Food Research International 51 (2013) 59–65

Contents lists available at SciVerse ScienceDirect

Food Research International

journal homepage: www.elsevier.com/locate/foodres

Oxidative evolution of (+)-catechin in model white wine solutions containing sulfur dioxide, ascorbic acid or gallotannins

Fabio Chinnici *, Francesca Sonni, Nadia Natali, Claudio Riponi

Department of Agri-Food Sciences and Technologies, University of Bologna, Viale Fanin, 40-40127, Bologna, Italy

ARTICLE INFO

Article history:
Received 24 August 2012
Accepted 13 November 2012

Keywords:
Oxidation
Sulfur dioxide
Ascorbic acid
Gallotannins
(+)-Catechin
Wine

ABSTRACT

The effects of some antioxidant (sulfur dioxide, ascorbic acid and gallotannins) and their mixtures, on the oxidative evolution of model wines containing (+)-catechin, have been compared by monitoring O_2 consumption, browning development and (+)-catechin decay. The contextual generation of xanthylium pigments has been further evaluated with the aim of deepening our understanding of the kinetics and the mechanisms underlying the oxidative spoilage of flavanols in wine-like conditions. Novel data on the efficacy of gallotannins in controlling the (+)-catechin oxidative decay in model wine solutions are furnished, together with its comparison with the ones offered by SO_2 and ascorbic acid.

Ascorbic acid was found to promptly reduce the amount of dissolved oxygen in samples, while the presence of SO_2 or tannins resulted in a significantly lower consumption. Under our experimental conditions and at least for 30 days, browning rate was best controlled by sulfite and ascorbic acid (even if to a different extent) while gallotannins failed in such a task. However, a longer storage (120 days) under oxidative conditions revealed a large augmentation of browning rate in samples with aa and/or SO_2, added which became yellower than untreated samples. The amounts of (+)-catechin declined the fastest in all the solutions with aa added Chemical reactions underlying the obtained results, have been discussed.

1. Introduction

During winemaking and aging, wines may be (intentionally or not) exposed to oxygen. For red wines, a moderate consumption of oxygen during storage or aging is generally assumed to be beneficial to improve some sensory (color and astringency) characteristics. On the other hand, in white wines oxygen exposure can result in a darkening of the color, impairing both the chromatic and aromatic features of the product.

Phenolic compounds bearing an *o*-diphenol group, such as caffeic acid, (+)-catechin, or (−)-epicatechin, have the ability to easily participate in the oxidative cascade (Cheynier, Rigaud, Souquet, Duprat, & Moutounet, 1990; Singleton, 1987) initiating redox reactions which result in the formation of quinones and yellow pigments (Waterhouse & Laurie, 2006). However, in matrixes such as white wine, other oxidizable constituents may be involved in the reactions, making the browning a quite complex phenomenon. In the presence of metal ions, for example, hydrogen peroxide oxidize ethanol and (+)-tartaric acid giving rise to acetaldehyde and glyoxylic acid respectively (Es-Safi, Le Guernevé, Fulcrand, Cheynier, & Moutounet, 1999; Waterhouse & Laurie, 2006), which directly react with flavanols to generate yellowish xanthylium ions via an aldehyde-mediated dimeric condensation, a dehydration and a final oxidation step (Fulcrand, Dueñas, Salas, & Cheynier, 2006). Other carbonyl compounds produced during fermentation (pyruvic acid, 2,3-butanedione, HMF, and others) may also act as bridging molecules (Oliveira, Silva Ferreira, De Freitas, & Silva, 2011). Further, the presence of some technological adjuvants and additives such as sulfur dioxide and ascorbic acid (aa), plays a pivotal role in the control (or the development) of browning.

Sulfur dioxide is widely used in winemaking due to its antimicrobial and antioxidant activities. It protects wine against browning and regulates the growth of yeasts and bacteria responsible for the wine spoilage (Ribereau-Gayon, Peynaud, Ribereau-Gayon, Sudraud, & Amati, 1988). Also, SO_2 can reduce the unpleasant aromatic impact of carbonyl compounds by reacting with them to form odorless bisulfite adducts (Singleton, 1987) Concerning its way of action, it is now believed that the main antioxidant function of sulfite is to quench hydrogen peroxide coming from the reduction of O_2, in this way inhibiting aldehyde formation and blocking oxidation of other easily oxidizable compounds (Boulton, Singleton, Bisson, & Kunkee, 1996; Elias & Waterhouse, 2010). In addition, it reduces quinones formed during oxidation back to their original *o*-diphenolic form (Danilewicz, Seccombe, & Whelan, 2008), regenerating the phenolic pool of the wine.

It is worth noting, nonetheless, that SO_2 can elicit allergic reactions (European Council, 2003) and, also due to the increased attention of consumers to food healthiness, there is a trend to minimize its usage in wine (Santos, Nunes, Saraiva, & Coimbra, 2012).

Ascorbic acid is another additive which has been largely used to prevent oxidation in white wines, primarily due to its fast reaction with

* Corresponding author. Tel.: +39 0512096002; fax: +39 0512096017.
E-mail address: fabio.chinnici@unibo.it (F. Chinnici).

0963-9969/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.foodres.2012.11.013

molecular oxygen, undergoing preferential oxidation over phenolic compounds (Bradshaw, Barril, Clark, Prenzler, & Scollary, 2011). As with SO_2, ascorbic acid was also claimed to converts the quinone back to its catechol precursors (Boulton et al., 1996; Danilewicz, 2003), even if this activity has recently been questioned (Makhotkina & Kilmartin, 2009). However, oxidation of aa to dehydroascorbic acid produces hydrogen peroxide which in turn, in the presence of metal ions, would promote the oxidative spoilage of wines (Barril, Clark, & Scollary, 2012). There has been, hence, a widely held opinion that aa represents an adequate protection against browning only if a suitable amount of free SO_2 is simultaneously present with the aim to scavenge the H_2O_2 produced by its oxidation (Ribereau-Gayon et al., 1988). Yet, both anecdotal and experimental evidences showed that aa can exhibit a "crossover" effect, acting as an antioxidant or pro-oxidant as a function of its level (Bradshaw, Cheynier, Scollary, & Prenzler, 2003; Peng, Duncan, Pocock, & Sefton, 1999). In addition, Barril, Clark, Prenzler, Karuso, and Scollary (2009) argued the involvement of one degradation product of dehydroascorbic acid (xylosone) on browning development of model white wine, suggesting that the use of aa in wines should be carefully weighted.

Enological tannins are aiding used in winemaking to impact chemical and sensory features of wines (Neves, Spranger, Zhao, Leandro, & Sun, 2010; Parker et al., 2007). These substances are plant derived extracts from several botanical species. Depending on the origin, tannins can be classified into two groups, namely (i) hydrolysable tannins (gallotannins and ellagitannins, derived from oak or other plant species); (ii) condensed tannins (derived mainly from grapes) (Haslam, 2007). Hydrolysable tannins, in particular, have been reported to possess a distinguished antioxidant capacity (Hagerman et al., 1998) supposedly due to their molecular structure rich in galloyl derivatives and their chelating properties (Haslam, 2007). Already published works have investigated the pre-fermentative utilization of gallotannins in sulfite-free white musts to prevent oxidative phenomena of volatile compounds (Sonni, Cejudo-Bastante, Chinnici, Natali, & Riponi, 2009; Sonni, Chinnici, Natali, & Riponi, 2011) but precise information on their efficacy in contrasting phenolic decay and browning are still lacking. More data on their antibrowning capability would be useful, for instance, in the optic to reduce the usage of sulfites in wine.

The purpose of this study was, hence, to investigate the effects of SO_2, ascorbic acid and gallotannins, alone or in mixture, on the oxidative evolution of (+)-catechin, the latter taken as white wine representative phenol.

A model solution, containing ethanol, (+)-tartaric acid and metal ions, was used to mimic constitutive compounds that, in white wines, participate in the oxidative pathway. Parameters such as oxygen consumption and browning development, together with SO_2 disappearance, (+)-catechin decay and the generation of xanthylium ions, were used to follow the evolution of oxidative phenomena.

2. Materials and methods

2.1. Chemicals and standards

HPLC grade acetonitrile and acetic acid were obtained from Merck (Darmstadt, Germany). Water was of MilliQ quality. (+)-catechin, ascorbic acid, (+)-tartaric acid, Fe(II) sulfate heptahydrate, Cu(II) sulfate pentahydrate and potassium metabisulfite were obtained from Sigma-Aldrich. A commercial formulation of liquid gallotannins (Excellence Gold White) was supplied by Oliver Ogar Italia (Verona, Italy).

2.2. Model wine solutions

Thirty six liters of a solution containing 6 g/L of (+)-tartaric acid and 12% (V/V) of ethanol was prepared. The pH was adjusted to 3.6 with 2.5 M NaOH before bringing to the mark progressively by adding water.

The model wine was stirred in open air until saturated with O_2 and (+)-catechin was added at 350 mg/L. These (+)-catechin amounts, somewhat higher than those found in white wines, were chosen with the aim to accelerate the oxidation without affecting the species being generated (Bradshaw et al., 2003).

Eight trials (in triplicate) were arranged by transferring aliquots (1.5 L) of the solution in 2.5 L glass bottles. Solutions of Fe(II) sulfate heptahydrate (2.5 g/L in water) and Cu(II) sulfate pentahydrate (600 mg/L in water) were separately made and added to each bottle to give a final concentration of 5 mg/L Fe and 0.15 mg/L Cu. When appropriate, sulfur dioxide (as potassium metabisulfite), ascorbic acid and gallotannins were added to achieve the concentrations outlined in Table 1.

For each glass bottle, a stirrer bar was introduced, to facilitate the successive oxygen measurement. Bottles, tightly closed, were stored at 20 °C in darkness a part from when withdrawn for the analysis as described in the following chapter.

2.3. Oxygen, browning and SO_2 measurement

An Orbisphere 2607 oxygen measurement unit (Orbisphere Laboratories, Geneva, Switzerland) was used to monitor the oxygen dissolved in the liquid phase. For this aim, before each reading, the bottle cap was rapidly removed and substituted by another hermetic cap in which the electrode had been mounted so as to remain at about 2 cm from the bottom of the bottle, and tightly sealed. Readings were completed in 1 min (including electrode stabilization) under stirring at 200 rpm (reading had been initially verified to be stable for 3 min). Before the repositioning of original caps, solutions were stirred in open air for 3 min to saturate the model wine with oxygen and an aliquot was withdrawn for SO_2, HPLC and spectrophotometric analysis.

Dissolved oxygen readings and SO_2 analysis were carried out on a daily basis for the first 4 days, followed by other readings at days 7, 10, 23, and 30. Saturation with air had the same timescale as oxygen measurements.

After 120 days of storage, a further sampling was performed. Free and total SO_2 concentrations were determined in accordance with official OIV methods (OIV, 2012) and browning development was measured as the increase of absorbance at 440 nm by using a Jasco 810 spectrophotometer (Tokyo, Japan).

2.4. RP-HPLC/ESI-MS analysis of (+)-catechin and xanthylium cations

HPLC separation and identification of (+)-catechin and xanthylium cations were performed on a Quadrupole HP 1100 MDS series (Agilent Technologies, Palo Alto, CA), equipped with an autosampler, and a diode array UV–vis detector. The column was a C18 Synergy 4 μ hydro RP 80A, 250×3.00 mm, operating at 35 °C with a flow of 0.5 mL/min. Elution solvents were 2% acetic acid in HPLC grade water (Eluent A) and 2% acetic acid in HPLC grade acetonitrile (Eluent B). Gradient

Table 1
Composition and codes of the model wines[a] investigated.

Code	Metal ions	Tn: gallotannin	S: SO_2	A: ascorbic acid
	Fe(II) + Cu(II)[b]	(150 mg/L)	(100 mg/L)	(150 mg/L)
C	+			
Tn	+	+		
S	+		+	
STn	+	+	+	
A	+			+
ATn	+	+		+
AS	+		+	+
ASTn	+	+	+	+

[a] Model wine consisted in a 12% V/V hydroalcoholic solution containing 6 g/L of (+)-tartaric acid, pH 3.6.
[b] Metal ions concentration were: Fe(II) at 5 mg/L and Cu(II) at 0.15 mg/L.