



Review

Updated knowledge about pyranoanthocyanins: Impact of oxygen on their contents, and contribution in the winemaking process to overall wine color



Cindy Quaglieri ^{a, b}, Michael Jourdes ^{a, b}, Pierre Waffo-Teguo ^{a, b},
Pierre-Louis Teissedre ^{a, b, *}

^a Univ. Bordeaux, ISVV, EA 4577 (Enologie, F-33140, Villenave d'Ornon, France

^b INRA, ISVV, USC 1366 (Enologie, F-33140, Villenave d'Ornon, France

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ABSTRACT

Background: Better knowledge of wine composition, especially that of anthocyanin-derived pigments, has helped improve wine quality over the years. The use of micro-oxygenation (MOX), which consists in adding low quantities of oxygen at different stages of the winemaking process, contributes to enhancing and stabilizing wine color through the formation of stable pigments called pyranoanthocyanins, while the cycloaddition of anthocyanins requires an oxidation step.

Scope and approach: This review describes the formation kinetics and the evolution of the concentrations of the various groups of pyranoanthocyanins. Both non-oxygenated and oxygenated varietal red wine samples are compared in order to determine the impact of MOX on pyranoanthocyanin contents.

Key findings and conclusions: During alcoholic fermentation, the concentration of vitisin A increases due to the availability of pyruvic acid and progressively decreases with aging. Higher contents are found in Port red wines. MOX can enhance the concentrations in dry red wines but the contents remain lower than those found in Port wines. The formation of vitisin B can be promoted by the oxidation of ethanol in acetaldehyde but the results depend on the varietal red wine used. Flavanol-pyranoanthocyanin contents also vary according to wine age, with a reported decreasing concentration during aging for Port and dry red wines. After MOX treatment, their concentrations increase with a more acidic pH and a higher oxygen rate. The increase of the content in pyranoanthocyanins after two years of ageing contributes to stabilize wine colour. Further studies will determine the impact of oxygen on phenylpyranoanthocyanins since data are still scarce on the subject.

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1. Introduction

Phenolic compounds are a large group of complex chemical compounds produced naturally in plants as secondary metabolite compounds (Pandey & Rizvi, 2009). They represent the largest category of phytochemicals and are widely distributed in the plant kingdom (Giada, 2013). Contained both in grapes and wines, flavonoids are one of the most important classes of phenolic compounds since they contribute to wine organoleptic qualities such as color, astringency and bitterness. The two most important groups

of flavonoids in red wines are anthocyanins and flavanols. These constituents are very reactive and undergo chemical modifications involving two important variables: acidity and oxygen.

Oxygen (O₂) also plays an important role during the winemaking process. Technical wine improvements have been achieved in the last 25 years through the controlled addition of O₂. Most studies have investigated the oxidation process in red wines owing to the occurrence or the increasing concentrations of certain polyphenols (catechol derivatives such as caffeic acid, (+)-catechin, (–)-epicatechin, proanthocyanidins, flavanol-anthocyanin derived-pigments ...), which are very reactive to O₂ and can easily be oxidized (Singleton, 1987). Recent studies on micro-oxygenation (MOX) have opened up the analysis of pyranoanthocyanins to color and sensory data. Indeed, color is one of the most important characteristics in red wines. The instability of anthocyanins during

* Corresponding author. Univ. Bordeaux, ISVV, EA 4577 (Enologie, F-33140, Villenave d'Ornon, France.

E-mail address: pierre-louis.teissedre@u-bordeaux.fr (P.-L. Teissedre).

the winemaking process leads them to react with other compounds such as carbonyl compounds, catechin units or vinylphenols to form stable pigments, the so-called pyranoanthocyanins.

Over the years, many studies have examined the effect of MOX in order to characterize the impact of the oxidation mechanism of catechols in quinones (Danilewicz, 2003; Waterhouse & Laurie, 2006), and that of ethanol in acetaldehyde (Wildenradt & Singleton, 1974). The central role of iron and copper as catalysts has also been highlighted (Danilewicz, 2011, 2013). The introduction of low and controlled quantities of oxygen at crucial steps through the winemaking process enhances red wine color through the formation of pyranoanthocyanins (Pechamat, 2014) and polymerized pigments. It then improves red wine structure and softens tannins to reduce astringency and bitterness. Finally, it removes reduction aromas and reduces herbaceous aromas (Heras, Rivero-Pérez, Pérez-Magariño, González-Huerta, & González-Sanjosé, 2007).

Following on previous studies on micro-oxygenation and its consequences on wines, this review first highlights the oxidation mechanism. In the second part, particular attention is paid to the formation of the various groups of pyranoanthocyanins. Owing to the significant modification of wine color and pigment composition due to MOX, the third part focuses on the comparison of pyranoanthocyanin contents in non-oxygenated and oxygenated red wines.

2. The oxidation mechanism

Oxidation is a chain reaction involving redox partners, where electron transfer takes a central place through the presence of iron (Fe) and copper (Cu), which have been known as catalysts of wine oxidation for decades. Catechols, such as flavan-3-ols ((+)-catechin, (–)-epicatechin ...), are oxidized in quinones by the sequential abstraction of two electrons, with the concomitant loss of two protons, corresponding to the transfer of two hydrogen atoms. However, oxygen (O_2) cannot directly oxidize polyphenols because of its diradical form (triplet ground state), which limits its reactivity. In nature, most phenols are in balance at a mean 50% or more with their phenolate ions. They present a high pKa value (9–10). At this level of pH, autoxidation is easier and extremely fast (Rossi & Singleton, 1966). However, at wine pH, such a reaction is very limited; it is nine times faster at pH 4 than at pH 3 (Singleton, 1987).

Several models of oxidation have been proposed. Wildenradt and Singleton (1974) described the oxidation of ethanol in acetaldehyde. In 2003, Danilewicz (2003) proposed a very detailed model of the catechol-quinone system by giving the dissociation constants and reduction potentials with corresponding equations. The first global summary of wine oxidation mechanism was published by Waterhouse and Laurie (2006). They postulated that phenolics directly reacted with the hydroperoxyl radical to be oxidized into semiquinones and then into quinones. According to them, catechol functional groups seem to be the primary reacting species with the hydroperoxyl radical, after the reduction of O_2 mediated by the redox couple Fe(II)/Fe(III). In 2011, the central role of iron was precisely defined (Danilewicz, 2011). Catalyzed by Fe(II), the hydroperoxyl radical disproportionates to yield O_2 and hydrogen peroxide (H_2O_2), which is preferable from a thermodynamic point of view (Bielski & Arudi, 1983). The analysis of the Fenton reaction with or without polyphenol in the wine-like model ((+)-catechin) led to the conclusion that the occurrence of such a molecule does not affect the reaction, i.e. it is not directly involved in O_2 reduction (Danilewicz, 2011). Furthermore, the hydroperoxyl radical cannot directly oxidize catechols. Danilewicz proposed that ethanol was in 130-fold molar excess and tartaric acid in 30-fold molar excess relative to (+)-catechin in the wine-like model. The probability of

hydroxyl radicals ($HO\cdot$) encountering a (+)-catechin molecule is around 0.5%.

On the oxidative side, ferrous ion Fe(II) is oxidized by O_2 in its ferric state Fe(III), the redox couple Fe(II)/Fe(III) playing a mediating role, as previously discussed (Clark, 1960; Danilewicz, 2016). In turn, Fe(III) slowly oxidizes catechols into semiquinones and then into quinones (Danilewicz, 2011), before returning to its ferrous state (Fig. 1). The oxidation rate of catechol by Fe(III) decreases when pH increases and totally stops when pH exceeds 5 (Avdeef, Sofen, Bregante, & Raymond, 1978). Furthermore, the rate of Fe(II) oxidation increases with the presence of copper (Danilewicz & Wallbridge, 2010; Danilewicz, 2011). On the reductive side, ferrous ion Fe(II) progressively reduces O_2 into hydrogen peroxide (H_2O_2) then into water (H_2O): O_2 also successively transfers two electrons leading to the formation of two radicals, superoxide ion O_2^- and perhydroxyl radical HO_2^- , both in balance with their protonated forms (Danilewicz, 2003). H_2O_2 , which is a strong oxidative molecule, is involved in the oxidation of ethanol into acetaldehyde (Wildenradt & Singleton, 1974).

Red wine can take up a larger amount of oxygen than white wine owing to the presence of polyphenols. Furthermore, measuring the total wine phenolic content is relevant to evaluate the capacity of a wine to take up oxygen (Singleton, 1987).

2.1. Impact of iron and copper

The impact of iron and copper is known to influence the oxidative or reductive evolution of wine and/or its turbidity (Ribéreau-Gayon, Glories, Maujean, & Dubourdieu, 2012). Iron and copper are involved in oxidation processes in wine. These metallic ions are naturally present in the soil (Almeida & Vasconcelos, 2003; Pohl, 2007; Taylor, Longerich, & Greenough, 2003) and are absorbed by the root system (Zoecklein, Fugelsang, Gump, & Nury, 1999). Exogenous contamination may occur before harvesting owing to vine treatments with copper fungicides (Volpe et al., 2009) and during the winemaking process with the use of enological equipment and fining products (Eschnauer, 1982; Pohl, 2007), e.g. bentonite (Catarino, Madeira, Monteiro, Curvelo-Garcia, & Bruno de Sousa, 2006; Nicolini, Larcher, Pangrazzi, & Bontempo, 2015). The concentrations of these metals decrease during alcoholic fermentation owing to the biosorption mechanism induced by yeast cells (Stafilov & Karadjova, 2009).

The impact of iron and copper has been evaluated in wine-like model solutions and white wines. Joint addition of iron and copper in wine-like model solutions has a significant impact on oxygen consumption, more so than with their addition separately (Morozova, Just, Schmidt, & Schwack, 2013). In white wines, results are not significant, suggesting an impact of phenolic compounds that are not added to the model solution, and the possible influence of other metals like manganese, zinc or aluminum (Carrascon, Fernandez-Zurbano, Bueno, & Ferreira, 2015; Morozova et al., 2013). In white wines, the presence of copper is correlated to oxidative and reductive processes, since it is involved in haze formation (copper casse) and linked to protein stability (Clark, Wilkes, & Scollary, 2015). Moreover, residual and cationic forms of copper seem to be closely correlated with oxygen consumption, compared to the impact of iron (Rousseva, Kontoudakis, Schmidtke, Scollary, & Clark, 2016).

In white wine model solutions, copper enhances the color but the result is detectable only in analytical form by measuring the absorbance at 420 nm. In Riesling wine, sensory properties are not affected by the addition of iron or copper (Morozova et al., 2013).

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