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Pre-drying and submerged cap winemaking: Effects on polyphenolic compounds and sensory descriptors. Part II: BRS Carmem and Bordô (*Vitis labrusca* L.)

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Peonidin 3,5-diglucoside (PubChem CID: 44256843)
Malvidin 3,5-diglucoside (PubChem CID: 12312725)
Malvidin 3-(6″-*p*-coumaroyl)-glucoside-5-glucoside (PubChem CID: 44256995)
Vitisin A (PubChem CID: 10325504)
Myricetin 3-glucoside (PubChem CID: 22841567)
Catechin (PubChem CID: 9064)
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ABSTRACT

Brazilian wine production is dominated by the use of American grape cultivars (*Vitis labrusca* L.) and their hybrids. In this context, this study analyzed the phenolic composition and sensory profile of Bordô and BRS Carmem red wines elaborated from traditional and two alternative winemaking technologies: grape pre-drying and submerged cap of chaptalized musts. Anthocyanins and pyranoanthocyanins apparently seemed to be affected by the thermal process (60 °C), causing their degradation. In addition, the decrease of the concentration of these compounds could be suggested as a result of possible oxidation and hydrolysis reactions of anthocyanin 3-glucosides. Stilbenes were also affected by thermal degradation; however, flavan-3-ols and HCAD seemed to be less affected by the drying process. Submerged cap winemaking resulted in an increase of the anthocyanin and pyranoanthocyanin compounds due to the constant contact between the must and pomace during the alcoholic fermentation. The antioxidant capacity seemed not to be affected by thermal degradation, since the products of Maillard reaction also present antioxidant properties. Pre-dried wines were described as structured due to their higher flavan-3-ols content, and with high color intensity probably due to the formation of Maillard reaction products. The submerged cap wines presented an intense violet hue due to their high anthocyanin derivative concentrations and showed strong correlation with all other classes of the phenolic compounds.

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1. Introduction

Vitis vinifera is the most used grape for wine production throughout the world, however in Brazil, the wines are mostly elaborated from the American grapes (*Vitis labrusca*) and their hybrids known as table wines, which have surpassed the production of wines elaborated from European grapes (Biasoto, Netto, Marques, & Da Silva, 2014). This fact is probably due to the tropical climatic conditions of the major viticulture regions of Brazil, which present features that are unfavorable for the growth of *V. vinifera* grape cultivars. Additionally, the American grapes present strong adaptation to hot climates, versatility in relation to the crop planning and their rusticity is an interesting feature related to their high resistance to the major diseases of the vine (De Castilhos, Conti-Silva, & Del Bianchi, 2012).

Despite the above-mentioned advantages, the American grapes and their hybrids present low soluble solids content and reduced color intensity on their optimal stage of ripening. Thus, there is a need to improve these features in order to produce table wines that are more attractive for the consumers, as a result of the enhancement of the red pigments extraction from grape berries by variation on the winemaking process or genetic improvement (Camargo & Ritschel, 2008).

In this context, the Brazilian agro-farming research agency EMBRAPA Grape and Wine has been developing new hybrid grape cultivars with higher sugar content and color indexes under normal growth conditions. Among the new cultivars developed, it is possible to highlight the 'BRS' type cultivars such as: BRS Carmem, BRS Rúbea, BRS Cora, BRS Violeta and others. Of these one can highlight the BRS Carmem, which was a grape originated in 2008 as a result of the crossing between Muscat Belly A and BRS Rúbea producing red wines with an intense violet hue and typical raspberry aroma and flavor (Camargo, Maia, & Ritschel, 2008). In addition to these grapes developed by means of genetic improvement, Bordô grape (*V. labrusca* L.), already a well-known grape cultivar in Brazil, which produces wines with intense red-purple color, fruity aroma and usually used as a blend with wines presenting low color hues (Lago-Vanzela, Da-Silva, Gomes, García-Romero, & Hermosín-Gutiérrez, 2011).

Additionally to the genetic improvement, the modifications on the winemaking process are usually carried out by wineries aimed at improving the quality of red wines by the enhancement of the phenolic compound extraction during the alcoholic fermentation. Among the possible variations in the winemaking process, grape drying (Marquez, Serratosa, Lopez-Toledano, & Merida, 2012) is one of the procedures applied in order to gain wine color as a result of the irreversible damage to the cellular structure of the grape skin caused by the heat that facilitates the extraction of anthocyanins and other phenolic compounds (Figueiredo-González, Cancho-Grande, & Simal-Gándara, 2013; Margaris & Ghiaus, 2007). The submerged-cap during the wine maceration is another alternative winemaking procedure that facilitates the contact between the pomace and the must, which promotes higher extraction of the phenolic compounds from the grapes (Bosso et al., 2011). However, these studies are restricted to the analysis of the phenolic compounds from red wines elaborated by *V. vinifera* grapes and studies that assessed the response of these winemaking procedures in wines elaborated from *V. labrusca* grapes and hybrids are practically non-existent.

The maximum levels of these wine pigments are observed during the early days of the maceration and approximately 30–40% of the anthocyanins remain in the crushed skins (Marquez et al., 2012). During the maceration, anthocyanins and tannins are extracted from the solid parts of the berries allowing the oxidation and condensation reactions and absorption phenomena that cause a balance between extraction and loss. The anthocyanin content decreases during the maceration time by the reactions of coupled oxidation catalyzed by polyphenoloxidase (PPO) in the presence of residual oxygen. The submerged-cap winemaking procedure aims at avoiding the contact between the solid parts and the residual oxygen in order to increase the anthocyanin content of the resulting wine (Bosso et al., 2011).

Considering that the quality of the red wines is based on the assessment of their sensory attributes, any variation in the winemaking process can change their phenolic composition, antioxidant capacity, as well as their sensory features, promoting changes on the wine quality. A similar previous work was done assessing the phenolic and sensory profiles of BRS Rúbea and BRS Cora red wines submitted to alternative winemaking procedures (De Castilhos et al., 2015) and another study with BRS Violeta, a *teinturier* grape, is being carried out. These studies present a strong contribution to the enological area since the response of these winemaking procedures on the chemical and sensory profiles of the red wines elaborated from these new grape cultivars are yet unknown.

Thus, the aim of this work was to evaluate the detailed composition of the most relevant phenolic compounds, the antioxidant capacity and sensory descriptive attributes of Bordô and BRS Carmem red wines elaborated from traditional (T) and two alternative winemaking procedures: grape pre-drying (PD) and submerged cap (SC). In addition to the influence of these techniques on chemical and sensory profiles, a chemometric approach was generated in order to allow for a relationship between both profiles.

2. Material and methods

2.1. Chemicals

All solvents were of HPLC quality, all chemicals were of analytical grade (>99%) and the water was of Milli-Q quality. The following commercial standards from Phytolab (Vestenbergsgreuth, Germany) were used for the identification of the phenolic compounds: malvidin 3-glucoside, malvidin 3,5-diglucoside, peonidin 3,5-diglucoside, *trans*-piceid, *trans*-caftaric acid, (−)-epigallocatechin and (−)-gallocatechin, as also the following commercial standards from Extrasynthese (Genay, France): cyanidin 3-glucoside, cyanidin 3,5-diglucoside, procyanidins B1 and B2, kaempferol, quercetin, isorhamnetin, myricetin, syringetin and the 3-glucosides of kaempferol, quercetin, isorhamnetin and syringetin. In addition, the following commercial standards from Sigma Aldrich (Tres Cantos, Madrid, Spain) were used: *trans*-resveratrol, caffeic acid, (+)-catechin, (−)-epicatechin, (−)-epicatechin 3-gallate and (−)-gallocatechin 3-gallate. Other non-commercial flavonol standards such as myricetin 3-glucoside, quercetin 3-glucuronide and laricitrin 3-glucoside were previously isolated from Petit Verdot grape skins (Castillo-Muñoz et al., 2009). Procyanidin B4 was kindly supplied by Prof. Fernando Zamora (Department of Biochemistry and Biotechnology, Universitat Rovira i Virgili, Spain). The *trans* isomers of resveratrol and its 3-glucosides (piceid) were converted into their respective *cis* isomers by UV irradiation (366 nm light for 5 min in quartz vials) of 25% MeOH solutions of the *trans* isomers.

All the standards were used for identification and quantitation by calibration curves covering the expected concentration ranges. When a standard was not available, the quantitation was done using the calibration curve of the most similar compound: malvidin 3,5-diglucoside for 3,5-diglucoside anthocyanin type and malvidin 3-glucoside for the 3-glucoside type, quercetin 3-glucoside for flavonol 3-glycosides and their free aglycones, caffeic acid for hydroxycinnamic acid derivatives, (+)-catechin for polymeric flavan-3-ols (total proanthocyanidins), and individual flavan-3-ol monomers and dimers by their corresponding standards considering their total sum as (+)-catechin equivalents.

2.2. Winemaking

Six red wines were produced: traditional Bordô wine (BT), pre-dried Bordô wine (BPD), submerged cap Bordô wine (BSC), traditional Carmem wine (CART), pre-dried Carmem wine (CARPD) and submerged cap Carmem wine (CARSC). The grapes were harvested in