

Development of Anthocyanins and Tannins in Pinot noir Grapes and their Relative Importance in Wine

James A. Kennedy, Jose Luis Pastor, Barney Watson
Department of Food Science and Technology
Oregon State University, Corvallis, OR 97331

INTRODUCTION

The objectives of this research are to monitor tannin and anthocyanin changes during berry development and over several growing seasons to understand how the vintage effects wine composition. Specifically, the objectives of this research project are:

- Determine the effect of berry development on the composition of phenolics (tannins and anthocyanins) in cv. Pinot noir grapes
- Isolate and purify sufficient quantities of tannin and anthocyanin for sensory and stability studies
- Determine the sensory properties of wines manipulated with anthocyanins and tannins representing extremes in composition based on grape and wine data.

These goals are designed to understand how tannin and anthocyanin composition in grapes affects the color stability and texture of wine, and to begin to understand the extent to which vineyard and winery practices could be used to influence their composition. This report is a summary of the first two years of this study. A justification for this study was reported after the first year of this project (Kennedy et al., 2002), and readers are encouraged to read this report to provide context and experimental detail to the following update.

RESULTS AND DISCUSSION

Growing Season

The 2001 and 2002 growing seasons were both considered to be exceptionally good vintages from a wine production standpoint. The period encompassing berry growth (mid June-early October) was for the most part free of adverse weather conditions. To the extent that plant growth in the cool growing regions

of Oregon are responsive to heat, the growing degree days for the 2001 and 2002 growing seasons are summarized in Figure 1. Based upon growing degree days, 2002 was a warmer year.

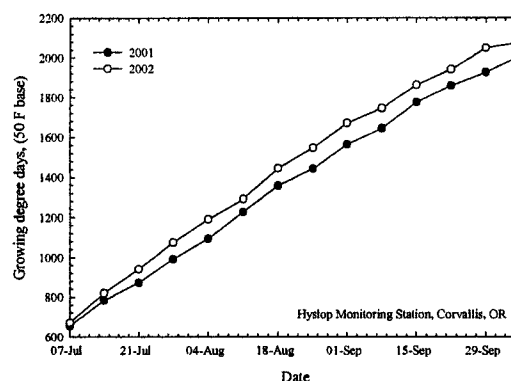


Figure 1. Cumulative growing degree-days during the period of berry growth and for the 2001-2002 growing seasons.

Temperature differences such as these could contribute to differences in anthocyanin and tannin production.

Berry Development

Overall berry development is summarized in Figures 2-4.

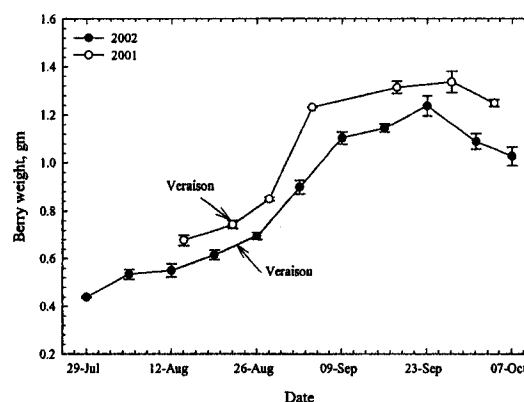


Figure 2. Berry weight change and véraison onset for the 2001 and 2002 growing seasons with error bars indicating \pm SEM (N=5).

Berry weight over the first two vintages, while generally developing in parallel, were significantly different in terms of berry weight differences (Figure 2). Large

differences in the production in this vineyard were noted between these two years (2001: 1.5 T/Ac; 2002: 2.4 T/Ac) due to less cluster thinning at véraison. This might explain differences in berry weight although other factors may have played a role. At the time of harvest, the berry weight for the 2001 vintage (1.3 g/berry) was considerably higher than for the 2002 vintage (1.1 g/berry). Given that the extraction of anthocyanins and tannins during wine production are dependent on berry size, the smaller berry size of 2002 would favor a more extracted wine.

Very little difference in the soluble solids between the two vintages was observed (Figure 3).

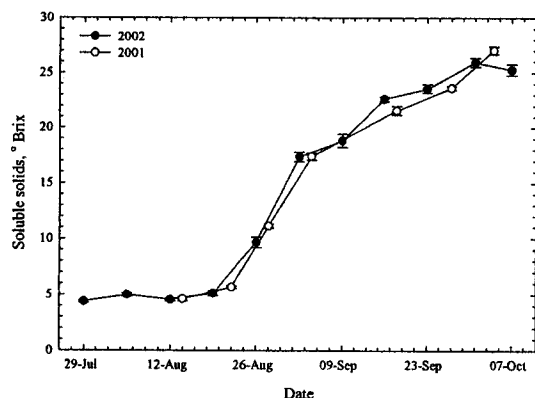


Figure 3. Soluble solids accumulation during the 2001-2002 growing seasons with error bars indicating \pm SEM (N=5).

The pH and titratable acidity (TA), summarized in Figure 4, followed expected trends, yet the final TA and pH suggest that extensive organic acid metabolism has taken place.

In addition to this, dramatic differences in must pH between the two vintages existed. The higher titratable acidity and lower pH for the 2002 growing season may have been due to the increased crop load.

Seed Development

The seeds developed similarly for the two vintages. Initially, prior to véraison, the seeds were green with a soft seed coat. Beginning

at véraison, and continuing through harvest, the seeds lost their green color and became progressively browner with time.

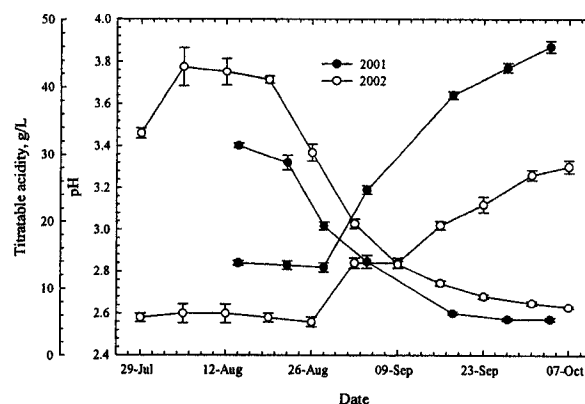


Figure 4. pH and titratable acidity change during the 2001 and 2002 growing seasons with error bars indicating \pm SEM (N=5).

The difference between fresh and dry seed weight provides some indication of dessication status, and can be used as an indicator of seed developmental status. For the two seasons, very similar patterns existed, with a increase in dry seed weight up to véraison, and a stabilization thereafter (Figure 4). The fresh seed weight on the other hand declined continuously up to and including harvest. This suggests that the seed were still developing at this time.

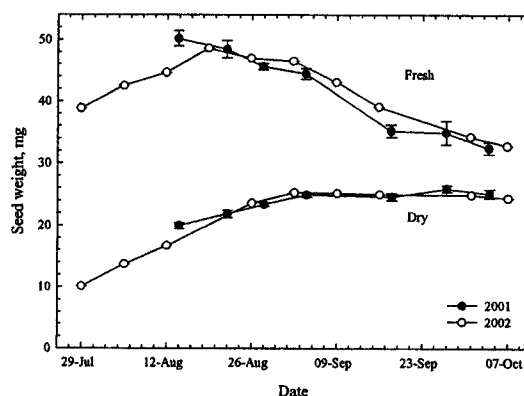


Figure 5. Fresh and dry seed weight for the 2001-2002 growing season, with error bars indicating \pm SEM (N=5).

Tannin Development: Seed

Seed tannins developed in a manner consistent with other varieties, although significant differences were apparent (Figures 6-8). Overall, the results for the 2001 and 2002 vintages were similar, although at harvest, the 2002 vintage had lower flavan-3-ol monomer and high tannin amounts.

Consistent with previous results, the seed flavan-3-ol monomers in Pinot noir were synthesized in the few weeks preceding véraison whereas the majority of the tannins were already present (Figure 6). As was discussed in the first year report, the abundance of flavan-3-ol monomer in Pinot noir is in stark contrast to other studied varieties where they make up a much smaller proportion of the total tannin pool (>6x).

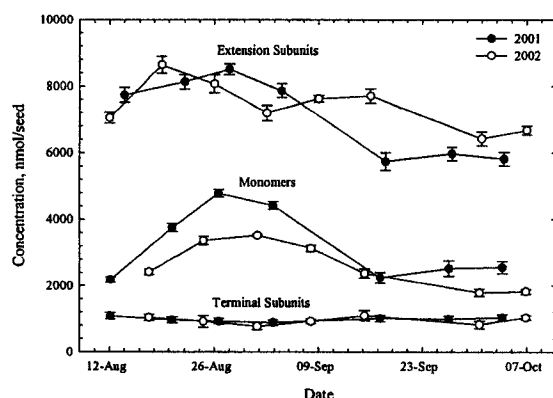


Figure 6. Development of the different tannin flavan-3-ol components in grape seed, with error bars indicating \pm SEM (N=5).

The presence of a large amount of flavan-3-ol monomers may have important implications in winemaking if the following is considered. First, because of their smaller size, low molecular weight tannins are expected to diffuse into wine more readily than larger molecules. This is significant because smaller tannins are dominated by the perception of bitterness, and have been described as hard in other beverages (Peleg et al., 1999). Second, because of their much higher concentration, wines made from Pinot noir grapes could easily have a much higher concentration present than varieties such as

Cabernet Sauvignon and Shiraz if it were not for differences in winemaking.

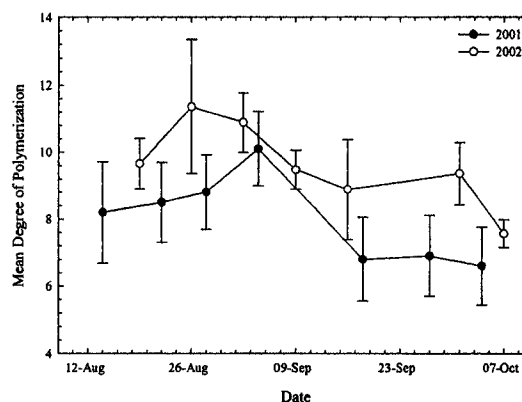


Figure 7. Mean degree of polymerization of grape seed tannins for cv. Pinot noir during berry development for the 2001 and 2002 growing season with error bars indicating \pm SEM (N=5).

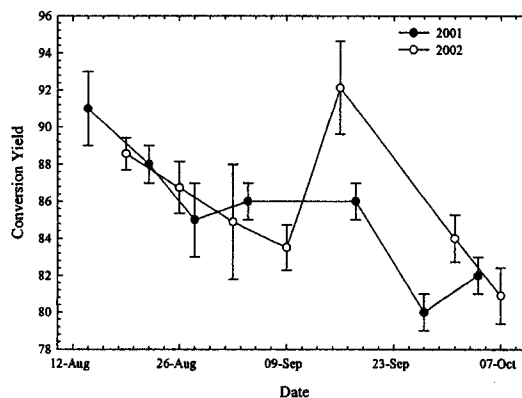


Figure 8. Conversion yield for seed tannins during berry development and for the 2001 and 2002 growing season with error bars indicating \pm SEM (N=5).

The tannin mean degree of polymerization (Figure 7) and the conversion of tannins into known subunits (Figure 8), followed similar trends over the two vintages. For the 2002 vintage, the mean degree of polymerization was generally higher although overall, the differences probably do not translate into differences at the sensory level.

This preliminary data suggests that while Pinot noir possesses tannins that are similar to other varieties, the preponderance of monomeric (bitter) material drives skin

contact time in Pinot noir production. This is consistent with current production techniques in use that are designed to minimize seed extraction (where the monomeric material resides). The current study is consistent with the desire to minimize seed extraction, and furthermore provides additional avenues that could be pursued if monomer concentration in wines is to be minimized. Of particular interest is the biosynthesis at different times between seed monomers and larger tannins in the grape (Figure 6). This indicates that it may be possible through grape production practices to manage monomer biosynthesis without affecting tannin biosynthesis.

Tannin Development: Skin

The development of tannins in the skin tissue is summarized in Figure 9. The amounts produced over the two vintages was very similar in both pattern of accumulation and in amount. The degree of polymerization however was very different (Figure 9 inset). These results should be considered preliminary.

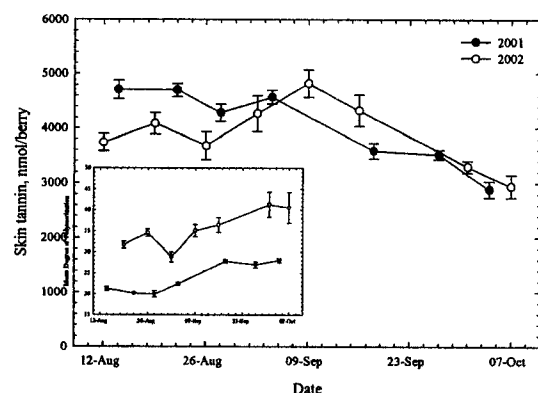


Figure 9. Development of the grape skin tannin and the corresponding mean degree of polymerization (mDP, inset) with error bars indicating \pm SEM (N=5) for the 2001 and 2002 growing seasons.

Anthocyanin Development

The development of anthocyanins during the 2001 and 2002 growing seasons is shown in Figure 10. While the per berry anthocyanin concentration was generally higher during the 2001 growing season, the lower harvest berry weight observed during the 2002 growing

season minimized these differences at the winemaking level (Figure 2).

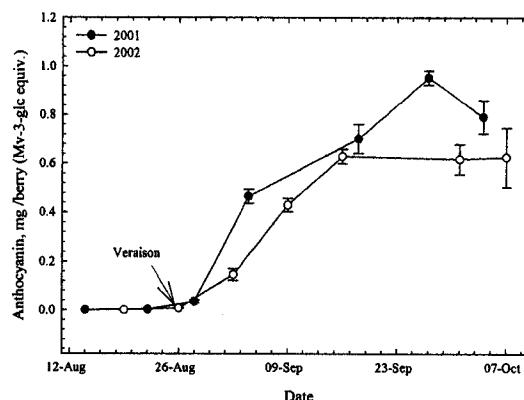


Figure 10. Development of anthocyanins with error bars indicating \pm SEM (N=5) for the 2001 and 2002 growing seasons.

Wine Phenolics

During the 2002 vintage, wines were made from grapes harvested at three levels of increasing ripeness (Table 1). The methods used to produce wines have been previously described in the last report. The three harvest dates were designed to investigate the extremes of what industry might observe. Here, the earliest harvest date was very clearly an underripe crop whereas the latest harvest date was tending towards an overripe crop.

In addition to the three harvest dates, one additional wine (Mid-L) was produced from grapes harvested at the intermediate level of ripeness. Here, the fermenting must was pressed on the 3rd day of fermentation to minimize tannin extraction (Table 2). For this wine, purified tannins will be added back to understand how tannin composition influences color stability and texture.

Table 1. Soluble solids at harvest and anthocyanin concentration of finished wines.

Wine	° Brix	Anthocyanin, mg/L
Early	20.1	208
Mid-E	23.4	308
Mid-L	23.4	255
Late	25.5	240

The anthocyanins were similar for all wines (as predicted by berry weight and anthocyanin data), with the mid harvest wines having the highest amounts.

In Table 2, the individual tannin components are reported for the wines produced in the 2002 vintage. As expected, the flavan-3-ol monomer concentration declined with increasing fruit maturity, particularly between the latter two pick dates. There was also a very clear decline in the overall amount of tannin extracted into wine across maturity. While this has generally been ascribed to a reduction in seed tannin extraction, the percentage of skin tannin indicates otherwise.

Table 2. Composition of tannin components in wine.

Wine	C ^a	EC ^b	Tannin ^c	mDP ^d	% skin ^e
Early	110	52	702	2.5	51
Mid-E ^f	42	20	343	3.2	87
Mid-L ^g	114	53	664	2.5	51
Late	99	43	559	2.4	44

Notes) ^a(+)-catechin, mg/L
^b(-)-epicatechin, mg/L
^cTotal tannin, mg/L
^dAverage tannin degree of polymerization
^e% tannin derived from skin tissue
^fWine pressed on 3rd day of fermentation
^gWine pressed on 7th day of fermentation

In comparing the total amount of tannin extracted with the % skin tannin extracted, the results in Table 2 indicate that while the amount of seed tannin remained fairly constant (325-348 mg/L), the amount of skin tannin declined (358, 339 and 224 mg/L for early, mid-L and late respectively). These results to our knowledge have not been previously reported.

In comparing the 2001 and 2002 vintages, the mid-maturity wines are comparable. The wines were made in a very similar manner. The results are of interest because they provide some indication of how the composition of grapes influences the resulting wines. In this case, the tannin was generally higher on a per berry basis during the 2002 vintage. In addition to that, the berries were considerably smaller. As predicted by these

results, the tannin in the 2002 vintage was higher than 2001. The anthocyanin was somewhat higher in the 2001 vintage (284 and 255 mg/L for the 2001 and 2002 vintage respectively), although these differences were minor. Overall then, the grape data in large part predicted the wine data. All wines are currently being stored under cellar conditions for sensory studies.

Table 3. Composition of tannin components in wine.

Wine	C ^a	EC ^b	Tannin ^c	mDP ^d	% skin ^e
2001	100	49	444	2.3	46
2002	113	56	664	2.5	51

Notes) ^a(+)-catechin, mg/L
^b(-)-epicatechin, mg/L
^cTotal tannin, mg/L
^dAverage tannin degree of polymerization
^eWine pressed on 7th day of fermentation

One of the primary goals of this study is to understand how the relative composition of tannins and anthocyanins affects both color stability and texture in red wine. An additional year of study is planned for this project. From this a better understanding of how phenolic production in grapes affects color stability and texture in wine will be made.

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Kennedy, J.A., Godard, M., Watson, B.T. (2002) Development of anthocyanins and tannins in Pinot noir grapes and their relative importance in wine. *Proceedings of the 2002 Oregon State University Winegrape Research Day* Corvallis, OR, pp.81-94.