# ALTERNATIVES FOR AVOIDING DEGRADATION IN ECOLOGICAL WINE

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ABSTRACT

Organic wines are prone to suffer from oxidative degradation due to the restrictions in the winemaking. This work studies the influence of different chemical routes, due to thermal and oxidative processes, in the wine aromatic profile. The resistance to these processes after the addition of compounds with a presumably antioxidant capacity was evaluated. Ascorbic acid, resveratrol, calcium disodium ethylenediaminetetraacetate (EDTA), sulphur dioxide ($SO_2$) and the polyphenols: gallic acid, epicatechin and caffeic acid, were tested. The oxidative estate by cyclic voltammetry, aromatic composition and general profiles and sensorial analysis were performed; obtaining interesting differences depending on the applied treatment. All samples gave a characteristic voltammetry signal; showing a remarkable decrease in the current intensity on those samples that suffer a deeper degradation. Regarding the chemical analysis results, the application of the metal chelator EDTA, apart from the $SO_2$ treatment, might be of interest to partly reduce the oxidative effect. Sensory differences were only found in samples treated with $SO_2$ and those that had the addition of polyphenols, due to the appearance in these last samples of a strong vegetable aroma not perceptible in the other treatments.

Key words: antioxidant capacity, EDTA, oxidative degradation, polyphenols, $SO_2$, voltammetry.

## INTRODUCTION

Oxidative degradation affects the final colour and aroma of wine, producing negative effects on its quality. The susceptibility for the development of the oxidative spoilage is related to three factors: the wine's redox potential, the dissolved oxygen concentration and the type and concentration of intrinsic and added antioxidants (Silva Ferreira *et al.*, 2003a). Most of the research about wine oxidation has been performed on white wines, as they are more prone to experience oxidation reactions. In the case of organic wines, this susceptibility to oxidation is more significant, as there are important restrictions during the wine making, such as the level of $SO_2$ that can be employed, broadening the problem to both, white and red wines.

The main aim of this work was to study the evolution of an organic red wine during spoilage conditions and to determine if the addition of specific compounds with a presumably antioxidant capacity could influence in the final oxidative level, aromatic profiles and sensorial characteristics. Obtaining alternatives to the use of sulphur dioxide could improve organic wines aromatic quality and thus encourage the market for them. Compounds such as ascorbic acid, $SO_2$, resveratrol, EDTA and some polyphenols were tested. The oxidative estate was evaluated in all samples by cyclic voltammetry. This technique has been recently incorporated for studies of resistance to oxidation of white wines (Oliveira *et al.*, 2002; Kilmartin *at al.*, 2001); considering its future application for monitoring aging processes and characterizing wines for their antioxidant protection. Volatile analysis and sensorial tests were as well performed for all the wine samples taken at different times of the degradation process.

## MATERIALS AND METHODS

*Chemicals: All the reagents used were analytical quality.*

Wine: Spanish ecological young red wine: *Viña Bosquera* 2007, D.O. Madrid.

Forced age wine protocol and preparation of wine samples: Wine was divided into 1.5 L portions and prepared as follows: 1. "T° Control" and 2. "T°&$O_2$ Control" were left without the addition of any chemical; 3. "Ascorbic acid": 0.5 mM ascorbic acid; 4. "Resveratrol": 7.5 mg/L resveratrol; 5. "Ascorbic acid + Resveratrol"; 6. "$SO_2$": 50 mg/L $SO_2$; 7. "EDTA": 500 mg/L EDTA and 8. "Polyphenols": 475, 50 and 400 mg/L gallic acid, caffeic acid and epicatechin, respectively. Sampling times were at 0, 1, 4 and 8 days and a gradient T° program from 60° to 40°C was followed. Samples were oxygenated till saturation level at the beginning of the experiment and resaturated at each sampling time, except the "T° Control".

Cyclic voltammetry: A potentiostat (Autolab type PGSTAT30, Ecochemie) controlled by the GPES 4.9 software provided by Ecochemie was used. Voltammograms were obtained in the oxidation range of potentials (between ca. 0.2 and 1.2 V) at a scan rate of 100 mV/s using a 3 mm glassy carbon disk (BAS M-2012) working electrode.

Volatile analysis: Liquid-liquid extraction – GC-MS analysis was performed based on the methodology described in the literature (Silva Ferreira *et al.*, 2003b).

Sensorial analysis: Samples were divided in the 3 time groups. For each group, the level of similarity in a 0-10 continuous scale was asked to established; always referring the similarity to the same "T°&$O_2$ Control" of the specific time group. In a second session the same methodology was followed but the comparison was established between a 10-year-old Porto wine and all the samples.

## RESULTS AND CONCLUSIONS

Voltammetry analysis. There was a decrease in the voltammetry intensity while the wine was suffering degradation, mostly due to oxidation. This gradual decrease indicates a reduction in the concentration of the species oxidized at these potential ranges. When all the samples were compared, the most remarkable observation was that all that have the addition of polyphenols, independently of the time that were taken during the spoilage period, had a very distinct voltammogram; showing significantly higher intensities from 0.42 V onwards. This was expected, as the voltage interval between 0.4 and 0.6 represents the most powerful reducing agents of wine; which are, apart from ascorbic acid and $SO_2$, that were present to some extent in all samples, polyphenols with a triphenol group on the flavonid B-ring (Martins *et al.*, 2008).

Volatiles analysis. The most remarkable volatiles, due to their behaviour along the experimental time, were methional, phenylacetaldehyde, furfural, 5-methyl-2-furfural, benzaldehyde and guaiacol. Except this last compound, the rest have previously been reported as typically present in aged and oxidized white wines and are responsible for the development of off-flavors characteristic of these type of wines, such as "honey-like", "boiled potato", "cooked vegetable", "liquorice" or "farm feed" (Escudero *et al.*, 2002; Silva Ferreira *et al.*, 2003b). All the mentioned compounds increased along the experiment due to thermal reactions; but methional, benzaldehyde and phenylacetaldehyde were highly sensible as well to the aeration action. It was observed that the combination of ascorbic acid with resveratrol and EDTA partly limited the increase with time of methional and that the $SO_2$, EDTA and polyphenols treatments could avoid as well part of the concentration increase of benzaldehyde. In both cases, the EDTA treatment was the most powerful one.

Levels of 1,3-dioxanes and 1,3-dioxolanes (characteristic of Porto wines) increase greatly along the spoilage protocol; mainly due to the oxygenation effect. They were partly limited with $SO_2$, but also, to a lesser extent, by EDTA and the polyphenols treatments.

Sensorial analysis. Sensorial data could be correlated with the main volatile analysis results. $SO_2$, EDTA and the polyphenols treatments were those ones with less similarity to the non supplemented control spoiled samples. It was confirmed that the "cooked" red wine has a very similar general odour with Porto wine and this can be due to the increase of compounds characteristic of oxidized wines, such as methional or benzaldehyde and the 1,3-dioxanes and 1,3-dioxolanes. The "$SO_2$" and the "Polyphenols" samples were the most dissimilar with respect to the Porto wine; showing lower concentrations of these types of compounds.

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