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Original Research Article

Adding oenological tannin vs. overripe grapes: Effect on the phenolic composition of red wines

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ABSTRACT

The effects on the phenolic composition (flavanols, phenolic acids and anthocyanins) and on CIELAB colour parameters of two different oenological practices (adding oenological tannin, using overripe grapes), whose purpose is to compensate wine quality deficiencies, have been evaluated in red wines made from Tempranillo grapes in two consecutive vintages. Both the addition of oenological tannin and the use of overripe grapes generally increased hydroxycinnamic acids and pigment contents. However, the effect of the former was noticeable above all in early stages of winemaking and ageing, whereas the effect of the latter was observable in late stages of ageing. In general, flavanol content increased in wines treated with oenological tannin, and decreased in wines made from overripe grapes in relation to control wines. Colour differences (ΔE^*_{ab}) between control and treated wines were in some stages higher than 3, indicating that the colour modifications caused by both treatments can be detectable by the human eye. Results showed that the addition of the oenological tannin to wine will be useful to address deficiencies in flavanol and pigment contents, whereas the use of overripe grapes will be useful when colour stabilization is required.

1. Introduction

The increase in the frequency of extremely hot days and the alteration of the rainfall patterns associated with global climate change are going to have an important impact in agriculture. Vineyards are also very sensitive to climate change but the effects of these changes on viticulture have been and are likely to be highly variable not only from a geographical point of view but also for the different grape varieties (Jones et al., 2005). Although these changes might cause short-term benefits in terms of more consistent and higher-quality production, viticultural and oenological strategies will be needed to reduce the long-term impact on wine quality (Jones et al., 2005; Ramos et al., 2008).

The effects of the climate change on grape composition and the consequences on wine quality have been recently reviewed by Mira de Orduña (2010). The concentrations of several grape metabolites are clearly affected by temperature and it has been observed that higher temperatures during berry development may increase pH and sugar concentration and affect the levels of flavonoids. In addition, it has been reported that harvest dates have advanced, especially in the last 10–30 years (Mira de Orduña, 2010).

Traditionally, grapes are harvested at technological maturity, i.e. when the grapes reach the optimal weight, sugar concentration, pH, total acidity, etc. in light of the particular wine being produced. In addition the quality of a wine also depends on polyphenol content, which changes as grape ripen. Thus, over the recent years not only technological maturity has been taken into account for the selection of harvest date but also phenolic ripeness, which refers, above all, to the contents of anthocyanins and tannins. Generally, after veraison the phenolic content of grape skin increases. Unlike skin tannins, anthocyanins reach a maximum and then they begin to decrease (Ribéreau-Gayon et al., 2000).

Seed tannins, on the contrary, tend to decrease or remain more or less constant as grapes ripen (Kennedy et al., 2000; Ribéreau-Gayon et al., 2000). Ideally, technological maturity and phenolic maturity should coincide, but environment and climatic conditions may cause a delay between them. The advancement of harvest date, which is related to earlier technological maturity, can

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increase the delay between these two kinds of maturity and, as a consequence, grapes collected at technological maturity might possess an inadequate phenolic composition, and the wines made from them might be too bitter or/and astringent and poor in anthocyanins. Furthermore, previous studies carried out in our laboratory (Ferrer-Gallego et al., 2012) have shown that the phenolic maturity patterns of grape skins and seeds are different and that they are differently affected by climatic conditions.

In order to obtain quality wines all these aspects have to be taken into account and harvest date should be a compromise date between technological and phenolic ripeness. However, it seems that global climate change is going to increase the delay between them (Mira de Orduña, 2010) making it even more difficult to choose the appropriate harvest date for the desired type of wine. Different approaches have been proposed to solve this problem. Adding exogenous tannins either in the form of grape seeds or in the form of commercial oenological tannins and the use of overripe (from a technological point of view) grapes, among others, aim at improving the phenolic quality of the wines and have been employed in winemaking based on practical experience.

However, until recently the effects of these techniques on phenolic composition have not been studied. Some of the positive effects of using oenological tannins that are reported by tannin suppliers are the improvement of wine colour and its stability, oxidative protection, and flavour and mouthfeel improvement. Recent studies (Bautista-Ortín et al., 2007) have shown that the effect of adding these oenological tannins can change from year to year and that they depend on grape characteristics at the moment of harvest. Furthermore, it has been reported that at the concentration recommended by tannin suppliers no significant differences with regard to colour properties could be observed between the tannin-treated wines and the control wines, and that tannin addition had only a minor effect on perceived astringency (Parker et al., 2007). Higher concentrations than those recommended can even produce a negative and measurable impact on wine sensory characteristics (Harbertson et al., 2012).

With respect to overripe grapes, winery experience shows that the wines made from these grapes possess more stable colour and more intense purple hues than those made from less mature grapes (Pérez-Magariño and González-San José, 2006). However, several aspects have to be taken into account. Not only does the evolution of phenolic compound levels need to be considered as grapes ripens but the changes in the extractability of these compounds must also be considered. In general, extraction of phenolic compounds from skins seems to be promoted as grapes ripen, due to the changes in the cell wall (Canals et al., 2005; Hernández-Hierro et al., 2012; Ortega-Regules et al., 2006; Río Segade et al., 2008). On the other hand, the evolution of grape seed cell wall composition and structure during ripening seems to decrease the extractability of these compounds from seeds (Cadot et al., 2006). However, longer maceration times and higher ethanol contents may facilitate the extraction of seed proanthocyanidins (Canals et al., 2005; Gil et al., 2012; González-Manzano et al., 2004) and compensate for the decrease in their extractability occurring during ripening. In addition, the evolution of phenolic content and extractability during ripening may differ from one grape variety to another (Ortega-Regules et al., 2006; Río Segade et al., 2008). In order to determine the utility of these different oenological practices in overcoming the deficiencies related to the delay between technological and phenolic ripeness, it is thus necessary to carry out specific studies for each grape variety.

Detrimental effects on grapevine growth and development and on wine yields and quality parameters have been projected for southern Europe because of increasing dryness and cumulative thermal effects during the growing season (Malheiro et al., 2010). In fact, mean temperatures in Spain during the 20th century showed a general increase, with a magnitude greater than the global average, and rainfall showed a downward trend. The temperature increase projected for the Iberian Peninsula is 0.4 °C/decade in winter and 0.6 or 0.7 °C/decade in summer. Concerning rainfall, a generalized tendency towards less annual accumulated rainfall has been projected with an important reduction in spring (Moreno-Rodríguez, 2005). From these data it can be deduced that Spanish vineyards are going to be especially sensitive to global climate change. Among red grape varieties grown in Spain, Tempranillo (*Vitis vinifera* L.) is the most cultivated (MAGRAMA, 2009). Studies on the impact of predicted climate changes on Tempranillo grape quality have been recently carried out in greenhouse experiments and have revealed that these changes (elevated CO_2, high temperature and partial irrigation) will affect phenology and berry quality (Salazar-Parra et al., 2010).

The objective of the present work was to evaluate the effect of two different oenological practices (adding oenological tannin during alcoholic fermentation or use of overripe grapes) on phenolic composition (flavanols, hydroxycinnamic acids and anthocyanins) and colour parameters in wines made from *Vitis vinifera* L. cv Tempranillo from D.O. Ribera de Duero (Spain). The final goal was to assess the usefulness of these oenological practices in lessening the negative effects on wine quality associated with the delay between technological and phenolic ripeness which are related, in turn, to global climate change.

2. Materials and methods

2.1. Samples

Three different wines elaborated in 2 consecutive vintages (2009 and 2010) by Bodegas La Horra S.L. (D.O. Ribera de Duero, La Horra, Spain) from *Vitis vinifera* L. cv. Tempranillo grapes were analysed. Two of these wines were elaborated from grapes collected at two different ripeness states: technological ripeness (*Control wine*) and 13 days after technological ripeness (*Overripe wine*). The third wine (*Tannin wine*) was elaborated from the same grapes as Control wine (collected at technological ripeness), to which oenological tannin (supplied by Laffort España, Errenteria, Guipúzcoa, Spain) was added twice during alcoholic fermentation in a dose of 15 g/hL each time, as recommended by manufacturer. The oenological tannin added was an extract from natural sources which was mainly constituted by proanthocyanidins (58.8%, with catechins and procyanidins representing by themselves 42% (25.7% monomers, 11.7% dimers and 4.6% trimers) of the oenological tannin), oak ellagitannins (11.2%) and hydroxybenzoic acids (7.5%).

Maceration and alcoholic fermentation were carried out in a stainless steel tank (1200 L). At the end of alcoholic fermentation, wines were transferred into new medium-toasted French oak barrels (225 L), where malolactic fermentation took place and where the wines were aged. All the barrels were manufactured by Societé Seguin Moreau et Compagnie (Merpins, France) from naturally seasoned oak wood (24 months of seasoning). During barrel ageing three rackings were performed (between points 5 and 6, 8 and 9 and 10 and 11). After barrel ageing (for ca. 14 months in 2009 vintage and ca. 12 months in 2010 vintage), wines were bottled and aged in bottle for 6 months.

Wine samples were collected at different moments during winemaking and ageing from the alcoholic fermentation to 6 months after bottling (Table 1).

2.2. HPLC-DAD-ESI/MS^n analyses

Analyses were performed in triplicate in a Hewlett-Packard 1100 series liquid chromatograph (Agilent Technologies, Waldbronn, Germany). The mass spectrometer was connected to HPLC