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Influence of the temperature and oxygen exposure in red Port wine: A kinetic approach

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Para-coumaric acid (PubChem CID: 637542)
Ferulic acid (PubChem CID: 445858)
Gallic acid (PubChem CID: 370)
Syringic acid (PubChem CID: 10742)
(+)-Catechin (PubChem CID: 9064)
(−)-Epicatechin (PubChem CID: 72276)
Malvidin-3-glucoside (PubChem CID: 443652)

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ABSTRACT

Although phenolics are recognized to be related with health benefits by limiting lipid oxidation, in wine, they are the primary substrates for oxidation resulting in the quinone by-products with the participation of transition metal ions. Nevertheless, high quality Port wines require a period of aging in either bottle or barrels. During this time, a modification of sensory properties of wines such as the decrease of astringency or the stabilization of color is recognized to phenolic compounds, mainly attributed to anthocyanins and derived pigments.
The present work aims to illustrate the oxidation of red Port wine based on its phenolic composition by the effect of both thermal and oxygen exposures. A kinetic approach toanthocyanins degradation was also achieved. For this purpose a forced red Port wine aging protocol was performed at four different storage temperatures, respectively, 20, 30, 35 and 40 °C, and two adjusted oxygen saturation levels, no oxygen addition (treatment I), and oxygen addition (treatment II). Three hydroxycinnamic esters, three hydroxycinnamic acids, three hydroxybenzoic acids, two flavan-3-ols, and six anthocyanins were quantitated weekly during 63 days, along with oxygen consumption. The most relevant phenolic oxidation markers were anthocyanins and catechin-type flavonoids, which had the highest decreases during the thermal and oxidative red Port wine process. Both temperature and oxygen treatments affected the rate of phenolic degradation. In addition, temperature seems to influence mostly the phenolics kinetic degradation.

1. Introduction

The main non-enzymatic reactions occurring during food and beverages processing or storage are the degradation of polyphenols, Maillard reaction, sugar caramelization, and oxidation, leading to browning and aroma/flavor formation. Polyphenols are reactive compounds, which can be degraded and polymerized through both enzymatic and non-enzymatic reactions during food and beverage processing and storage. Polyphenols chemical reactions have been particularly studied in wine (Cheynier, 2005), where these reactions include mainly oxidations and/or polymerizations.

Constituents of both red and white wines are capable of reacting with significant amounts of oxygen, polyphenols being among the most readily oxidized wine constituents (Oliveira, Silva Ferreira, De Freitas, & Silva, 2011; Singleton, 1987). Nevertheless, red wines contain higher levels of polyphenols, among which, anthocyanins, procyanidins, and flavan-3-ols are in particularly highest levels (Kilmartin, 2009; Waterhouse & Laurie, 2006).

The oxidative processes of wine begin by the oxidation of polyphenols containing a catechol or a galloyl group such as (+)-catechin/(−)-epicatechin, gallocatechin, gallic acid and its esters, and caffeic acid, which are the most readily oxidized wine constituents (Kilmartin, Zou, & Waterhouse, 2001; Makhotkina & Kilmartin, 2009). These substrates are sequentially oxidized to semi-quinone radicals and *ortho*-quinones, while oxygen is reduced to hydrogen peroxide (Oliveira et al., 2011). Quinones are therefore key reactive electrophilic oxidation intermediates in wine (Nikolantonaki & Waterhouse, 2012)

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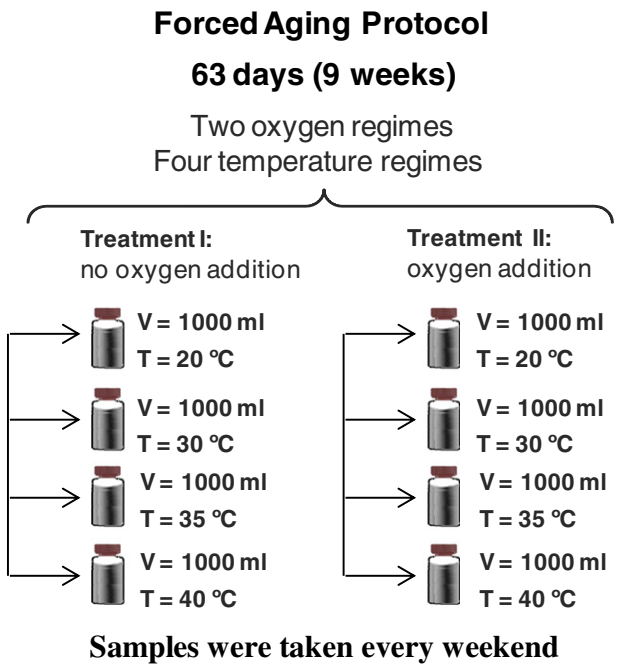

Fig. 1. Forced aging protocol.

and can undergo many reactions with wine nucleophiles like sulfur dioxide, ascorbic acid, amino acids, thiols, and other phenolics, including the formation of yellow or brown products (due to the polymerization of *ortho*-quinones) and the loss of varietal aromas.

It is established that oxygenation could improve the evolution of red wines during aging, by color stabilization and decrease on astringency. On the other hand, a long oxidation process will reduce wine antioxidants, such as sulfur dioxide or ascorbic acid, and the oxidation of desirable volatile compounds (Oliveira et al., 2011). Concomitantly, temperature will accelerate the oxidation process (Palacios, Caro, & Perez, 2001).

Considering monomeric anthocyanins, several reports on the effects of temperature and oxygen on this class of phenolics have been studied in red wines and wine-model solutions.

Simpson (1985) suggested that thermal degradation of anthocyanins could occur via two mechanisms: (i) from the hydrolysis of the 3-glycoside linkage to form the more labile aglycon; and (ii) from the hydrolytic opening of the pyrilium ring to form a substituted chalcone, which then degrades to brown insoluble phenolic compounds. Degradation of anthocyanins, under different temperatures, has been reported in model solutions (Romero & Bakker, 1999; Romero & Bakker, 2000; Tseng, Chang, & Wu, 2006) where it was found that, the discoloration of anthocyanins in ethanolic solutions is faster than in aqueous solutions (Tseng et al., 2006), and the increase of pH induces the rate of consumption of these phenolics (Romero & Bakker, 1999). Considering red wines, it was observed that, after 6 months of storage of young red wines, the content of anthocyanins was lower in wines stored at 25 °C compared to wines stored at 15 °C, possibly because oxidation of anthocyanins occurs faster at higher temperatures causing their decrease (Ivanova, Vojnoski, & Stefova, 2012). Moreover, wine SO_2 additions (0–100 mg/L) decrease the anthocyanins (malvidin-3-glucoside, malvidin-3-*O*-acetylglucoside, and malvidin-3-*O*-coumaroylglucoside) degradation rate through temperature (12 to 42 °C) (Dallas, Ricardo-da-Silva, & Laureano, 1995). Considering red Port wines the losses of free anthocyanins followed first-order kinetics during time aging (Bakker, Preston, & Timberlake, 1986; Mateus & De Freitas, 2001).

Micro-oxygenation in red wines has confirmed the loss of monomeric anthocyanins (Cano-López, Pardo-Minguez, López-Roca, & Gómez-Plaza, 2006; Gambuti, Rinaldi, Ugliano, & Moio, 2013; Kontoudakis et al., 2011; Pérez-Magariño, Sánchez-Iglesias, Ortega-Heras, González-Huerta, & González-Sanjosé, 2007) along with the formation of polymeric pigments, resistant to sulfur dioxide (SO_2) bleaching (Cano-López et al., 2008; Gonzalez-del Pozo, Arozarena, Noriega, Navarro, & Casp, 2010; Rayne, Sheppard, Di Bello, & Eggers, 2011).

Other monomeric phenolics (non-anthocyanins) have been evaluated in both white and red wines during bottle storage and after accelerated browning. Accelerated browning of white wines subjected to heating at a constant temperature of 55 °C (during 12 days) did not significantly change the concentrations of hydroxycinnamic esters (*trans*-caftaric acid, *trans*-coutaric acid, and *trans*-fertaric acid) but it significantly increased the concentrations of their corresponding hydroxycinnaminc acids (caffeic acid, *para*-coumaric acid, and ferulic acid) (Kallithraka, Salacha, & Tzourou, 2009). In fact, a decrease in the concentration of the hydroxycinnamic esters and an increase in their respective acids have been already reported (Recamales, Sayago, Gonzàlez-Miret, & Hernanz, 2006), although some authors have state opposite results (Cejudo-Bastante, Hermosín-Gutierrez, Castro-Vazquez, & Pérez-Coello, 2011; Mayen, Baron, Merida, & Medina, 1997). Moreover, (+)-catechin concentration was not affected by browning, while (−)-epicatechin concentration has decreased during accelerated browning (Kallithraka et al., 2009). Concerning fortified Madeira wines (white and red varieties) kept for 3 months at 45 °C, and for 1 month at 70 °C, a noticeable decrease of *trans*-caftaric acid, *trans*-coutaric acid, and *trans*-fertaric acid was

Table 1
Phenolics identification based on HPLC-DAD of Port wines.

No.	Retention time (min)	λ_{max1}	λ_{max2}	λ_{max3}	Compound name	Identification
1	2.9	270			Gallic acid	Available standard
2	3.0	258	292		Protocatechuic acid	Available standard
3	9.8	(296)	328		*trans*-Caftaric acid	Gutiérrez et al. (2005), Mozetič et al. (2006)
4	10.6	280			Catechin	Available standard
5	11.9	(296)	326		Caffeic acid	Available standard
6	12.0	276			Syringic acid	Available standard
7	12.3	(296)	314		*trans*-Coutaric acid	Gutiérrez et al. (2005), Mozetič et al. (2006)
8	12.7	280	(328)	528	Delphinidin-3-glucoside	Guerrero et al. (2009)
9	13.4	280			Epicatechin	Available standard
10	14.0	278	(328)	528	Petunidin-3-glucoside	Guerrero et al. (2009)
11	14.4	(300)	328		*trans*-Fertaric acid	Mozetič et al. (2006)
12	14.9	278	(334)	516	Peonidin-3-glucoside	Guerrero et al. (2009)
13	15.2	280	(348)	528	Malvidin-3-glucoside	Guerrero et al. (2009)
14	15.6	(296)	308		*para*-Coumaric acid	Available standard
15	16.3	(278)	320		Ferulic acid	Available standard
16	18.4	280	(324)	528	Mv-3-*O*-acetylglucoside	Guerrero et al. (2009)
17	20.7	282	(312)	534	Mv-3-*O*-coumaroylglucoside	Guerrero et al. (2009)