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Effect of the prefermentative addition of copigments on the polyphenolic composition of Tempranillo wines after malolactic fermentation

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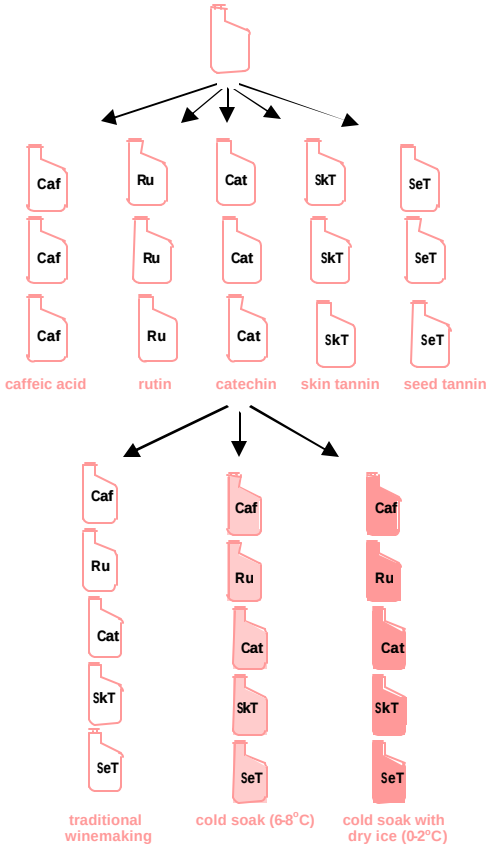
• The total color of a wine is the sum of three components: 1) copigmented anthocyanins, 2) non-copigmented free anthocyanins, and 3) polymeric pigments. Copigmentation is the interaction between anthocyanins and other phenolic components in wine -called cofactors or copigments- that result in an enhancement of wine color. (Even though "cofactor" and "copigment" are often used interchangeably, "cofactor" is probably the most correct word.) Known examples of cofactors belong to one of these categories: flavonols, flavanols, and hydroxycinnamic acids. Extending the maceration time of a must before fermentation would seem an important parameter to prolong the contact between anthocyanins and cofactors, and thus favor copigmentation reactions.

• Keeping the above in mind, these Spanish authors evaluated the effect of adding various **cofactors** (caffeic acid, rutin, catechin, skin tannin, seed tannin, all at 90 mg/L rate), as well as using various **pre-maceration techniques** (traditional winemaking, cold soak at 6-8°C, and cold soak with ice at 0-2°C), on the color parameters of Tempranillo grapes grown in Valencia, Spain. (See original text for concentrations). The authors conducted all the fermentations and analyses in triplicate.



• Before moving on with the results, let's get familiarized with the nature of the cofactors added. **Caffeic acid** is a hydroxycinnamic acid which is the product of the hydrolysis of caftaric acid, a compound naturally formed in grapes when they are exposed to sunlight. Clusters from open canopies, such as the Tempranillo from this study, would tend to exhibit high levels of caffeic acid. **Rutin** is a flavonol, the category of polyphenols that gives rise to the best cofactors. Natural levels of rutin in grapes tend to be low. **Catechin** is a flavanol, which along with epicatechin, represent the building units of tannins. Finally, **skin tannins** and **seed tannins** are polymeric flavanols. These may have undergone hydrolysis upon addition to the musts, in which case the tannin addition would partially mimick a catechin (and epicatechin) addition.

• **Effect of addition of copigments:** Adding cofactors caused a significant increase in color intensity and in the percentage of color due to copigmented anthocynins. (For a protocol to measure copigmented anthocyanins see http://boulton.ucdavis.edu/copig.htm).

• **Effect of pre-fermentation maceration:** Similar to the addition of cofactors, pre-fermentation maceration increased the concentration of anthocyanins, increased the percentage of ionized anthocyanins (the ones that contribute to color), and increased the copigmented anthocyanin contribution to color. Additionally, pre-fermentation maceration increased total polyphenols, total tannins, and the percentage of tannins combined with polysaccharides. Finally, it also decreased astringency measurements. (See original text for methods used).

• **Effect of adding copigments and pre-fermentation maceration combined:** The effects of adding cofactors were enhanced when the winemaking technique included a pre-fermentation maceration with ice. Among the five cofactors compared (rutin, caffeic acid, catechin, skin tannin, seed tannin), the highest effects were observed with the white grape *skin tannins* and the *seed tannins*; and between the two cold-soaks (6-8^{o}C or dry ice), the highest effects were obtained with dry ice.

• **Sensory evaluation:** The sensory panel consisted of 30 trained judges from the Polytecnic University of Valencia, who ranked the wines according to selected attributes (*color, flavor intensity, flavor quality, astringency, bitterness, structure, balance*). The evaluation was replicated to ensure reproducibility. The panel found the wines with added cofactors combined with pre-fermentation maceration to score lower for *astringency*, and higher for the attributes *structure* and *balance*. The panel did not observe significant differences for *color, flavor intensity*, and *bitterness.*

• **Discussion highlights:**
_ even though pre-fermentation maceration failed to show a clear increase in color intensity early on, the fact that it increased the percentage of "copigmented" color may mean higher color stability and intensity later on;
_ in a previous study, "cryomaceration" caused an important increase in caffeic acid, which is a cofactor. The current authors believe that "cryomaceration" may have enhanced not only caffeic acid, but also polysaccharide extraction, which in turn would complex with tannins to result in a fuller structure, more softness, and less astringency in the pre-fermentation macerated wines. This is in agreement with what was observed in this and several other studies;
_ even though in this study grape tannins were the most effective cofactors of the five studied, we cannot rule out the possibility of this effect being actually due to their hydrolysis products (catechins and epicatechins and olygomers), or the presence of impurities, as the authors point out.

In brief, pre-fermentation addition of cofactors combined with a pre-fermentation maceration caused an increase in various polyphenolic parameters related to color. It also increased the perceived *structure* and lowered *astringency*, when the wines were evaluated right after malolactic fermentation. These effects were greatest when white grape tannin was added, and when the pre-fermentation maceration involved dry ice. It would be interesting to see what happens to the color of these wines "down the road".

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