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Evolution of pigments, tannins and acetaldehyde during forced oxidation of red wine: Effect of tannins addition

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ABSTRACT

During wine-making and aging, the phenolic composition gradually changes, mainly owing to oxidation reactions, which may result in a decrease in astringency as well as in color stabilization. Anthocyanins and tannins are the main compounds involved in these changes. The influence of enological tannins on the outcome of red wine oxidation has been evaluated in this study. Oligomeric tannins were added to red wine so as to have wines with three different anthocyanin A/tannin T ratios W (ratio 1A: 0.5T) WT (ratio 1A: 1T) WTT (ratio 1A: 3T). Samples were then treated with hydrogen peroxide to trigger the Fenton reaction. Chromatic characteristics, phenolic composition and acetaldehyde were monitored during oxidation. The samples treated with a higher concentration of tannins showed a clear improvement of color intensity with oxidation mainly due to an increase in polymeric pigments. The higher the content of tannins were, the lower the production of acetaldehyde. These are the first data showing the effect of different A/T ratios on the production of acetaldehyde during an oxidation process.

1. Introduction

Some of the organoleptic characteristics of red wines depend on the amount, type, composition and distribution of phenols. Among wine polyphenols, anthocyanins and tannins constitute the most important classes since they mainly contribute to the color and astringency caracteristics of wines (Arnold, Noble, & Singleton, 1980; Peleg, Gacon, & Schlich, 1999). The first sensory feature noticed in a wine is its color. The principal compounds in a young red wine that are responsible for its color are the native anthocyanins. During wine production, aging and storage the degradation and transformation of native anthocyanins results in more stable colored pigments (Gao, Girard, Mazza, & Reynolds, 1997; Garcìa-Puente Rivas, Alcalde-Eon, Santos-Buelga, Rivas-Gonzalo, & Escribano-Bailòn, 2006). The tannins, the compounds responsible for astringency (Robichaud & Noble, 1990), participate in reactions stabilizing wine color (Francia-Aricha, Guerra, Rivas-Gonzalo, & Santos-Buelga, 1997). They are also responsible for wine bitterness (Brossaud, Cheynier, & Noble, 2001; Robichaud & Noble, 1990) and both sensory attributes change with the molecular structure of tannic polymers (Kallithraka & Bakker, 1997). Elevated tannin levels may have a negative impact on wine quality.

Oxygen influences phenolic composition and determines changes in sensory characteristics linked to phenolics, such as color and astringency, all of which determine wine quality. Small amount of oxidation can improve red wines by contributing to softening of tannin harshness, stabilizing color, and decreasing vegetative aromas (Atanasova, Fulcrand, Cheynier, & Moutounet, 2002; E Gómez-Plaza, 2011). Wine oxidation consists of a series of reactions: first oxygen is reduced to hydrogen peroxide by interacting with transition metals, iron and copper ions, in the presence of catechol (Danilewicz, 2011). In a subsequent step, ferrous or cuprous species react with hydrogen peroxide in the Fenton reaction to yield the most reactive oxidant, the hydroxyl radical. It reacts with all organic constituents in proportion to concentrations (Elias, Andersen, Skibsted, & Waterhouse, 2009). As a consequence, native anthocyanin pigments are quickly transformed into more stable pigments via various types of reactions (Mateus, Silva, Santos-Buelga, Rivas-Gonzalo, & de Freitas, 2002) such as aldehyde-mediated condensation reactions with tannins and cyclo-addition reactions leading to the formation of pyranoanthocyanins (Blaauw, 2009; Oliveira, Ferreira, De Freitas, & Silva, 2011). Oxidation reactions are also involved in the change in wine astringency because oxygen is responsible for intra and inter molecular reactions changing tannin structure (Mouls & Fulcrand,

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2012). Essentially oxygen reacting with both classes of phenolics (anthocyanins and tannins) contributes to production of a "stabilized" anthocyanin or pigmented tannin which persists much longer in wine than the initial form (Waterhouse, 2002). A large number of these reactions are due to acetaldehyde. This molecule is produced by ethanol oxidation and reacts readily with flavan-3-ols to increase their polymerization (Drinkine, Glories, & Saucier, 2005). However an excessive production of acetaldehyde can result in the appearance of oxidation off-flavour (Carlton, Gump, Fugelsang, & Hasson, 2007).

It is known that the presence of a proper ratio between native anthocyanins and tannins could affect the reactions of pigment stabilization and changes in this ratio could be important for proper wine aging as already proposed (Singleton & Trousdale, 1992; Francia-Aricha et al., 1997; Morel-Salmi, Souquet, Bes, & Cheynier, 2006). This is why the addition of enological tannins is an accepted enological practice (OIV: ENO 5/2008), aimed at stabilizing wine color and improving wine structure (Obreque-Slíer, Peña-Neira, López-Solís, Ramírez-Escudero, & Zamora-Marín, 2009). Although several studies evaluating the effect of adding enological tannins to red wine have been reported (Bautista-Ortin, Martinez-Cutillas, Ros-Garcia, Lopez-Roca, & Gomez-Plaza, 2005; Harbertson, Parpinello, Heymann, & Downey, 2012; Versari, du Toit, & Parpinello, 2013), never has a study been undertaken to understand and evaluate the impact of different anthocyanin tannin ratios during oxidation.

In this study a mixture of oligomeric tannins (OT) was added to a wine rich in anthocyanins so as to have wine with three different anthocyanin tannin ratios. Samples were then treated with hydrogen peroxide to trigger the Fenton reaction; color, phenolic compounds and acetaldehyde were evaluated.

2. Experimental

2.1. Wines

The experiment was performed on a red wine produced in South Italy with thermovinification technique, which allowed a wine with a high concentration of native anthocyanins to be obtained. The base parameters were: alcohol 13.59 ± 0.3%V/V, titratable acidity 5.28 ± 0.2 g/l of tartaric acid, pH 3.55 ± 0.04, volatile acidity 0.50 ± 0.06 g/l of acetic acid, the sum of native anthocyanins were 3.43 ± 0.1 g/l (at least 5 times higher than normal concentration of native anthocyanins in a red wine) and BSA reactive tannins were 683.2 ± 18.8 mg/l. Base parameters were determined according to the OIV compendium of international methods of wine and must analysis (2007). The samples were treated to change the anthocyanin tannin ratios. Oligomeric Tannins O.T. (Tannin VR grape Biotan, Laffort Oenologie, France) were added to red wine so as to have three wines with three different anthocyanin/tannin ratios: W (anthocyanin/tannin ratio 1:0.5) WT (anthocyanin/tannin ratio 1:1) WTT (anthocyanin/tannin ratio 1:3). The concentration of O.T. has been reported by Fontoin, Saucier, Teissedre, & Glories (2008). Wines were prepared by adding different concentration of tannin in 5 liter flask previously saturated with nitrogen. Three hours late hydrogen peroxide 3% V/V was added to wines to eliminate the present total sulfur dioxide and to add an extra amount of 74 mg/l of oxygen equivalent. This quantity was chosen to simulate two year of aging in barrel (Nevares & Del Alamo-Sanza, 2015) or wine micro oxygenation (Tao, Dykes, & Kilmartin, 2007). After the addition, samples were stored at the temperature of 18 °C and monitored for thirty days. Two replicates of the experiment were performed.

2.2. Spectrophotometric analyses

Chromatic characteristics and spectrophotometric measures were determined using a spectrophotometer (Jenway 7305 Spectrophotometer). Color intensity C.I., abs420, abs520, abs620 nm and hue were evaluated according to the Glories methods (Glories, 1984). Total anthocyanins, short polymeric pigments (SPP) and large polymeric pigments (SPP) were determined by the Harbertson– Adams assay (Harbertson, Picciotto, & Adams, 2003). Briefly, pH changes allowed the evaluation of total anthocyanins while the large polymeric pigments (LPP) were obtained by combining analysis of supernatant obtained after protein precipitation using bovine serum albumin (SIGMA Life Science USA) with the bisulfite bleaching of pigments in wine. To determine vanillin reactive flavans (VRF), the method described by Di Stefano and Guidoni (1989) was scaled down and volumes were adjusted to decrease the consumption of organic solvents. All analyses were conducted through two experimental replicas and two analytical replicas.

2.3. High-performance liquid chromatography determination of acetaldehyde

Acetaldehyde was determined using the method of Han, Wang, Webb, and Waterhouse (2015). Briefly, wine sample aliquots (100 μL) were dispensed to a vial, followed by addition of 20 μL of freshly prepared 1120 mg/L SO_2 solution. Next, 20 μL of 25% sulfuric acid (Carlo Erba reagent 96%) was added, which was followed by 140 μL of 2 g/L 2,4-dinitrophenylhydrazine reagent (Aldrich chemistry). After mixing, the solution was allowed to react for 15 min at 65 °C and then promptly cooled to room temperature. Analysis of carbonyl hydrazones was conducted by HPLC (HPLC Shimadzu LC10 ADVP apparatus (Shimadzu Italy, Milan)), consisting of a SCL-10AVP system controller, two LC-10ADVP pumps, a SPD-M 10 AVP detector, and an injection system full Rheodyne model 7725 (Rheodyne, Cotati, CA) equipped with a 50 μL loop. A Waters Spherisorb column (250 × 4.6 mm, 4 μm particles diameter) was used for separation. The chromatographic conditions were: sample injection volume, 50 μL; flow rate, 0.75 mL/min; column temperature, 35 °C; mobile phase solvents, (A) 0.5% formic acid (Sigma Aldrich ≥ 95%) in water milli-Q (Sigma Aldrich) and (B) acetonitrile (Sigma Aldrich ≥ 99,9%); gradient elution protocol, 35% B to 60% B (t = 8 min), 60% B to 90% B (t = 13 min), 90% B to 95% B (t = 15 min, 2-min hold), 95% B to 35% B (t = 17 min, 4-min hold), total run time, 21 min. Eluted peaks were compared with derivatized acetaldehyde standard. All analyses, were conducted through two experimental replicas and two analytical replicas.

2.4. High-performance liquid chromatography analyses of anthocyanins

The separation of anthocyanins was carried out according to the OIV Compendium of International Methods of Analysis of Wine and Musts (2007). Analyses were performed in a HPLC Shimadzu LC10 ADVP apparatus (Shimadzu Italy, Milan), consisting of a SCL-10AVP system controller, two LC-10ADVP pumps, a SPD-M 10 AVP detector, and an injection system full Rheodyne model 7725 (Rheodyne, Cotati, CA) equipped with a 50 μL loop. A Waters Spherisorb column (250 × 4.6 mm, 4 μm particles diameter) with pre-column was used. Fifty μL of wine or calibration standards were injected onto the column. Detection was performed by monitoring the absorbance signals at 518 nm. All the samples were filtered through 0.45 mm, Durapore membrane filters (Millipore - Ireland) into glass vials and immediately injected into the HPLC system. The HPLC solvents were: solvent A: water milli-Q (Sigma Aldrich)/formic acid (Sigma Aldrich ≥ 95%)/acetonitrile (Sigma Aldrich ≥ 99,9%) (87:10:3) V/V; solvent B: water/formic acid/acetonitrile (40:10:50) V/V. The gradient used was: zero-time conditions 94% A and 6% B,