Aromatic stability of Syrah and Petit Verdot tropical wines from Brazil

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ABSTRACT
The production of fine wines in the Sub-middle of the São Francisco River Valley, Northeast of Brazil, is relatively recent, about twenty-five years ago. This region presents different characteristics, with a tropical semiarid climate, in a flat landscape. Presenting high annual average temperature, solar radiation and water in abundance for irrigation, it’s possible the scaling the grape harvests for winemaking throughout the year, allowing to obtain until two harvests per year. Several factors may affect the aromatic compounds in wines, such as viticulture practices, climatic conditions, cultivars and winemaking process. This study aimed to evaluate the aromatic stability of Syrah and Petit Verdot tropical wines elaborated in two different periods in the year. The grapes were harvested in the first and second semesters of 2009, in June and November. The wines were elaborated and then, they were bottled and analyzed in triplicate. thirty days and one year after bottling, by gas chromatography with ionization detector flame (GC-FID), to evaluate the profile and the stability of the aroma compounds. Principal component analysis was applied to discriminate between wine samples and to find the compounds responsible by the variability. The results showed that Syrah and Petit Verdot tropical wines presented different responses, for stability of higher alcohols, esters and carboxylic acids.

Keywords: grapes, red wines, tropical climat, aroma.

1 INTRODUCTION
Brazilian tropical wines have been studied few years ago and researches are being developed to characterize the effect of climate and soil conditions on adaptation of different cultivars, by determination of grape and wine composition (1-5).

The terroir effect has been showed that influences the wine characteristics (6). Climate, soil, and vineyard management are important factors playing a very important role on grape maturation and wine composition. Many compounds have been determined and related to the wine identity, like phenolic and aroma characteristics (5-8). Wine flavors have been recently studied in wines from tropical conditions in Brazil and are linked to the local terroir. In this condition, grapes and wines can be elaborated in different months, presenting variations in their composition, quality and typicity (5, 9).

There are several molecules taking part in the volatile compounds in wines, showing high complexity, presenting antagonistic as well as synergistic effects between them. Technological advances have allowed for the analysis of the aroma composition and can be widely used to differentiate cultivars and determine the quality and typicality of wines (10-13). In this way, this study aimed to evaluate the aroma stability of Syrah and Petit Verdot tropical wines elaborated in two different periods of the year, in Brazil.

2 MATERIAL AND METHODS
The wines were elaborated from grapes of two cultivars, Petit Verdot and Syrah, harvested in a commercial winery localized in Casa Nova-BA, in the Northeast region of Brazil, in two harvests of the year 2009, in June (Harvest 1-HI) and November (Harvest II-HII). The winemaking process adopted was the traditional method, with control of fermentation temperature (25°C and 18°C, for alcoholic and malolactic fermentations respectively) and one month of cold stabilization at 0°C (14-15). All wines were analyzed thirty days after the bottling (TI) and one year after the first analysis (TII). The volatiles were evaluated in triplicate by gas chromatography with ionization detector flame (GC-FID) and quantified using internal standardization. For the isolation of the volatile compounds, there were used two methods of extraction (11-13). The first one was a liquid-liquid extraction by solvent (LLE), realized utilizing a mixture of hexane and ether (1:1) in acidified medium with phosphoric acid. Two internal standards were added, 3-octanol and heptanoic acid. The wines were also distillated to the quantification of the higher alcohols, after the addition of 4-methyl-2-pentanol as internal standard. By both methods it was possible to identify and quantify 25 compounds, between esters, higher alcohols, carboxylic acids, and aldehydes. The data were analyzed by multivariate statistical analysis.

3 RESULTS AND DISCUSSION
Principal Component Analysis (PCA) was used to show groups of samples and to explain differences among the aroma profile of the wines in function of the harvest date, cultivar and wine aging. PCI and PCII explained 58.72% of the total variation (Figure 1). Wines from both cultivars responded differently and results varied according to the harvest date. For Petit Verdot, differences were observed in the wines elaborated in both harvests and the aging factor, while for Syrah wines, only the first semester played important role to distinguish wines according to the aging. Syrah wines from November presented similarities for the aging factor.

PC1 explained 33.21% of total variability and separated wines from Petit Verdot wines elaborated with grapes harvested in November, analyzed just after bottling, in the positive side of the axis x, of the same Petit Verdot wines analyzed after 12 months, that are located in the negative side of the axis x, with wines of Syrah and Petit Verdot from June, twelve months aging. The main compounds characterizing the wines were, for the positive side of PC1, phenyl-ethyl acetate, isoamyl acetate, octanoic acid, 2-methyl-l-butanol and hexanol. Characterizing the Petit Verdot from November and Syrah and Petit Verdot from June aging wines, in the negative side of PC1, the compound identified was 3-methyl-l-butanol. PC2 explained 25.51% and separated Petit Verdot and Syrah wines elaborated in June, analyzed after bottling, located in the positive side of the PC2, in the y axis, from both wines of Syrah elaborated in November, analyzed after the bottling and twelve months aging, in the negative side of PC2. The compounds identified characterizing the positive side of PC2 were hexanol, ethyl dodecanoate, ethyl decanoate, 2-methyl-1-propanol and
1-propanol for Petit Verdot and Syrah wines, and 2-phenylethanol, ethyl butanoate and ethyl acetate for Syrah wines from November, in the negative side of PC2. These results showed that the climate, represented here by the harvest date, and variety factors played important role on aroma compounds and wine stability (14, 16).

Figure 1. PC1 x PC2 explaining 58.72% of variation of aroma compound data of Syrah and Petit Verdot wines, from two crops in 2009 and two periods of analysis, after bottling and 12 months aging. A) Distribution of the wine samples analyzed; and B) Distribution of the 25 volatile compounds quantified by GC-FID. The wines are: PV: Petit Verdot and SY = Syrah. H1 (crop I, in June); HII (crop II, in November); T1 (thirty days after bottling) and TII (one year after the first analysis).

The higher alcohols 1-propanol, 2-methyl-1-butanol, 3-methyl-1-butanol and 2-phenylethanol were present in higher concentrations, participating in the aroma complexity of the wine (data not shown). The alcohols 2-methyl-1-butanol and 3-methyl-1-butanol are formed during the fermentation and therefore the final content of these two higher alcohols in wine is proportional to the ethanol formed. The 2-phenylethanol is described with pleasant terms as “rose”. This alcohol is associated with the typical aroma characteristics in red wines produced in the region of Berry, Portugal (17). This compound was the main volatile responsible for the differentiation of the Syrah wines from November, analyzed after bottling and aging.

The esters are present in lower concentrations in the wines, usually among 1 mg.L$^{-1}$ to 100 mg.L$^{-1}$, and may be synthesized by microorganisms, generating aroma notes of fruit, such as “apple”, “pear”, “pineapple”, “strawberry” and “melon” (18). In the present work different concentrations were found (data not shown). According to the literature, few acids effectively contribute to the aroma of the wine. In general, the most important acids are the acetic acid ("odor of vinager"), propanoic acid ("odor of cheese"), butyric acid ("odor of rancidness"), hexanoic, octanoic and decanoic acids ("sweet aroma") and 2-hydroxypropanoic acid ("odor of cheese") (19-20). Acids participated also of the aroma profile of the wines in Northeast of Brazil.

4 CONCLUSIONS
The differences found among the concentrations of volatiles and the stability of these compounds after 12 months aging may be explained by the particular
genetic expression of the Syrah and Petit Verdot varieties and its interaction with the climatic conditions in both seasons in the Northeast of Brazil. Future researches are necessary using gas chromatography associated to mass spectrometry (GC-MS) to identify compounds that were not identified contributing to the tropical wine quality.

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