Anthocyanins and tannins in four grape varieties (Vitis vinifera L.). Evolution of their content and extractability


• To find out whether fermentation length or extraction protocol should be adjusted in those red varieties that might be prone to produce unripe seeds leading to astringent wines, these authors followed the evolution of anthocyanins, tannins, and extractability index of four Spanish varieties (Cabernet Sauvignon, Syrah, Merlot and Mourvedre, aka Monastrell) during 3 seasons (2002-2004). (In the case of the local variety Mourvedre, the authors included grapes from 2 locations: Mourvedre-Jumilla and Mourvedre-Bullas).

• At various ripening intervals, the authors measured anthocyanins by extracting the skins with methanol and quantifying them using high pressure liquid chromatography (HPLC). They measured skin and seed tannins by a protein precipitation assay, using bovine serum albumin (Harbertson and Adams assay). Finally, to measure “extractability index”, they macerated the grapes at two different pH values (3.6 and 1.0) and calculated the difference in anthocyanin content between the two macerations:

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\text{Extractability index} = \frac{\text{Anthocyanins}_{pH1} - \text{Anthocyanins}_{pH3.6}}{\text{Anthocyanins}_{pH3.6}} \times 100
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• The above formula is based on the fact that at pH 1.0 there is a complete disorganization of the vacuolar membrane that facilitates the release of all skin phenolic compounds. This contrasts with what happens at pH 3.6, at which the vacuolar integrity is preserved, a situation that mimics what takes place during fermentation. A grape will have good extractability when the difference between these two values is small (fermentation extraction close to total extraction). Please notice that, according to this formula, a low value of extractability index represents a good extraction.

• Results:
  Berry weight: 1) The smallest grapes were found in Cabernet Sauvignon, whereas the largest were in Mourvedre, particularly Mourvedre-Bullas. 2) Cabernet, Syrah and Merlot increased berry size throughout the berry season, whereas Mourvedre reached a maximum early on, after which berry weight remained stable.
Sugars: Cabernet Sauvignon, and particularly Syrah and Merlot, reached a high sugar level early in the season (short ripening period), whereas Mourvedre had a particularly long ripening period. The short ripening period of Syrah and Merlot could mean that pulp maturity is reached before seed maturity, something with detrimental consequences for wine quality.

Anthocyanins: 1) Merlot presented the lowest anthocyanin concentrations, whereas Mourvedre, and particularly Mourvedre-Jumilla, presented the highest. 2) Cabernet, Syrah and Merlot showed continuous anthocyanin synthesis throughout ripening, followed by a slight decrease at the end of ripening, whereas Mourvedre showed a slower accumulation, with maximum anthocyanin concentration reached one month later (mid-September).

Extractability index: In Cabernet, Merlot and Syrah, anthocyanin values at pH 3.6 were high, indicating a high quantity of easily-extracted anthocyanins, whereas in Mourvedre, anthocyanins at pH 3.6 were less than half those at pH 1, indicating poor extractability in winemaking conditions.

Tannins: 1) Regarding skin tannins, the highest concentrations were found in Cabernet and Mourvedre. However, Cabernet showed an important decrease in tannins early in the ripening process. As a consequence, Mourvedre (from both locations) was the variety with the highest quantity of skin tannins at harvest. (This was true both when tannins were expressed per unit of skin weight or per unit of berry weight.) 2) As for seed tannins, they decreased gradually during ripening, but this decrease was highest in Mourvedre, and lowest in Merlot. As a result, Cabernet and Merlot had the highest seed tannin values at harvest. A previous study had shown a good correlation between seed tannin content and wine tannin content ($r^2=0.9$), as well as between seed tannin and total phenolic content ($r^2=0.7$).

• Effect of year: In this part of Spain, year 2002 of the trial was characterized as rather cool, year 2003 as very hot, and year 2004 as warm. When authors looked at the effect of year on the parameters studied, they found that the extreme heat stress in 2003 had caused smaller berry sizes that year, as well as lower levels of both anthocyanins and seed tannins. However, the extractability index was not affected by the year, suggesting that this is a very stable parameter, closely linked to the type of grape.

In conclusion, of the parameters studied, berry weight and extractability index were closely related to the variety, whereas anthocyanin content and tannin content, although also related to variety, showed more influence of the growing location or the growing season. The authors found that, for the warm conditions of SE Spain:

- the short ripening period of Merlot promotes a rapid sugar accumulation and an incomplete seed maturation that may lead to excessively astringent wines;
- the long ripening period of Mourvedre is more suited to these warm conditions, allowing for seed maturity to be reached at harvest. However, when processing this variety, it should be taken into account that anthocyanins are not easily extracted, and so the fermentation protocol needs to be adjusted (longer macerations, more frequent pump-overs, etc) to promote extraction.

Author: Bibiana Guerra, Editors: Kay Bogart, Linda Bisson. This summary series funded by J. Lohr Vineyards & Wines.