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The kinetics of oxygen and SO_2 consumption by red wines. What do they tell about oxidation mechanisms and about changes in wine composition?

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ABSTRACT

This work seeks to understand the kinetics of O_2 and SO_2 consumption of air-saturated red wine as a function of its chemical composition, and to describe the chemical changes suffered during the process in relation to the kinetics. Oxygen Consumption Rates (OCRs) are faster with higher copper and epigallocatechin contents and with higher absorbance at 620 nm and slower with higher levels of gallic acid and catechin terminal units in tannins. Acetaldehyde Reactive Polyphenols (ARPs) may be key elements determining OCRs. It is confirmed that SO_2 is poorly consumed in the first saturation. Phenylalanine, methionine and maybe, cysteine, seem to be consumed instead. A low SO_2 consumption is favoured by low levels of SO_2, by a low availability of free SO_2 caused by a high anthocyanin/tannin ratio, and by a polyphenolic profile poor in epigallocatechin and rich in catechin-rich tannins. Wines consuming SO_2 efficiently consume more epigallocatechin, prodelphinidins and procyanidins.

1. Introduction

Nowadays, the use of oxygen in winemaking is widespread around the world to obtain high quality wines. A mild oxidation is known to produce improvements in red wines: more color stability due to reactions of oxygen with anthocyanins (Atanasova, Fulcrand, Cheynier, & Moutounet, 2002; Cano-Lopez et al., 2008), softening of astringency and bitterness due to reactions of tannins (Cejudo-Bastante, Hermosin-Gutierrez, & Perez-Coello, 2011), aroma modulation and decrease of vegetative and green perceptions (Cejudo-Bastante et al., 2011; Ortega Heras, Rivero-Perez, Perez-Magarino, Gonzalez-Huerta, & Gonzalez-Sanjose, 2008). However, oxygen can also produce undesirable and unpredictable effects. In this context, research is required concerning the different effects that oxygen consumption has on wine composition, together with a better understanding about the mechanisms implied in wine oxidation. Undeniably, models able to predict how the wine is going to respond to contact with oxygen would be useful for helping winemakers to make wines more resistant towards oxidation.

Sulfur dioxide (SO_2) is the most important chemical used to prevent wine oxidation. It is used worldwide and it has not only antioxidant, but also antimicrobial and antioxidasic properties. Furthermore, SO_2 binds to certain compounds, such as aldehydes, preventing the detection of many oxidation-related off-odors even if they are already present (Bueno, Carrascón, & Ferreira, 2016). On the other hand, SO_2 produces allergic reactions in some individuals, so the maximum levels are legally restricted (European Comission Regulation 606/2009, 2009) and there is an increasing tendency to produce wines containing lower levels of sulfite. For all of this, SO_2 has been used for many years, and although many studies are now being conducted to replace it by new chemicals with similar properties but with less harmful effects (Guerrero & Cantos-Villar, 2015), no replacement has been yet found.

Recently, wine oxidation chemistry has been broadly studied (Danilewicz, 2007, 2011; Danilewicz, Seccombe, & Whelan, 2008; Laurie et al., 2012; Singleton, 1987; Ugliano, 2013), and the general mechanism has been already established. In the first place, molecular oxygen accepts electrons from iron and copper ions – Fe(II) and Cu(I) – which act as catalysts forming a superoxide ion $O_2^{\cdot -}$ (hydroperoxyl radical $OH\text{-}\dot{O}$ at wine pH). Phenolic compounds with a catechol group are oxidized by Fe(III) to a quinone, and the hydroperoxyl is reduced by

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Fe(II) to hydrogen peroxide. If sulfur dioxide is present, it reacts with hydrogen peroxide, giving sulfate and water, and with the quinone, reducing it back to the catechol form or forming a product with a sulfonate group. The precise outcome depends on pH and on the structure of the polyphenol. Polyphenols having an ortho dihydroxy-or trihydroxy- substitution pattern on the aromatic ring, namely B ring of flavanols, or hydroxy-cinnamic acids (caftaric) or hydroxybenzoicacids (gallic or protocatechuic acids) are more prone to suffer nucleophilic addition. If there is no sulfur dioxide in the wine, hydrogen peroxide can take part in further oxidation steps, such as the Fenton reaction (Gambuti, Han, Peterson, & Waterhouse, 2015). In this case, iron and copper ions interact with hydrogen peroxide to form the hydroxyl radical HȮ, a strong oxidant that reacts with many organic compounds in wine. The most important oxidation product of this reaction is acetaldehyde, in as much as ethanol is the most concentrated organic compound present in wine.

Acetaldehyde can further react with flavanols and anthocyanins forming pigments with a methylmethine bridge, usually referred as ethyl bridge, between the two units of flavanol and anthocyanin (Somers, 1971; Timberlake & Bridle, 1976). Pyranoanthocyanins are also indirect oxidation products of anthocyanins. In this case a new pyran ring is formed from the nucleophilic addition of alkenes rich in electrons to anthocyanins, such as the addition of acetaldehyde (Bakker & Timberlake, 1997), 4-vinylphenol (Fulcrand, dosSantos, SarniManchado, Cheynier, & FavreBonvin, 1996) or pyruvic acid (Fulcrand, Benabdeljalil, Rigaud, Cheynier, & Moutounet, 1998).

Previous works on wine oxidation kinetics have shown that oxygen consumption rates are strongly wine-dependent (Vivas & Glories, 1993; Vivas, Vivas de Gaulejac, & Nonier, 2014). In wines, higher pH and added ellagitannins can increase oxygen consumption rates (Singleton, 1987; Vivas & Glories, 1996). In a previous report, initial OCRs were positively related to levels of copper, of tannins rich in epigallocatechin structural units and of absorbance at 620 nm (blue pigments) (Ferreira, Carrascón, Bueno, Ugliano, & Fernández-Zurbano, 2015). Studies in model systems reported a strong dependence of the rate on copper and iron concentrations (Danilewicz, 2007) and a positive effect of SO_2 in presence of catechin and epicatechin (Danilewicz, 2007; Danilewicz et al., 2008). In wines undergoing micro-oxygenation, OCR strongly increased when free SO_2 was exhausted, which was attributed to the Fenton reaction in which radicals are being continuously formed and reacting (Gambuti et al., 2015).

In a previous report two different OCRs were defined: a highly variable initial OCR and a rather stable average OCR. Initial OCRs were much higher and determined oxygen consumption in the first air saturation, notably in the first moments after contact with O_2; average OCRs remained constant in 3 to 4 consecutive cycles of air-saturation (Ferreira et al., 2015). Unfortunately, in that experiment no specific analyses were performed after the first air-saturation, which made it difficult to assess the specific chemical changes linked to the fast oxygen uptake in the first saturation.

This work seeks to study in detail the kinetics of oxygen and sulfur dioxide consumption during a single air saturation, to determine the relationship between those kinetics and the wine chemical composition and also to evaluate their effects on the chemical changes taking place during the process. For that, commercial red wines have been extensively analytical characterized before and after the oxidation. Chemical analyses have included dissolved oxygen, sulfur dioxide, acetaldehyde, color, total phenolic index (TPI), Folin-Ciocalteu index, metals, phenolics, tannins, amino acids and aroma compounds.

2. Materials and methods

2.1. Solvents and chemicals

Dichloromethane, ethanol and methanol for gas chromatography analyses were purchased from Merk (Darmstadt, Germany). Methanol and acetonitrile of HPLC quality were obtained from Fluka Analytical (Buchs, Switzerland). Hydrochloric acid 37%, formic acid and ammonium formate high purity grade were purchased from VWR Prolabo (Fontenay sous Bois, France). Phloroglucinol, ascorbic acid (≥99%), acetaldehyde (≥99.5%), 2-chloroethanol (≥99.0%), methyl 2-methylbutyrate (≥99%), 2-buthanol (≥99%), Folin-Ciocalteu's phenol reagent, sodium carbonate (≥99%), gallic acid (≥99%) and (+)-catechin (≥99%) were supplied by Sigma-Aldrich (Madrid, Spain). Sodium metabisulfite 99% ($Na_2S_2O_5$), tartaric acid (99%), glycerol (99.5%), 1,2-propanediol (99.5%), sodium hydroxide (98%), ortho phosphoric acid (85%), hydrogen peroxide 3 % stabilized w/v VINIKIT, indicator 4,4, mixed (methyl red-methylene blue) VINIKIT, sodium hydroxide 0.01 mol/L VINIKIT were from Panreac (Barcelona, Spain). Standards and reagents for aroma compounds and amino acids determination were purchased from Sigma-Aldrich, Fluka, Panreac, Lancaster, PolyScience, Chemservice and Firmenich, and details of the chemicals have been already reported (Hernandez-Orte, Ibarz, Cacho, & Ferreira, 2003; Lopez, Aznar, Cacho, & Ferreira, 2002; Ortega, Lopez, Cacho, & Ferreira, 2001). Water was purified in a Milli-Q system from Millipore (Bedford, Germany) to get a resistance of 18.2 MΩ·cm at 25 °C.

2.2. Samples and oxidation procedure

For this study, eight Spanish wines of different vintages, between 2009 and 2014, and two different grape varieties, Garnacha (Grenache) and Tempranillo, were purchased at a local store. Details of the samples together with some compositional parameters are shown in Table 1.

Samples were oxidized in duplicate by saturating the wine with air. For each wine, two separate saturation replicates with 500 mL each, were carried out. This was done by gentle shaking 500 mL of wine in a 1 L closed flask for 10 s, after which the cap was opened to allow fresh air to enter, and the shaking operation was repeated 2 more times. Air-saturated wine was then distributed in screw capped 60 mL vials strictly

Table 1
Basic details about the wines used in the study together with chemical data relevant to the oxidation process.

Wine Code	DO	Grape Variety	Vintage	Ethanol (v/v)	Total acetaldehyde (mg/L)	Total SO_2 (mg/L)	Free SO_2 (mg/L)	pH	Fe (mg/L)	Cu (μg/L)	Tannins (mg/L)	mDP	Anthocyanins (mg/L)/ Tannins (mg/L)
G1_09	CB	G	2009	14.0	15.90	31	2.6	3.32	1.59	28.7	688	4.8	0.029
G2_13	CB	G	2013	15.0	17.63	31	10.5	3.26	1.25	97.8	729	5.2	1.155
G3_14	Cl	G	2014	14.5	20.33	43	14.8	3.29	1.37	55.2	1468	7.8	0.943
G4_14	CB	G	2014	13.5	16.38	37	14.4	3.31	1.50	55.4	1155	6.5	1.350
T1_11	Rj	T	2011	13.5	19.61	76	24.7	3.51	1.25	59.2	819	6.9	0.236
T2_12	Tr	T	2012	14.5	17.78	77	33.7	3.60	0.87	145.3	1363	9.5	0.416
T3_10	Rj	T	2010	13.5	13.90	40	13.3	3.61	1.18	44.3	757	7.6	0.164
T4_14	Rj	T	2014	13.5	17.25	24	10.1	3.58	2.17	239.7	1066	8.4	1.302

DO: Denomination of origin; CB: Campo de Borja; Cl: Calatayud, Rj: Rioja; Tr: Toro.
G: Garnacha; T: Tempranillo.