POLYPHENOLIC AND CHROMATIC CHARACTERIZATION OF TROPICAL RED WINES PRODUCED IN THE SÃO FRANCISCO RIVER VALLEY (NORTHEAST BRAZIL)

L. L. A. LIMA[1*] ; G. E. PEREIRA[2], S. A. C. ANDRADE[3], N. B. GUERRA[3]

[1]Universidade Federal Rural de Pernambuco (UFRPE-DTR),52171-900, Recife, Brasil.
[2]Embrapa Uva Vinho/Semi-árido, 56302-970, Petrolina, Brasil.
[3]Universidade Federal de Pernambuco (UFPE-DN), 50670-901, Recife, Brasil.
* Corresp. author: Luciana Leite de Andrade Lima, 55 81 3320-6284, 55 81 3320-6284, lucianalima.ufrpe@gmail.com

Summary

Young varietal and experimental wines from *Vitis vinifera* – Petit Verdot, Tempranillo and Syrah – cultivated in a tropical semiarid region (Northeast Brazil) were evaluated with regard to their phenolic composition and chromatic characteristics during a storage period of 12-month. The wine was stored in bottles and evaluated using spectrophotometry and high efficiency liquid chromatography to determine color, total polyphenols, anthocyanins, flavanols and flavonols. The Petit Verdot had a less color variation when compared to wines from temperate climates. Although the wines followed the traditional pattern of decreasing polyphenol concentration during storage, the concentrations of these compounds remained higher than those reported in literature, such as for the anthocyanins in Petit Verdot wines and trans-resveratrol in Syrah, showing possible beneficial health effects even after storage.

Key-words: tropical wines, phenolic composition, chromatic characteristics.

INTRODUCTION

The upper middle region of the São Francisco River Valley, northeast Brazil is situated between the 8th and 9th parallels of the southern hemisphere. It has a semiarid tropical climate with intra-annual variability characterized by warm days and nights and produces grapes during different seasons (Pereira *et al.*, 2007). Interactions between the vine and the edaphoclimatic conditions produces typical variations in the phenolic compositions (anthocyanins, flavonols, stilbenes and flavanols) of the grapes and consequently of the wines (Rastija *et al.*, 2008). The variations mentioned above have an impact on color, which is one of the principal attributes of wine quality and is of great importance for winemaking. In addition, these compounds are found to be associated with biochemical and pharmacological effects that are beneficial to human health (Guerrero *et al.*, 2009; Kumar *et al.*, 2009).

This evidence, in addition with the scarcity of information about tropical wines, motivated this study, which aims to evaluate the phenolic composition and chromatic characteristics of the monovarietal and experimental tropical wines produced in the upper middle region of the São Francisco River valley.

MATERIAL AND METHODS

Winemaking

Young monovarietal wines were produced in the Semiarid Oenology Laboratory of Embrapa, Petrolina/PE, with *V. vinifera* L. cv. Petit Verdot, Syrah and Tempranillo grapes, cultivated in the northeast of Brazil (Casa Nova/BA). A starting material of 80-kg of grapes from each variety was vinified on a semi-industrial scale, followed by manual bottling (Peynaud, 1997). The determinations of the polyphenolic composition and colorimetric characterization were performed after 3, 6 and 12-months of storage in 750-mL bottles with agglomerated cork stoppers in a wine cellar heated to 18° ± 1°C and with an average relative humidity of 60%.

Determination of the phenolic composition

Polyphenols: the index at 280-nm (I_{280nm}) was found by reading the absorbance of wines diluted in water at 2%, and using Varian 50 Bio UV/Vis spectrophotometer (Harbertson and Spayd, 2006).

Total anthocyanins: this analysis was done using the spectrophotometer method of differential pH by changing the chromophoric structure of anthocyanins in acidic medium according to OIV (*Office International de la vigne et du vin*,1990).

Flavonols and trans-resveratrol: flavonols (rutin, quercetin, myricetin and kaempferol) and trans-resveratrol were identified and quantified in the *Ultimate* 3000 *Dionex*® liquid chromatograph with an *Acclaim*®120 *Dionex* C-18 analytical column (250 mm x 4.6 mm, 5 µm), wavelengths 370 and 306 nm. The mobile phase was prepared by mixing formic acid to 1% ultra pure water (Milli-Q, Millipore ®) and acetonitrile (HPLC grade), before pH adjusted to 2.5. The compounds were quantified in an analytical curve by external pattern (Voureinen *et al.*, 2000) (modified).

Tannins: total concentration was determined in a spectrophotometer at 725 nm after dilution of the wines in water and reaction with the Folin-Denis phenolic agent, stabilized with a saturated solution of sodium carbonate. The results are shown in mg.L^{-1} of tannic acid (*Association of Official Analytical Chemistry* - AOAC, 1990).

Determination of colorimetric characteristics

The Varian 50 Bio UV/Vis spectrophotometer was used to determine absorbance at 420, 520 and 620 nm. The intensity of color (IC) was found by adding the absorbancies at 420, 520 and 620 nm, tonality (T) expressed by the ratio between the absorbencies at 420 and 520 nm (Caillé *et al.*, 2009).

Statistical Analysis

The results were obtained in triplicate and submitted to ANOVA and Duncan Test for comparison among averages ($p<0.05$) and analysis of the principal components (APC). All statistical analysis was performed using the *Statistics for Windows 7® So*ftware

RESULTS AND DISCUSSION

Phenolic characterization and its evolution during aging

The results shown in Table 1 corroborate the findings of Falcão *et al.* (2007) with regards to the influence of grape variety upon the amount of polyphenols in wines and demonstrate that although the Petit Verdot wine showed the highest levels of total polyphenols, the Tempranillo and Syrah wines had the highest stability during 12-months of storage. With respect to the anthocyanin concentration, the Petit Verdot had the greatest amount, approximately 25.0%, and the Tempranillo had the smallest drop (49.0%) during storage. Concerning Tempranillo, they were superior to the value for Spanish wines obtained by Monagas *et al.* (2005), which was 360.0 $mg.L^{-1}$.

The significant variation of total tannins ($p < 0.05$) among all wines after 12-months of storage (Table 1) show that the flavanols also depend upon variety and *terroir*.

This study confirmed that myricetin, quercetin and kaempferol are the main flavonols in red wines (Table 2). Results found by several researchers show that the content of each flavonol in wines is caused by several factors, including winemaking techniques, exposure to solar light during maturation, climate conditions of the harvest, and genetic factors of the grapes (Gutierréz *et al.*, 2005; Vuorinen *et al.*, 2000). Trans-resveratrol stilbene has multiple benefits for human health and was found in all samples, table 2.

Table 2. Composition of flavonols in tropical wines, before 12-months of storage in the bottle.

Variety	Flavonóis ($mg.mL^{-1}$)				Stilben ($mg.mL^{-1}$)
	rut[a]	mir[b]	que[c]	kam[d]	t-resv[e]
Petit Verdot	ND	7.5±0.09	6.1±0.35	0.4±0.04	3.0±0.05
Tempranillo	ND	10.8±0.12	7.4±0.06	ND	2.9±0.08
Syrah	ND	5.3±0.02	1.2±0.05	0.1±0.01	12.1±0.01

a: rutin-3-glicose; b: myricetin-3-glicose; c: quercetin-3-glicose; d: kaem-3-glicose; e: trans-resveratrol.

Chromatic characterization

The decrease of anthocyanin concentration is characteristic of the aging process, during which absorbancy at 520-nm decreases and absorbance in the 400-430-nm spectrum increases, and this behavior was observed in this study.The chromatic characterization (Figure 1) shows significant differences among varieties with regard to color intensity and tonality, highlighting the stability of the IC of the Syrah wines during twelve months of storage.

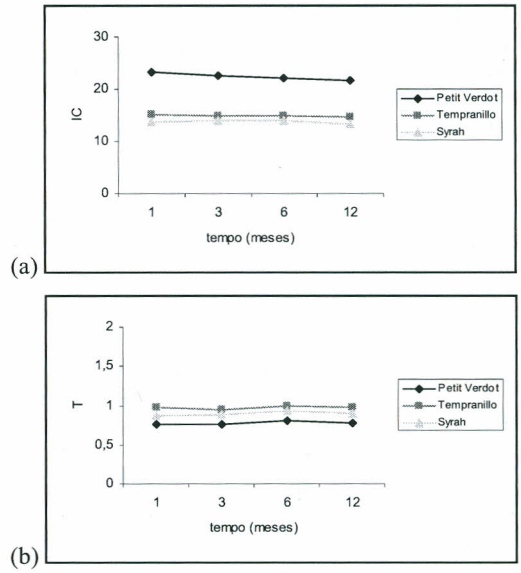


Figure 1. Chromatic characterization of the tropical red wines, during storage in the bottle, (a) color intensity and (b) tonality.

Table 1. Stability of polyphenols in tropical red wines, during storage in the bottle.

variety / months	Petit Verdot			Tempranillo			Syrah		
	3	6	12	3	6	12	3	6	12
POL[a] (I_{280nm})	70.4 ±0.04	66.3 ±0.01	70.0 ±0.01	69.1 ±0.36	61.7 ±0.06	68.4 ±0.08	56.9 ±0.08	53.0 ±0.01	58.8 ±0.03
ANT[b] ($mg.L^{-1}$)	508.0 ±0.86 ^{Ab}	496.8±0.54 ^{Ab}	431.1±0.34 ^{Ac}	356.6 ±0.72 ^{Cb}	312.5 ±0.54 ^{Bc}	225.3±0.18 ^{Cd}	395.1 ±0.78 ^{Bb}	314.8 ±0.98 ^{Bc}	234.7±0.12 ^{Cd}
Total Tannins ($mg.L^{-1}$)	-	-	2076.1± 13.1^{C}	-	-	2759.8± 11.8^{A}	-	-	2546.5± 11.4^{B}

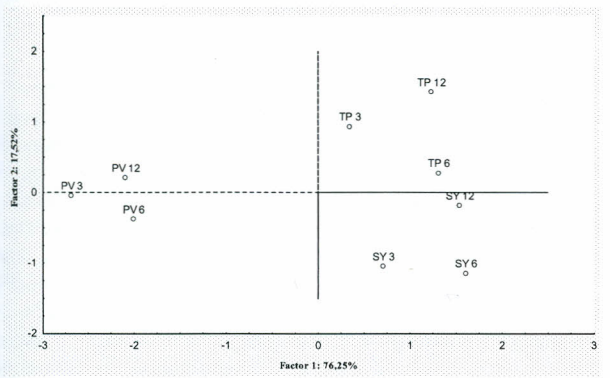
a: polyphenols total índex of 280nm; b: total anthocyanins. Average followed of diferent letter significant difference according to the test of Duncan ($p<0,05$). Average followed of capital letter – comparation beteween variety in the same storage time – and the small letters – comparation between storage time in the same variety.

Multivariate analysis

Separation of the tropical red wines was performed using values of total polyphenols ($I_{280\ nm}$), total anthocyanins and chromatic parameters during 3, 6 and 12 months of storage in bottles. The first two principal components extracted 93.77% of the total variance, from which the first principal component (PC1), which represents 76.25%, was dominated by colorimetric intensitivy, tonality and total anthocyanins, while the second (PC2), was 17.52% and was dominated by percentage of total polyphenols (Figure 2).

The Petit Verdot wines, which were characterized by positive values of the total polyphenols and by negative values of the total anthocyanins and colorimetric intensity, are grouped in the left of the graphic. The Tempranillo wines, indicated by positive values of tonality are found at the rigth of the PC1.

(a)



(b)

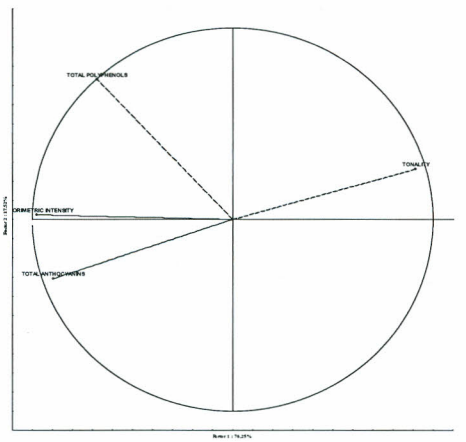


Figure 2. The distribuition of the red wines (a) (SY= Syrah; PV= Petit Verdot e TP = Tempranillo) and variable contribuition (b), during storage for 3, 6 and 12-months in the bottle, in two dimension with the coordinates system defined the first and second principal component.

Characterization and aging in the bottle confirmed the variation in phenolic composition and color in red wines, made from different cultivars. These results will ~~be~~ contribuite to the establishment of Geographical Indication of Origin. Moreover, the analytical results, during storage, followed the traditional pattern of decrease of phenolic compounds.

LITERATURE

Association of Official Analitycal Chemists – *Office methods of anaysis.* 1990. 15 ed. Washington.

CAILLÉ S., SAMSON A., WITH J., DIÉVAL J.-B., VIDAL S., CHEYNIE V. 2009. Sensory characteristics changes of red Grenache wines submitted to different oxygen exposures pre and post bottling. *Analytical Chimica Acta*, Doi: 10.1016/j.aca.2009.11.049.

FALCÃO A.P., CHAVES E.S., KUSKOSKI E.M., FETT R., FALCÃO L.D., BORDIGNON-LUIZ M.T. 2007. Índice de polifenóis, antocianinas totais e atividade antioxidante de um sistema modelo de geléia de uvas. *Ciência e Tecnologia dos Alimentos*, 27, 637-642.

GUERRERO R.F., LIAZID A., PALMA M., PUERTAS B., GONZÁLEZ-BARRIO R., GIL-IZQUIERDO A., GARCIA-BARROSO C., CANTOS-VILLAR, E. 2009. Phenolic characterisation of red grapes autochthonous to Andalusia. *Food Chemistry*, 112, 949-955.

GUTIÉRREZ I.H., LORENZO E.S.P., ESPINOSA A.V. 2005. Phenolic composition and magnitude of copigmentation in young and shortly aged red wines made from the cultivars Cabernet Sauvignon, Cencibel and Syrah. *Food Chemistry*, 92, 269-283.

HARBERTSON J., SPAYD S. 2006. Measuring phenolics in the winery. *American Journal of Enological and Viticultural*, 57, 280-288.

KUMAR A., MALIK A.K., TEWARY D.K. 2009. A new method for determination of myricetin and quercetin using solid phase microextraction-high performance liquid chromatography-ultra violet/visible system in grapes, vegetables and red wines samples. *Analytical Chimica Acta*, 631,177-181.

MONAGAS M., MARTIN-ALVAREZ P.J., GOMÉZ-CORDOVÉS C., BARTOLOMÉ B. 2006. Time course of the colour of young red wines from *Vitis vinifera* L. during ageing in bottle. *International Journal of Food Science and Technology*, 41, 892-899.

PEREIRA G.E., SOARES J.M., GUERRA C.C., ALENCAR Y.C.L., LIRA M.M.P., LIMA M.V.O, SANTOS J. 2007. Caractérisation de vins rouges tropicaux produits au Nord-Eut du Brésil. In: *PROCEEDINGS OF THE 59TH GERMAN VICULTURE CONGRESS WINE IN MOTION*. Stuttgart, Alemanha.

PEYNAUD E. 1997. *Connaissance et travail du vin.* Paris :Editora Dunod, 341p.

RASTIJA V., SRECNIK G., SARIC M.-M. 2008. Polyphenolic composition of Croatian wines with different geographical origins. *Food Chemistry*, Doi: 101016/i-foodchem.

VUORINEN H., MÄÄTTÄ K., TÖRRÖNEN R. 2000. Content of the flavonols myricetin, quercetin and kaempferol in finnish berry wines. *Journal of Agricultural and Food Chemistry*, 48, 2675-2680.

ACKNOWLEDGEMENTS

The authors thank the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for financial support, the Miolo Wine Group for maintenance of the grapevines.