**Investigation on oenological tannins and their role in enhancing the longevity of white wines**

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The aim of this PhD research project is finding one or more strategies to help winemakers to produce long-lived white wines. The experimental plan takes into consideration two main stages of the productive process, the pre-fermentative operations, and the fining period. Among all the techniques and additives that can be used in winery, this paper shows the results obtained using oenological tannins. We considered tannins as adjuvants that can be applied as fining agents before and after white wine stabilization. Tannins play an important role in wine quality, they are frequently added during winemaking, but their impact on white wine is poorly documented.

**Studio sui tannini enologici e sul loro ruolo nel promuovere la longevità dei vini bianchi**

Lo scopo di questo progetto di dottorato è individuare strategie enologiche che possano aiutare l’enologo nella produzione di vini bianchi longevi. Il piano sperimentale prende in considerazione due momenti fondamentali del processo produttivo, le operazioni pre-fermentative e il periodo di affinamento. Tra tutte le possibili tecniche e utilizzi di coadiuvanti, si vuole mostrare i risultati ottenuti dall’analisi dei tannini ad uso enologico. I tannini sono considerati coadiuvanti che possono essere utilizzati sia prima che dopo la stabilizzazione del vino. I tannini al giorno d’oggi rivestono una parte importante nella qualità del vino finale e per questo sono sempre più spesso utilizzati nella vinificazione, ma il loro impatto sui vini bianchi è poco studiato.

**Key words**: redox evolution, cyclic voltammetry, proteins, polyphenols

# **1. Introduction**

In Europe the use of oenological tannins in winemaking is allowed (Council Regulation (EC) No 1493/1999) and an increasing number of commercial preparations from different origin are available. In this view, the analytical characterisation of oenological tannins is important because they have different chemical and biological activities according to their chemical composition. Oenological tannins are commercial natural products extracted from different botanical sources. This class of natural additives can be broadly classified as either hydrolysable or condensed tannins. The first class includes glucosides, either from gallic acid (gallotannins) or from ellagic acid (ellagitannins), whereas condensed tannins, also called proanthocyanidins, are polymers of flavan-3-ol monomers, such as (+)-catechin, (−)-epicatechin and their gallates (Laghi et al., 2010). The addition of tannin powder to wines during winemaking is a longstanding technological practice in wine industry for different purposes. Considering that oenological tannins are obtained from a wide array of botanical sources with a large diversity of chemical composition, the effects on wine properties are diverse. In fact, some works have shown that oenological tannins should be used with great care; in fact, depending on the characteristics of the tannin extract and its composition and concentration of phenolic substances, their addition sometimes have a negative effect on wine characteristics (Cliff et al., 2012; Harbertson et al., 2012). While the industry relies on tannin for many applications, in white wines the use of oenological tannins aims at improving mouthfeel and body, as well as at protecting wine against oxidation; in fact there are studies for understanding the role of tannins in the redox processes occurring in wine (Magalhães et al., 2014). When we talk about white wine, we must take into consideration the total content of polyphenols (TPC) in fact in white wines the average TPC range between 100 and 300 mg/L (Simonetti et al., 1997). This is important because the use of oenological tannins in white wines can modify severely the structure and the sensory perception of the product. Even a small addition of oenological tannins can have important sensory consequences in poorly structured white wines.

# **2. Materials and Methods**

All the oenological tannins were characterized using the analytical methods described below. Different commercial tannins were supplied by Dal Cin Gildo S.p.A. (Concorrezzo, Italy). The samples were prepared at final concentration of 100 mg/L according to the guideline suggestions. Solutions of each tannin were prepared in a synthetic model wine solution MS (12% v/v ethanol, 5 g/L tartaric acid adjusted to pH 3.2 with sodium hydroxide) and in two types of wine, one supplied by an Italian winery of the north-east (unstable wine, UW) and the other bought from the supermarket (stable wine, SW). All the analyses were carried out at least in triplicate. All the samples were analysed by measuring the UV and visible spectra. Also, the reactivity with wine proteins was measured with the aid of a turbidimeter. At the same time, cyclic voltammetry (CV) profile was acquired using screen-printed electrode (SPCE) model DRP-C110 Metrhom Dropsense (Metrohom Italiana S.r.l., Origgio, Italy) and EmStat pico potentiostat (PalmSens BV, Houten, The Netherlands). Finally, the sensory impact of the different tannins was evaluated in wine solutions.

# **3. Results and Discussion**

## **3.1 Characterization of different oenological tannins**

It is known that UV and visible spectra allow classifying the different tannins based on their botanical origin. however, in winemaking practice, tannins from the same source may give different performances. CV may allow a better characterization of tannins concerning their effect on wine redox potential. In fact, as we can see in Fig. 1, four different lots of gall tannins give four different voltammograms, and this results in a different mechanism of action on white wines.

***Fig 1.*** *Voltammograms of four different lots of gall tannins.*

## **3.3 Reactivity of oenological tannins with white wine’s proteins**

|  |  |
| --- | --- |
|  | ∆NTU |
| **Wine**  | **Gall** | **Thè** | **Mix 1** | **Mix 2** |
| UW | 20,6 | 117,8 | 34,2 | 74,5 | 71,8 |
| SW | 0,4 | -0,2 | 0,2 | 7,35 | 2,2 |

The tannin-protein interaction is deeply studied for red wines but when we talk about white wines there are less information. Table 1 shows the different response of the wine after the adding of oenological tannins in stable and unstable wine and the consequent heat treatment. Data can be explained in this way, if the addition is made in an unstable wine, oenological tannins react with the more reactive protein fraction that is already present in wine and the increment of turbidity is consequently higher. Instead, when the oenological tannins are added in a stabilized wine, this phenolic fraction creates a lesser increase of turbidity, and we can say that in this way these adjuvants ***Table 1.*** *Differences of NTU pre and post heat treatment* can exploit their action by regulating redox potential. *of the wines. Wine = UW and SW without tannins*

## **3.2 Different behaviors of the same oenological tannin in different wines**

Fig. 2 presents the voltammograms illustrating the behaviour of a particular tannin in various mediums. It is evident from the results that the introduction of gall tannin elevates the potential of the wine, while no noticeable disparity is observed between the two wine types. This observation appears counterintuitive since the presence of abundant unstable proteins in UW would typically lead to a reduction in the curve. However, it is important to note that the absence of a direct correlation at this moment may be attributed to the possibility that a longer duration is required for the tannin to establish binding and effectively fulfil its intended role.

***Fig 2*.**  *Voltammograms of the same gall tannins in different mediums.*

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