integral grape juice (Aurora, lot 001/2009)
7. Alcoholic aroma: characteristic aroma of ethanol.	Weak: Brandy 40% vol. (Pitu, lot L41203434B) diluted (1:9)	Strong: 20ml Brandy 40% vol. (Pitu, lot L41203434B) + 30ml Water
8. Fermented aroma: aroma of fermentation.	None: Water	Strong: Instant dry yeast (Dr. Oetker, lot T291) + 25ml water
9. Buttery aroma: aroma of butter.	None: Water	Strong: Butter (Aviação, lot 5mar09)
10. Vanilla aroma: sweet aroma characteristic of vanilla.	None: Water	Strong: 2% solution of artificial vanilla flavoring (Dr. Oetker, lot TM072)
11. Fruity aroma: sweet aroma reminiscent of a mixture of fresh berries.	None: Water	Strong: Blend of strawberries, plums and red grapes Niagara Rosada crushed (1:1:1)
12. Dried fruit aroma: characteristic aroma of dried fruits such as, for example, raisin or prune.	None: Water	Strong: Blend of raisins (Bompreço, lot 008) and prune (Bompreço, lot 1893/S) crushed (1:1)
13. Ripe fruit aroma: aroma reminiscent of cooked fruits or jams.	None: Water	Strong: Blend of strawberry jam (Bompreco lot03G) and blackberry (Queens Berry, lot 29D4) (1:1)
14. Pungent aroma: pungent aroma of spices such as black pepper.	None: Water	Strong: 15g black pepper ground black (Kitano, lot F3L-B9C5)
15. Floral aroma: characteristic aroma of flowers, such as violet or roses.	None: Water	Strong: 50ml de water + 5 drops of artificial flavoring of red roses (Palácio das Essências, lot 9886)
16. Olive aroma: characteristic aroma of olives in brine.	None: Water	Strong: Black olives in brine (Rivoli, lot 27/01/09)
17. Vinegary aroma: aroma of acetic acid.	None: Water	Strong: Red wine vinegar (Minhoto, lot 2680)
18. Sulphur aroma: characteristic aroma of rotting eggs or sulfur.	None: Water	Strong: Sulphur stone

Cont. Table 1. Descriptive terminology and respective references of intensity developed by sensorial team to the red wine samples

19. Sour taste: characteristic sour taste of citric acid solution. Associated with the presence of acids in wine.	Weak: Citric acid food grade solution 0.02%	Strong: Citric acid food grade solution 0.9%
20. Bitter taste: characteristic bitter taste of caffeine solution.	Weak: Caffeine food grade solution 0.01%	Strong: Caffeine food grade solution 0.1%
21. Sweet taste: characteristic sweet taste of sucrose solution. Associated with the presence of sugars and alcohol in wine.	None: Water	Strong: 2% sucrose solution
22. Alcoholic flavor: flavor of alcohol in beverages by the perceived sensation of warmth in the mouth and throat.	Weak: Brandy 40% vol. (Pitu, lot L41203434B) diluted (1:9)	Strong: 20ml Brandy 40% vol. (Pitu, lot L41203434B) + 30ml Water
23. Fruity flavor: flavor associated with berries and grapes.	None: Water	Strong: 50ml Grape cooler (Keep Cooler Classic, lot 001/2008) + 50ml grape soda (Fanta Uva, lot P270209)
24. Vinegary flavor: flavor associated with the presence of acetic acid in wine.	None: Water	Strong: 3ml red wine vinegar (Minhoto, lot 2680) + 50ml water
25. Fermented flavor: flavor of fermented beverages. Associated with the presence of yeast.	None: Water	Strong: 10mL Pilsen beer (Skol, lot JP02:15) + 50mL de water
26. Astringence: feeling of "dryness", "mooring", "trevor" and "roughness" perceived in the oral cavity. Associated with the presence of tannins.	Weak: Slice of banana ripening process in silver	Strong: Slice of banana silver green full
27. Body: sense of opulence or perceived density of red wine in your mouth. Synonym: oral viscosity, mouth filling, full bodied.	Low: 50ml Cabernet Sauvignon wine (Salton Classic-Special Reserve, lot 0908916) 2007 + 50ml water	High: Cabernet Sauvignon wine (Salton Classic-Special Reserve, lot 0908916) 2007
28. Softness: harmony between sugars and alcohols present in wine.	Low: Cabernet Sauvignon / Shiraz wine (Carrancas do São Francisco) 2007	High: Cabernet Sauvignon wine (Salton Classic - Special Reserve, lot 0908916) 2007

Extraction, separation and identification of volatile compounds

The volatile compounds were isolated by using HS-SPME. The fiber used was 100-μm polydimethylsiloxane (PDMS) (Supelco, USA). Approximately 3 mL of each sample were placed in amber sealed vials, and the PDMS fiber was exposed to the headspace at 30°C 30 min^{-1}. The separations were conducted on a Shimadzu QP5000 gas chromatograph with detector quadrupole mass spectrometry. A capillary column (HP-5; Hewllett-Packard, USA) 30m x 0.32mm x 0.25mm (5% diphenyl and 95% dimethylpolysiloxane) was used. The carrier gas was helium (1 mL min^{-1}). The column temperature had the following schedule: initial temperature of 60°C with an increasing temperature gradient (3°C min^{-1}) to reach the final temperature of 246°C. The temperature of the detector and injector was 250°C, and the form of injection used was splitless. Desorption time was 2 min. An ionization voltage of 70eV was used, and the mass spectrum was obtained in a scan interval of 30m/z to 350m/z. The identification of volatile compounds was performed using the Automated Mass Spectral Deconvolution System (AMDIS v.2.62) and was compared with the NIST library using the Mass Spectral Search Program (NIST v.2.0, Washington D.C., USA).

Statistical analysis

The results of the descriptive analysis were subjected to ANOVA with Tukey's test at 5% significance using the SAS statistical software (version 8.2; SAS institute, Cary, NC). The graphics of the principal component analysis (PCA), hierarchical cluster analysis (HCA) and Pearson's correlation were performed with Minitab statistical software (version 15.1; Minitab Inc.).

Results and discussion

All selected judges correctly identified at least 60% of the aromas presented in the odor recognition test. The eucalyptus aroma was the most easily detected by the judges (100% correct), and paprika was the aroma with the lowest rate of recognition (7% correct). In the test of basic tastes, all of the judges were able to recognize at least one concentration of each basic taste in addition to astringency. Most participants (77%) acknowledged at least 75% of the taste solutions presented with the lowest recognition rate (54%) assigned to the sour taste at the 0.02% concentration.

A total of 28 descriptors were raised for samples of red wine (Table 2). In previous sensory study involving Brazilian red wines (FALCÃO et al., 2007), descriptors were also raised that were common to those developed in this work, demonstrating its importance in the development of the sensory profile of Brazilian red wines. At least two samples differed significantly in all attributes. The most important descriptors in determining wine samples by variance analysis were red, violet, pungent aroma, vinegary aroma and softness.

Table 2. Results of Analysis of Variance (ANOVA) for sensory attributes of red wine samples

Attribute	Samples					
	A*	B*	C*	D*	E**	F**
Red (RD)	5.20[a]	3.15[b]	3.12[b]	4.64[a]	5.43[a]	5.52[a]
Reddish-orange (RO)	2.51[d]	6.15[a]	6.48[a]	3.68[b]	2.75[cd]	3.49[cb]
Violet (VI)	5.16[a]	2.10[b]	2.11[b]	3.79[a]	4.55[a]	4.07[a]
Amount of tears (AOT)	5.50[a]	4.35[ba]	3.86[b]	4.66[ba]	4.31[ba]	4.53[ba]
Visual viscosity (VIS)	5.72[a]	4.09[b]	3.73[b]	4.37[ba]	4.24[b]	4.32[ba]
Turbidity (TUR)	5.93[a]	3.55[bc]	4.01[bc]	4.75[ba]	3.94[bc]	3.27[c]
Alcoholic aroma (ALA)	3.79[b]	4.72[a]	3.95[ba]	4.74[a]	4.24[ba]	4.60[ba]
Fermented aroma (FEA)	1.67[cb]	4.04[a]	4.52[a]	1.43[c]	2.44[b]	2.32[b]
Buttery aroma (BUA)	1.53[a]	0.79[ba]	1.27[ba]	0.72[b]	1.40[ba]	1.35[ba]
Vanilla aroma (VAA)	3.05[a]	1.05[d]	0.72[d]	2.82[ba]	1.13[dc]	2.05[bc]
Fruity aroma (FRA)	4.08[ba]	2.76[bc]	2.23[c]	4.61[a]	3.52[bac]	3.52[bac]
Dried fruit aroma (DFA)	2.87[ba]	1.83[c]	1.30[c]	3.48[a]	1.60[c]	2.64[b]
Ripe fruit aroma (RFA)	3.53[a]	2.21[ba]	1.90[b]	3.39[a]	2.72[ba]	3.37[a]
Pungent aroma (PUA)	1.48[b]	1.80[b]	2.93[a]	1.48[b]	1.71[b]	1.52[b]
Floral aroma (FLA)	1.63[bc]	1.23[dc]	0.87[d]	2.21[a]	1.93[ba]	2.04[ba]
Olive aroma (OLA)	1.47[b]	1.86[ba]	2.65[a]	1.70[b]	1.48[b]	1.31[b]
Vinegary aroma (VIA)	1.56[b]	3.09[a]	3.22[a]	1.54[b]	3.23[a]	3.56[a]
Sulphur aroma (SUA)	0.89[bc]	1.76[ba]	2.53[a]	0.53[c]	0.91[bc]	1.33[bac]
Sour taste (SOT)	4.70[ba]	4.44[bac]	5.00[a]	3.70[c]	4.42[bac]	3.98[bc]
Bitter taste (BIT)	4.55[ba]	3.85[b]	5.39[a]	4.50[ba]	4.05[b]	2.56[c]
Sweet taste (SWT)	1.48[c]	1.82[bc]	1.23[c]	2.49[ba]	3.18[a]	2.76[a]
Alcoholic flavor (ALF)	4.83[ba]	3.81[c]	5.14[a]	5.16[a]	4.35[bc]	4.38[bc]
Fruity flavor (FRF)	2.43[ba]	2.24[ba]	1.71[b]	3.25[a]	3.34[a]	2.76[ba]
Vinegary flavor (VIF)	2.26[b]	3.07[ba]	3.55[a]	2.57[ba]	2.57[ba]	2.85[ba]
Fermented flavor (FEF)	2.34[ba]	3.06[a]	3.18[a]	2.46[ba]	1.87[b]	1.93[b]
Astringency (AST)	5.07[ba]	4.48[bc]	5.47[a]	4.04[dc]	2.96[e]	3.21[de]
Body (BOD)	5.44[a]	4.24[d]	4.30[d]	5.21[ba]	4.92[bc]	4.65[dc]
Softness (SOF)	4.22[a]	3.09[b]	2.05[c]	4.60[a]	4.66[a]	4.27[a]

Means in the same row followed by same letter do not differ significantly feom Tukey's test ($p \leq 0.05$); *São Francisco Valley; **Serra Gaúcha; A=Cabernet Sauvignon/Shiraz; B=Cabernet Sauvignon; C=Cabernet Sauvignon; D=Cabernet Sauvignon/Shiraz; E=Cabernet Sauvignon; F=Merlot.

With respect to appearance, samples B and C (Cabernet Sauvignon, São Francisco Valley) significantly differed from the other samples with the lowest averages for red and violet. These samples were considered to have the most reddish-orange color. Samples A, E and F had the highest average for the red and violet.

Aroma descriptors, such as vanilla, ripe fruit, and floral were considered positive in red wines. The highest averages of vanilla aroma were observed in composite samples with a blend of Cabernet Sauvignon and Shiraz (Table2) without significant differences between them. Moreover, sample D did not differ from sample F (Merlot). Furthermore, no significant difference in the vanilla aroma was found between samples

F and E (Cabernet Sauvignon), which were produced in the same geographical region. The aroma similarity between Merlot and Cabernet Sauvignon varieties, produced in different localities, has also been described (GÜRBÜZ et al., 2006). Wines from these varieties have many flavor compounds in common, and differ only by their caramel aroma (higher in Merlot).

Several studies have described the aromas of certain wine varietals. Aromas of gooseberry, green pepper, smoke, hay, vanilla, blueberry and cinnamon are considered typical in Cabernet Sauvignon wines produced in China (TAO et al., 2009). In another study, the aroma of Merlot wine was described as vegetation, fresh caramel, quince, gooseberry, butter, grass, liquorice, and oak (GAMBARO et al., 2003). The pungent aroma was important to differentiate significantly sample C (Cabernet Sauvignon, São Francisco Valley) from the others samples, and it was perceived by the sensory panel with greater intensity in this sample (Table2). Higher scores for the dried fruit aroma were obtained from samples A and D. The addition of Shiraz grapes may have contributed to this. During a comparison of the Shiraz and Cabernet Sauvignon varietal wines by Lattey et al. (2010), Shiraz wines were associated with the aroma of cooked dark fruits in addition to being classified with a greater purple colour and sweet taste.

Negative aromas were also perceived by judges. Samples B and C (Cabernet Sauvignon) achieved the highest averages for the fermented and sulphur aromas (Table2). Regarding vinegary aroma, samples B and C had high scores but did not significantly differ from the Serra Gaúcha region wines, which had the highest averages. The vinegary aroma was important to differentiate significantly samples A and D (Cabernet Sauvignon/Shiraz, São Francisco Valley) from the other samples. By olfactometry, Falcão et al. (2008) related vinegar odor to acetic acid. Small amounts of acetic acid (0.2 to 0.4g/L) in wine can be produced by the action of *Saccharomyces cerevisiae* during the fermentation process (FALCÃO et al., 2007). However, high concentrations of acetic acid are related to a failure in the drink sanity.

Although all the wines were dry, sweet taste was detected, with sample E having the highest average. The amount of residual sugar in this sample, and the sensitivity of each individual judge may have allowed this perception. Moreover, the alcohol and glycerol contents also reinforce a perception of sweetness in wine (JACKSON, 2008). As for the sour taste, samples C and A had the highest mean ,and the sample D had the lowest average for this attribute, with no significant difference being found between sample D and the samples produced in the South. The lowest score for bitter taste was observed in sample F (Merlot) (Table2).

The samples from the São Francisco Valley region had the highest mean of astringency (Table 2). Astringency in red wines is usually related to phenol compounds. Lucena et al. (2010) found high levels of phenol compounds in samples of red wines produced in the São Francisco Valley (3.2 to 5.9gGAE/L). They suggest that climate, high levels of sunshine, and use of controlled irrigation typical of this region may contribute to the higher phenol content of wines. Wines that had high polyphenol levels were characterized as astringent, bitter, sour and pungent (GOLDNER; ZAMORA, 2010).

Body and softness were also two important descriptors to discriminate wine samples. Body attribute was defined by the sensory panel as a sense of opulence or density of the red wine perceived in mouth, while the softness attribute was described as the harmony between the amounts of sugar and alcohol in the samples perceived by the mouth. Samples A and D (São Francisco Valley) presented the highest body (5.44 and 5.21, respectively). Possibly, this increased sense of body is related to its alcohol content since, at high concentrations, alcohol may contribute to the feeling of weight or body, especially in dry wines (JACKSON, 2008). These same samples (A and D) were considered as the softest along with samples of the Serra Gaúcha region (E and F), thus more balanced in sugar and alcohol content. Softness was important to significantly differentiate samples B and C (Cabernet Sauvignon, São Francisco Valley) from the others.

Pearson's correlation showed that among the following sensory attributes there were strong positive correlations (Table 3): sweet taste and softness (r=0.78); body and softness (r=0.76); bitter taste and astringency (r=0.74); sweet taste and red color (r=0.68); sour taste and astringency (r=0.67). The positive association between red color and intensity of sweet taste in a variety of drinks was cited by Durán and Costell (1999) to demonstrate the influence of color on perceived sweetness. According to Delwice (2003), color has a profound effect on the perception of food and drink aromas, and the techniques used by winemakers to enhance the color of red and white wines can often distort the perception of their real flavor.

The following strong negative correlations also were observed: sweet taste and astringency (r=-0.98); astringency and softness (r=-0.73); sweet and acid tastes (r=-0.68); sweet and bitter tastes (r=-0.63). Some authors have suggested that sweetness can have a dampening effect on the perception of acidity, bitterness and astringency with the opposite also being true (BEHRENS; SILVA, 2000), explaining the negative correlations obtained between these attributes in the current study.

There were negative correlations between astringency and the fruity aroma and bitter taste attributes; as well as a positive correlation between fruity aroma and sweet taste (Table3). These results agree with those obtained by Sáenz-Navajas et al. (2010), who found that sweetness of dry wines is closely related to the fruity aroma, and that perceptions of astringency and bitterness are inversely related to this aroma.

Table 3 - Pearson correlation coefficient (r) between means of sensory attributes

	RD	RO	VI	AOT	VIS	TUR	ALA	FEA	BUA	VAA	FRA	DFA	RFA	PUA	FLA	OLA	VIA	SUA	SOT	BIT	SWT	ALF	FRF	VIF	FEF	AST	BOD
RO	-0.95*																										
VI	0.93*	-0.98*																									
AOT	0.53	-0.68	0.74																								
VIS	0.53	-0.68	0.77	0.97*																							
TUR	0.25	-0.46	0.56	0.77	0.83*																						
ALA	-0.10	0.20	-0.33	-0.21	-0.43	-0.60																					
FEA	-0.83*	0.89*	-0.87*	-0.73	-0.66	-0.52	-0.05																				
BUA	0.50	-0.41	0.50	0.13	0.32	0.17	-0.74	-0.06																			
VAA	0.57	-0.67	0.71	0.87*	0.80*	0.71	-0.02	-0.87*	-0.02																		
FRA	0.68	-0.79*	0.75	0.74	0.64	0.56	0.15	-0.97*	-0.15	0.89*																	
DFA	0.48	-0.55	0.54	0.72	0.60	0.51	0.26	-0.84*	-0.27	0.94*	0.90*																
RFA	0.82*	-0.83*	0.83*	0.78	0.71	0.47	0.07	-0.94*	0.14	0.92*	0.90*	0.88*															
PUA	-0.71	0.75	-0.69	-0.72	-0.59	-0.22	-0.36	0.82*	0.09	-0.69	-0.82*	-0.71	-0.82*														
FLA	0.81*	-0.78	0.69	0.41	0.29	0.11	0.38	-0.89*	-0.07	0.63	0.86*	0.71	0.82*	-0.80*													
OLA	-0.87*	0.84*	-0.79*	-0.63	-0.55	-0.11	-0.22	0.78	-0.20	-0.58	-0.70	-0.55	-0.81*	0.93*	-0.81*												
VIA	-0.15	0.38	-0.42	-0.71	-0.67	-0.87*	0.17	0.62	0.28	-0.79*	-0.74	-0.74	-0.54	0.37	-0.31	0.13											
SUA	-0.76	0.86*	-0.79*	-0.67	-0.57	-0.44	-0.17	0.95*	0.09	-0.76	-0.96*	-0.76	-0.83*	0.86*	-0.90*	0.79	0.60										
SOT	-0.42	0.37	-0.25	-0.19	0.00	0.18	-0.79*	0.63	0.52	-0.47	-0.68	-0.69	-0.60	0.70	-0.84*	0.60	0.21	0.68									
BIT	-0.51	0.34	-0.27	-0.14	-0.04	0.49	-0.55	0.28	-0.09	-0.11	-0.19	-0.20	-0.42	0.64	-0.50	0.75	-0.42	0.28	0.56								
SWT	0.68	-0.58	0.44	-0.04	-0.13	-0.37	0.45	-0.51	0.01	0.07	0.43	0.18	0.40	-0.58	0.80*	-0.69	0.22	-0.61	-0.68	-0.63							
ALF	0.05	-0.09	0.15	0.07	0.12	0.53	-0.34	-0.28	0.03	0.42	0.30	0.39	0.24	0.27	0.12	0.31	-0.55	-0.12	0.01	0.61	-0.26						
FRF	0.72	-0.74	0.62	0.26	0.16	0.04	0.34	-0.77	-0.12	0.39	0.75	0.47	0.60	-0.72	0.91*	-0.72	-0.24	-0.88*	-0.74	-0.38	0.88*	-0.02					
VIF	-0.81*	0.93*	-0.92*	-0.85*	-0.82*	-0.61	0.11	0.92*	-0.18	-0.79*	-0.88*	-0.68	-0.86*	0.85*	-0.74	0.83*	0.60	0.92*	0.41	0.28	-0.43	-0.04	-0.69				
FEF	-0.98*	0.90*	-0.85*	-0.39	-0.38	-0.06	0.01	0.74	-0.48	-0.42	-0.59	-0.36	-0.72	0.69	-0.80*	0.87*	0.01	0.70	0.45	0.61	-0.79	0.08	-0.75	0.73			
AST	-0.66	0.53	-0.40	0.05	0.14	0.46	-0.50	0.45	-0.03	-0.30	-0.36	-0.14	-0.38	0.59	-0.75	0.72	-0.32	0.54	0.67	0.74	-0.98*	0.38	-0.82*	0.38	0.78		
BOD	0.74	-0.87*	0.89*	0.79*	0.79*	0.78	-0.28	-0.92*	0.20	0.87*	0.90*	0.75	0.85*	-0.63	0.68	-0.59	-0.76	-0.85*	-0.32	0.03	0.25	0.45	0.59	-0.90*	-0.61	-0.16	
SOF	0.88*	-0.91*	0.83*	0.56	0.48	0.24	0.20	-0.91*	0.06	0.63	0.86*	0.63	0.82*	-0.88*	0.94*	-0.90*	-0.35	-0.95*	-0.69	-0.49	0.78	-0.03	0.92*	-0.89*	-0.87*	-0.73	0.76

* $p \leq 0.05$.

Most analytical methods tend to generate a lot of information. The use of multivariate techniques has helped in the interpretation of results obtained with wines. Campo et al. (2008) suggest that the use of HCA can be an interesting tool to differentiate the quality of Spanish monovarietal white wines. Thus, HCA was performed to verify the grouping of samples (Figure 1). There were two major clusters at level 9.17 (y-axis). Samples B and C were clearly separated in a smaller cluster, and another larger cluster was associated with samples A, D, E and F. The dendrogram showed that samples A and D (Cabernet Sauvignon and Shiraz) from the São Francisco Valley had a higher degree of similarity with samples E (Cabernet Sauvignon) and F (Merlot) from Serra Gaúcha. These same samples were perceived as the softest by the sensory team (Table 2). Even though the wines E and F were made from different grape varieties, their similarity can be justified by the same soil and climatic conditions during the cultivation of grapes and preparation of the beverage, demonstrating the influence of conditions resulting from a geographical region in the final sensory characteristics of red wine. Although there was some differentiation of the samples by HCA, no information about the importance of sensory attributes was indicated by it.

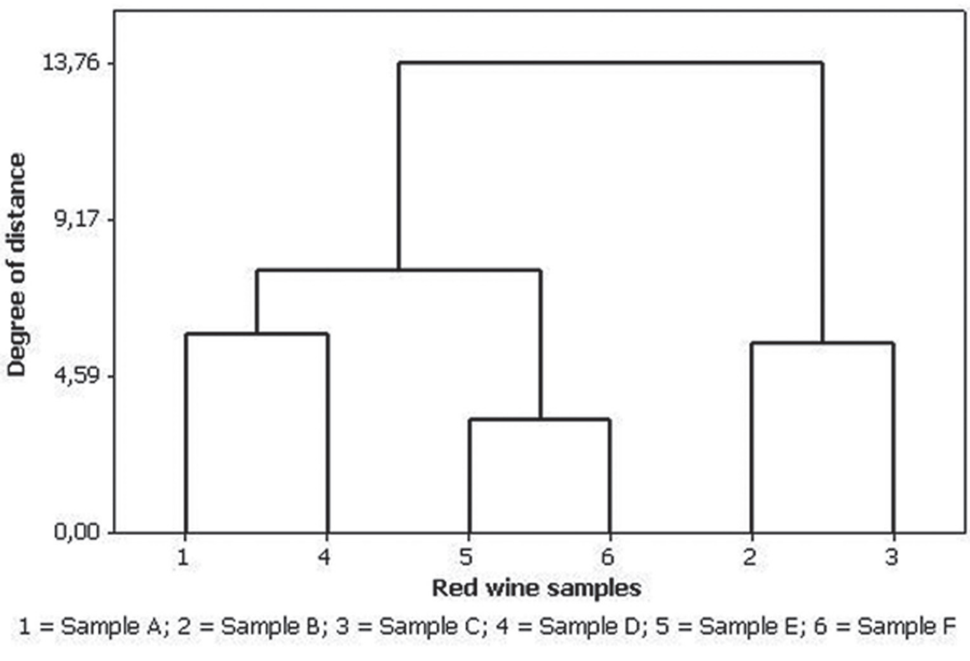

Figure 1. Multivariate analysis demonstrated in the form of hierarchical clustering of samples of red wine.

Thus, PCA was performed after HCA. PCA was divided into categories of attributes as represented in Figures 2, 3 and 4 (correlation matrix). The first two principal components of the category of appearance attributes, explained 95.8% of the total variation of the data, and they showed that the turbidity, amount of tears and visual viscosity were important to characterize samples A and D. The red color was more important to characterize samples E and F, and the reddish-orange characterized samples B and C (Figure 2). It was possible to discriminate samples based in the production region by means of Component I of PCA with regard to the attributes of appearance (Figure 2).

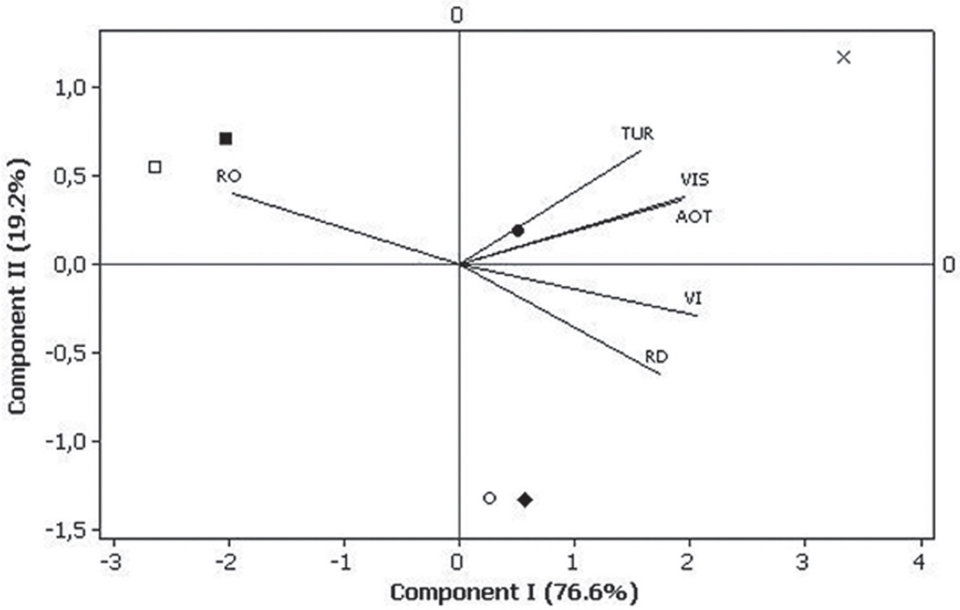

Figure 2. Two-dimensional projection of the results obtained from the principal components analysis I and II for the class of attributes that include the appearance.

With regard to the attributes of aroma (Figure 3), components I and II accounted for 83.2% of the explanation for variability. The axis of component I objected to the terms of fruity aromas related to the terms of fermented, olive and sulphur aromas vectors that had long and near to the axis, indicating the relevance of this attributes in the characterization of samples. The vanilla aroma, ripe fruit aroma and fruity aroma were important in characterizing sample A. The buttery aroma characterized sample E. The samples D and F were characterized by a floral aroma in addition to a dried fruit aroma and alcoholic aroma. The pungent aroma, olive aroma, sulphur aroma, vinegary aroma and fermented aroma (correlated positively with Component I) differed the samples B and C from the others. Thus, these aromas were responsible for the characterizing of these samples. It was possible to discriminate the samples based in grape variety only by means of Component II of PCA with regard to the attributes of aroma (Figure 3).

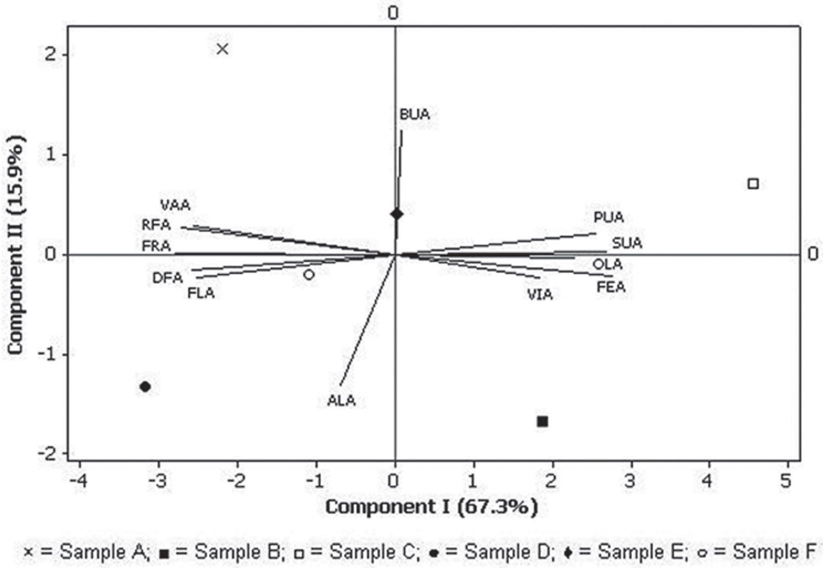

Figure 3. Two-dimensional projection of the results obtained from the principal components analysis I and II for the class of attributes that include aroma.

Regarding the attributes of mouth perceptions (Figure 4), components I and II totaled 83.3%. Alcoholic flavor was important in characterizing sample A, and sample D was mainly characterized by body, softness and fruity flavor. Sample C was characterized by a higher intensity of astringency, sour taste and bitter taste. The vinegary and fermented flavors were important to characterize sample B while samples E and F were characterized by higher intensity of sweet taste, although all the samples were dry red wine and probably contained a low content of total sugars.

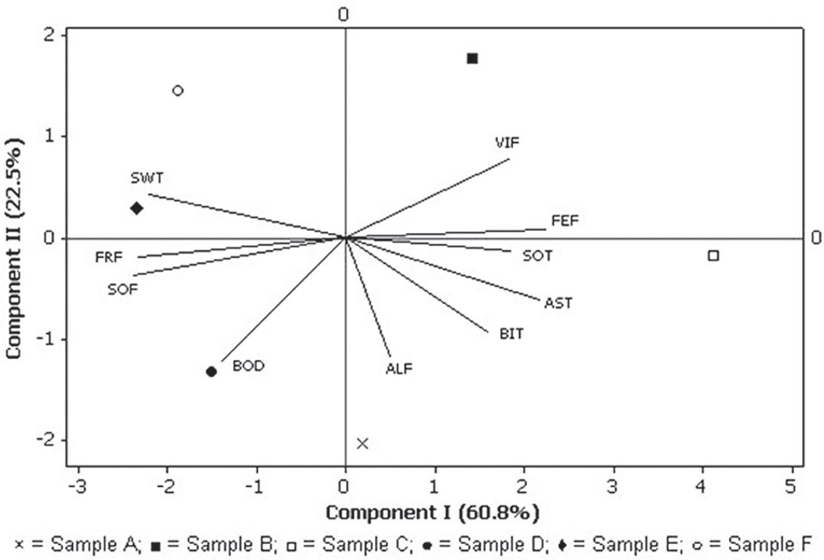

Figure 4. Two-dimensional projection of the results obtained from the principal components analysis I and II for the class of attributes that include mouth sensations.

A qualitative study of volatile compounds for the six brands of red wines analyzed was conducted. 42 volatile compounds were identified, including 8 alcohols, 8 acids, 11 ethyl esters, 4 acetates and 11 compounds belonging to other chemical classes (Table 4).

Table 4. Volatiles compounds identified in red wine samples

Volatile compound	Occurrence							
Alcohols	R_t	A*	B*	C*	D*	E**	F**	Descriptor
1-hexanol	3.54	+	+	+	+	+	+	Vegetable[3]
1-propanol	1.60	+	+	+	+	+	+	
2,3-butanediol	2.53			+	+	+		Cream[1]
2-ethyl-1-hexanol	8.15	+	+	+	+	+	+	
2-methyl-1-butanol	2.10	+	+	+	+	+	+	
3-methyl-1-butanol	2.08	+	+	+	+	+	+	Malty[1]
Decanol	18.09			+				Greasy, sweet aroma[1]
Phenethyl alcohol	10.49	+	+	+	+	+	+	Rose, flowery[4]
Acids and fatty acids								
Acetic Acid	1.59		+	+		+	+	Vinegary[4]
Decanoic acid	22.08			+				Sour odor[1]
Formic acid	1.52					+		
Heptanoic acid	6.40			+				
Hexanoic acid	6.59	+						Grass, buttery[2]
Lactic acid	9.57			+				
Octanoic acid	13.94			+				Sweat[3], rotten fruit[1]
Propanoic acid	2.78	+			+			
Ethyl esters								
9-ethyl decenoato	22.18					+	+	Roses[1]
2-methylethyl butanoate	3.56			+				Apple, sweet[1]
3-methylethyl butanoate	3.64			+				Fruity, floral[1]
Ethyl butanoate	2.65			+	+	+		
Ethyl decanoate	22.58	+	+	+	+	+	+	Fruity, waxy[6]
Ethyl dodecanoate	30.69					+		
Ethyl hexanoate	6.58	+	+	+	+	+	+	Apple[3]
Ethyl isovalerate	3.32				+			Frity[5]
Ethyl lactate	2.83		+		+	+		
Isobutanoate ethyl	2.27					+		
Ethyl octanoate	14.02	+	+	+	+	+	+	Fruity[5]
Acetates								
Ethyl acetate	1.56	+	+	+	+	+	+	Fruity[7]
Phenylethyl acetate	17.23			+				Herbaceous[5], olive[6]
Isoamyl acetate	3.74	+	+	+	+	+	+	Banana[2]
Isoamyl phenyl acetate	4.05			+				
Other compounds								
Decanal	14.32	+		+	+			Dried grass[2]
Ethylbenzene	3.83			+				
Hexadecane	31.64			+				
Isopropylbenzene	6.01			+				
O-xylene	4.43			+				
Propylbenzene	5.88			+				
P-xylene	3.98			+				
Tetradecane	23.59			+				
Toluene	2.56			+				
Tridecanal	19.62			+				
2,4-Di-tert-butyl-phenol	27.41	+					+	

*São Francisco Valley; **Serra Gaúcha; Rt=retention time (min); (+) identified compound. Identification considering only similarity > 90%; 1Gürbüz et al. (2006); 2 Guarrera et al. (2005); 3 Vilanova et al. (2010); 4 Falcão et al. (2008); 5 Goldner et al. (2009); 6 Antalick et al. (2010); 7 Tao et al. (2008).

Identification of each aromatic compound may help in understanding the individual contribution of each volatile compound in the aroma of wine. In all samples, 1-propanol, 2-methyl-1-butanol and 3-methyl-1-butanol were detected. These compounds are among the quantitatively most important higher alcohols in wine (JACKSON, 2008). Phenethyl alcohol (found in all samples) may have contributed to the perception of a floral aroma during the QDA (Table 1).

The increased intensity of the fermented aroma for sample C (Table2) may be associated with the presence of decanoic acid (Table 4). Hexanoic acid was found only in sample A , in agreement with the sensory analysis (Table 2) which indicated that sample A had the highest average for the buttery aroma. Octanoic acid was observed only in sample C and is associated with unpleasant odors (Table 4). Octanoic acid may be related to a more intense aroma of sulphur (characteristic of rotten egg), which was perceived by the sensory panel for sample C (Table 2).

One important organic acid present in *Vitis vinifera* wines is lactic acid, which was identified only in sample C. Lee et al. (2006) found negative correlation between the lactic acid content in red wines and their intensity of ripe fruit aroma. Thus, presence of lactic acid may have contributed to the lower ripe fruit aroma scores in sample C (Table 2). Acetic acid, in turn, was detected in samples B, C, E and F, which was also in agreement with the sensory perception of the vinegary aroma (Table 2).

Among all the aroma compounds identified, the group of esters was one of the most abundant (Table 4). Ethyl octanoate, ethyl decanoate and ethyl hexanoate were found in all samples. Tao et al. (2008) found ethyl hexanoate, ethyl octanoate and ethyl lactate in their wine samples, which gave a nice positive floral and fruity odor with hints of ripe fruits. In the current study, ethyl lactate was detected in samples B, D and E. The highest intensity of fruity aroma, which was perceived in sample D (Table 2), may also be related to the presence of ethyl isovalerate, found only in this sample. The 9-ethyl decenoate may have favored high scores of floral aroma in the samples produced in Southern Brazil (Table 2).

Ethyl acetate and isoamyl acetate were observed in all samples. Phenethyl acetate was found only in sample C, and it may have contributed to a greater perception of an olive aroma by the judges (Table 2), and to the characterization of this sample (Figure 3).

With regard to the compounds belonging to other chemical classes, the only volatile phenol identified was 2,4-di-tert-butyl-phenol (A and F). Tao et al. (2008) also identified this compound, but they did not report a specific aromatic description.

Tao and Zhang (2010) found that ethyl acetate, ethyl isovalerate, ethyl hexanoate, ethyl lactate, 1-hexanol, ethyl octanoate, hexanoic acid and octanoic acid among other compounds have intense odors. The 2,4-di-tert-butyl-phenol and phenyl ethyl acetate compounds have been identified with moderate aromatic impact.

Many atypical compounds in red fine wines were detected in sample C (Table 4) as toluene. Goldner et al. (2009) also detected toluene in samples of wine, but they did not discuss this compound. The presence of these compounds may contribute to aromas and flavors in sample C indicating a possible contamination of the wine. According to Comuzzo et al. (2006), derivatives of benzene (toluene, alkyl benzenes) are among the contaminants commonly detected in various foodstuffs including wine. Although sample C presented several flavor compounds that gave fruity notes, such as various esters and acetates, it may be possible that the aromatic effect was masked due to compounds, such as acetic acid, octanoic acid and the atypical compounds described above (Table 4).

This study helped to identify the aromatic components of the red wine samples produced in the São Francisco Valley and Serra Gaúcha regions. Moreover, it is also important to explain the descriptors of aroma of red wine as follows: a synergistic interaction between volatile components, the association between wine compounds and the chemical composition of wine.

Conclusions

The ANOVA method of investigation showed that color attributes, "pungent aroma", "vinegary aroma" and "softness" were important attributes to discriminate samples B and C (São Francisco Valley) from sample E (Serra Gaúcha) produced from the same grape variety (Cabernet Sauvignon). The multivariate analysis (HCA and PCA) collaborated for the interpretation of sample discrimination, as it was possible to verify the formation of two groups of samples from different regions, characterized mainly by the attributes of color, in the case of PCA. The 9-ethyl decenoate was identified only in samples from the Southern region and it may have contributed to the higher intensity of floral aroma in these wines.

Acknowledgments

Fundings from Fundação de Amparo à Pesquisa do Estado da Bahia (FAPESB) are gratefully acknowledged. The authors would like to thank the Miolo, Botticelli, Bianchetti and Rio Sol wineries, the Laboratory of Analytical Chemistry (UNICAMP), especially Professor Fabio Augusto, and all the judges who participated in the sensory analysis.

References

ANTALICK, G.; PERELLO, M-C.; REVEL, G. Development, validation and application of a specific method for the quantitative determination of wine esters by headspace-solid-phase microextraction-gas chromatography-mass spectrometry. *Food Chem,* v. 121, p. 1236-1245, 2010.

AUGUSTO, F.; LEITE, A.; ZINI, C.A. Sampling and sample preparation for analysis of aromas and fragrances. *Trends Anal Chem,* v. 22, p. 160-169, 2003.

BEHRENS, J.H.; SILVA, M.A.A. Sensory profile of Brazilian varietal white wines by quantitative descriptive analysis. *Ciênc Tecnol Aliment,* v. 20, p. 60-67, 2000.

CADOT, Y.; CIALLÉ, S.; SAMSON, A.; BARBEAU, G.; CHEYNIER, V. Sensory dimension of wine typicality related to a terroir by Quantitative Descriptive Analysis, Just About Right analysis and typicality assessment. *Anal Chim Acta,* v. 660, p. 53-62, 2010.

CÂMARA, J.S.; ALVES, M.A.; MARQUES, J.C. Classification of Boal, Malvazia, Sercial and Verdelho wines based on terpenoid patterns. *Food Chem,* v. 101, p. 475-484, 2007.

CAMPO, E.; BALLESTER, J.; LANGLOIS, J.; DACREMONT, C.; VALENTIN, D. Comparison of conventional descriptive analysis and a citation frequency-based descriptive method for odor profiling: an application to Burgundy Pinot noir wines. *Food Qual Pref,* v. 21, p. 44-55, 2010.

CAMPO, E.; DO, B.V.; FERREIRA, V.; VALENTIN, D. Aroma properties of young Spanish monovarietal white wines: a study using sorting task, list of terms and frequency of citation. *Aust J Grape Wine R,* v. 14, p. 104-115, 2008.

COMUZZO, P.; TAT, L.; TONIZZO, A.; BATTISTUTTA, F. Yeast derivatives (extracts and autolysates) in winemaking: release of volatile compounds and effects on wine aroma volatility. *Food Chem*, v. 99, p. 217-230, 2006.

DAMÁSIO, M.H.; COSTELL, E. Análisis sensorial descriptivo: generación de descriptors y selección de catadores. *Rev Agroquim Tecnol Aliment,* v. 31, p. 165-178, 1991.

DELWICE, J.F. Impact of color on perceived wine flavor. *Foods Food Ingredients J Jpn,* v. 208, p. 349-352, 2003.

DURÁN, L.; COSTELL, E. Percepción del gusto. Aspectos fisicoquímicos y psicofísicos. *Food Sci Technol Int,* v. 5, p. 299-309, 1999.

FALCÃO, L.D.; REVEL, G.; PERELLO, M.C.; MOUTSIOU, A.; ZANUS, M.C.; BORDIGNON-LUIZ, M.T. A survey of seasonal temperatures and vineyard altitude influences on 2-methoxy-3-isobutylpyrazine, C13-norisoprenoids, and the sensory profile of Brazilian Cabernet Sauvignon wines. *J Agric Food Chem*, v. 55, p. 3605-3612, 2007.

FALCÃO, L.D.; REVEL, G.; ROSIER, J.P.; BORDIGNON-LUIZ, M.T. Aroma impact components of Brazilian Cabernet Sauvignon wines using detection frequency analysis (GC-olfatometry). *Food Chem,* v. 107, p. 497-505, 2008.

GAMBARO, A.; VARELA, P.; BOIDO, E.; GIMENEZ, A.; MEDINA, K.; CARRAU, F. Aroma characterization of commercial red wines of Uruguay. *J Sens Stud,* v. 18, p. 353-366, 2003.

GOLDNER, M.C.; ZAMORA, M.C. Effect of polyphenol concentrations on astringency perception and its correlation with gelatin index of red wine. *J Sens Stud*, v. 25, p. 761-777, 2010.

GOLDNER, M.C.; ZAMORA, M.C.; LIRA, P.D.L.; GIANNINOTO, H.; BANDONI, A. Effect of ethanol level in the perception of aroma attributes and the detection of volatile compounds in red wine. *J Sens Stud*, v. 24, p. 243-257, 2009.

GUARRERA, N.; CAMPISI, S.; ASMUNDO, C.N. Identification of the odorants of two Passito wines by gas chromatography-olfactometry and sensory analysis. *Am J Enol Vitic,* v. 56, p. 394-399, 2005.

GÜRBÜZ, O.; ROUSEFF, J.M.; ROUSEFF, R.L. Comparison of aroma volatiles in commercial Merlot and Cabernet Sauvignon wines using gas chromatography-olfatometry and gas chromatography-mass spectrometry. *J Agric Food Chem,* v. 54, p. 3990-3996, 2006.

JACKSON, R.S. *Wine science*: principles and applications. San Diego: Elsevier Academic Press, 2008.

LATTEY, K.A. ; BRAMLEY, B.R. ; FRANCIS, I.L. Consumer, acceptability, sensory properties and expert quality judgments of Australian Cabernet Sauvignon and Shiraz wines. *Aust J Grape Wine R,* v. 16, p. 189-202, 2010.

LEE, S-J.; LEE, J-E.; KIM, H-W.; KIM, S-S.; KOH, K-H. Development of Korean red wines using *Vitis labrusca* varieties: instrumental and sensory characterization. *Food Chem,* v. 94, p. 385-393, 2006.

LUCENA, A.P.S.; NASCIMENTO, R.J.B.; MACIEL, J.A.C.; TAVARES, J.X.; BARBOSA-FILHO, J.M.; OLIVEIRA, J.E. Antioxidant activity and phenolics content of selected Brazilian wines. *J Food Compos Anal,* v. 23, p. 30-36, 2010.

MEILGAARD, G.K.; CIVILLE, G.V.; CARR, B.I. *Sensory evaluation techniques:* Marketing and R & D approaches. Boca Raton: CRC Press, 2007.

MOSKOWITZ, HR. *Product testing and sensory evaluation of foods:* marketing and R & D approaches. Westport: Food and Nutrition Press, 1983.

SÁENZ-NAVAJAS, M-P.; CAMPO, E.; FERNÁNDEZ-ZURBANO, P.; VALENTIN, D.; FERREIRA, V. An assessment of the effects of wine volatiles on the perception of taste and astringency in wine. *Food Chem,* v. 121, p. 1139-1149, 2010.

STONE, H.; SIDEL, J.L. *Sensory evaluation practices*. San Diego: Elsevier Academic Press, 2004.

TAO, Y.; LI, H.; WANG, H.; ZHANG L. Volatile compounds of young Cabernet Sauvignon red wine from Changli County (China). *J Food Compos Anal,* v. 21, p. 689-694, 2008.

TAO, Y.; ZHANG, L. Intensity prediction of typical aroma characters of Cabernet Sauvignon wine in Changli County (China). *LWT-Food Sci Technol,* v. 43, p. 1550-1556, 2010.

TAO, Y-S.; LIU, Y-Q.; LI, H. Sensory characters of Cabernet Sauvignon dry red wine from Changli County (China). *Food Chem,* v. 114, p. 565-569, 2009.

VILANOVA, M.; GENISHEVA, Z.; MASA, A.; OLIVEIRA, J.M. Correlation between volatile composition and sensory properties in Spanish Albariño wines. *Microchemical J,* v. 95, p. 240–246, 2010.

ZHANG, J.; LI, L.; GAO, N.; WANG, D.; GAO, Q.; JIANG, S. Feature extraction and selection from volatile compounds for analytical classification of Chinese red wines from different varieties. *Anal Chim Acta,* v. 662, p. 137-142, 2010.

Artigo recebido em: 31 jul. 2012
Aceito para publicação em: 28 ago. 2012