Grape seed tannins: impact on red wine

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Winemakers and wine writers alike describe tannins in red wine using qualitative terms,[19] (Table 1). It is readily apparent from periodicals devoted to wine appreciation that tannin quality is an important attribute in red wine quality.

Table I
Descriptive terms given to red wine astringency

Terms generally recognized as positive:	Terms generally recognized as negative:
ripe[1], soft, round, velvety, silky, supple	unripe[1], hard, green, harsh, aggressive

notes: [1] Qualitative terms related directly to fruit maturity.

It is important therefore to understand the factors affecting tannin quality so that better wines can be made. It is recognized that enological practices, such as extended maceration and ageing (cooperage, oxygen exposure, and time), can influence the tannin quality in red wine. It is also recognized that tannin concentration and quality are initially determined in the vineyard, with seed number and fruit maturity playing leading roles.[10, 15]

While a definitive explanation for tannin quality does not exist, speculations typically fall into one of the following two categories:

The *concentration (i.e.* the "quantity effect"): tannins are described (positively or negatively) based on their ***concentration*** relative to other wine components *(i.e.* acidity, sugars, flavor components, and alcohol).

The *structure (i.e.* the "quality effect"): tannins are described (positively or negatively) based on their ***structure***, which changes during fruit ripening.

Presented with a problematic wine, and given these explanations, two very different approaches would be taken by a winemaker to improve the tannin quality. For the wine's concentration, adjusting the tannin levels in the wine relative to other wine components would result in an improvement in quality.

Conversely, for the wine's structure, a modification in tannin structure would be required for the same improvement in quality. Since definitive studies on grape tannin structure variability during fruit ripening have not been done, it is not at all clear whether tannin structure even changes.

Since grape seed tannins normally make up a significant proportion of the tannins found in red wine,[23] observed modifications in their structure during fruit ripening could lead to a testable theory for red wine tannin quality.

Initial research efforts toward an understanding of how tannin structure could affect the quality of extracted tannin in red wine have focused on grape seed tannins. This report is a summary of the research conducted on grape seed tannins and subsequent development of testable hypotheses that could explain differences in red wine tannin quality.

Grape seed tannin structure, changes during fruit ripening

Grape seed tannins are a complex group of compounds based on the flavonoid ring system.[1] While most flavonoid compounds have this three-ring system in common, the complexity of the tannins arises from their polymeric nature, composed of different flavan-3-ol subunits linked together (Figure 1).

Individual tannin molecules can vary in length from oligomers (containing two subunits) to polymers (reportedly containing over 19 subunits). Based on the most prevalent linkage between subunits, grape seed tannins are predicted to adopt a helical three dimensional structure with the B-ring radiating around the perimeter of the central helical core.[2, 8, 5, 11]

From microscopic and sensory examinations of developing grape berries, tannins are synthesized beginning at a very early stage of development (essentially from anthesis).[9] Based on our knowledge of the development of tannins in the peach, it is likely that tannins increase steadily during Stage I and the early part of Stage II of berry development.[22]

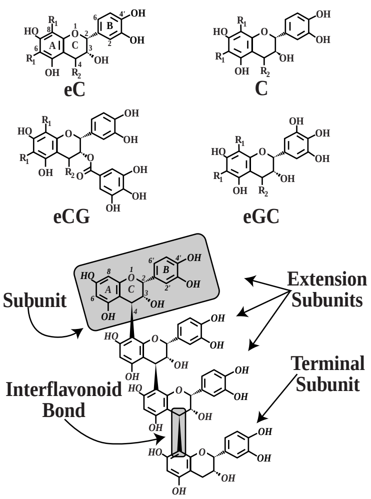

Figure 1

Extractability of seed tannins, from bloom through harvest, probably increases to a maximum during, or just prior to, Stage II of berry development, and thereafter declines (Figure 2). The increases in tannin extractability during Stage I and II of berry development would be due to the biosynthesis of tannins. The decreases in extractability during Stage III (fruit ripening) however, suggest that a developmental change has occurred.

From rigorous examinations of grape seeds and their tannin structure during fruit ripening, it is clear that there are indeed changes that the seed goes through, and furthermore, that these changes affect the tannin structure.[13] The most obvious visual change in the seed is a change in the seed coat color,[3] from a bright green to a dark brown. From the development of other plant seed coats, these changes are consistent with the final oxidation of the seed coat.[16, 24]

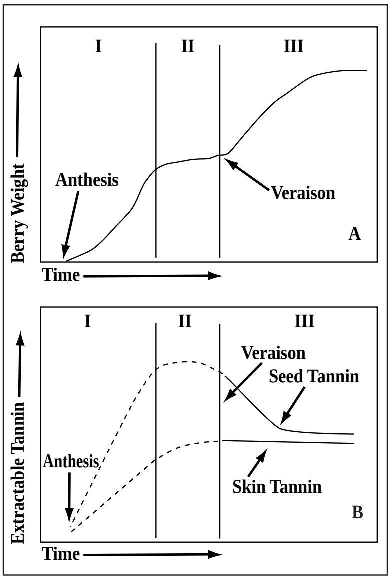

Figure 2

The changes in tannin structure are also consistent with oxidation. These changes include:

- decreasing extractability, with the decline in extraction consistent with an oxidation model,
- apparent increase in the average tannin length when analyzed intact and a decrease in length when analyzed after degradation,[12]
- upon degradative analysis, there is a decreasing conversion of tannins to known degradation products.

In order to understand how these changes in tannin structure during fruit ripening could play a role in the quality of red wine astringency, it is necessary to review the sensory properties of the tannins, and the way in which the tannins elicit their response.

Sensory Properties of Tannins

Mouth feel is the tactile perception of a wine in the mouth and is the sum of all components that can elicit a tactile perception including polysaccharides, ethanol, glycerin, as well as the tannins.

Tannins extracted from grapes during red wine production have two sensory properties associated with them: bitterness and astringency.[18, 21] In addition to sweetness, sourness, and saltiness, bitterness is a taste perception, and as such, there are taste receptors specific for bitterness.[19] For bitterness, these receptors tend to be concentrated on the back of the tongue.

Of the tannins extracted from grapes during red wine production, the low molecular weight molecules are predominantly bitter, whereas the higher molecular weight tannins are predominantly astringent.

Astringency is the feeling of dryness and roughness in the mouth. In red wine, this perceived dryness is associated with intensity and duration (Figure 3). The primary reaction responsible for this dryness is believed to be the precipitation of lubricating salivary proteins by tannins.[1] Because of their complimentary structure, salivary proteins and tannins are uniquely suited for complex formation.[4, 8, 9, 25] Presumably, the formation of a salivary protein-tannin complex inactivates the tannins before ingestion and minimizes the loss of dietary and digestive proteins.[17]

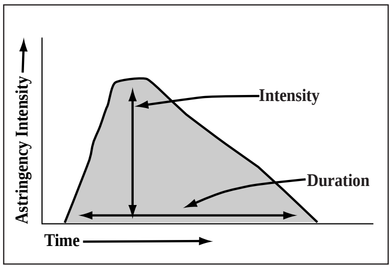

Figure 3

The complimentary structural features of the salivary proteins and the tannins are responsible for two effects which are expected to occur during their complexation: hydrophobic interactions and hydrogen bonding. Of these, the hydrophobic interactions are considered to be the driving force for complex formation.

Following the initial formation of a salivary protein-tannin complex from hydrophobic interactions, the complex is strengthened considerably by additional hydrogen bonding. The salivary protein-tannin complex is still soluble and requires additional aggregation to cause precipitation and subsequent astringency prerception, (Figure 4).[7] All of these processes are reversible and can have varied stoichiometries.

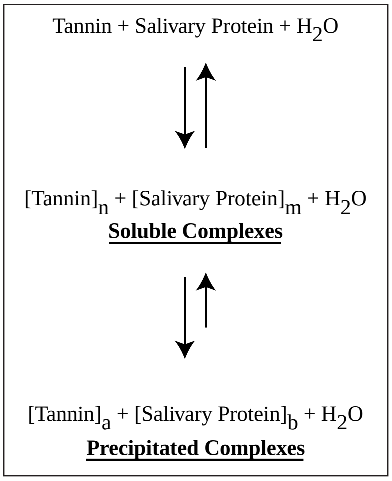

Figure 4

Tannin structure can influence protein interaction. Molecular weight, substitution pattern, and flexibility have been shown to affect the ability of tannin to interact with protein.[20] Based on the changes that the grape-based tannins undergo during fruit ripening, it is expected that their interactions with salivary proteins will become modified.

Concept of Tannin Quality

Given our current understanding of tannins, what precisely are desirable and undesirable tannins, and how could grape maturity affect their levels? From personal experience, conversations with winemaking professionals, current understanding of tannin changes during fruit ripening, and-tannin interaction with salivary proteins, three explanations for the change in tannin quality can now be given.

Theory I: Balance hypothesis

The first explanation is that changes in tannin quality have nothing to do with tannin structure at all, but are dependent on “balance” (see “concentration” above). If tannins are too high in concentration relative to other sensory components, then they overwhelm the perception of the other components in red wine and therefore are deemed hard and aggressive.

It is clear that tannins are more easily extracted from underripe grapes. Moreover, there are many biochemical processes that occur during fruit ripening, most of which lead to a reduction in perceived astringency, including a reduction in acidity, increases in sugar, soluble pectins, and flavor components.

The net effect is that, with fruit ripening, the possibility of having too much perceived astringency in wine is diminished because of the increasing role that other negating factors play in wine perception, and the increased development of flavor and aroma compounds.[6] To use winemaker terminology, underripe tannins would be considered to be tannins that are excessively present, and those that are ripe are in balance with other components.

Theory II: Bitterness/Astringency hypothesis

The second explanation for tannin quality is based on changes in tannin size. During fruit ripening, the average size of the tannin extracted from grape seeds increases. Therefore, as grapes ripen, the extracted tannins should elicit less bitterness and more of an astringent response.

Now the semantics: Some winemakers, when describing the tannin transition from unripe to ripe, describe the corresponding astringency as moving from a centralized and intense response in the back of the mouth for unripe tannins (bitterness sensed in back of the mouth), to one that is more general in location for ripe tannins. Additionally, unless bitterness is exceedingly high, winemakers rarely use it as a descriptor; it is part of the perception of mouth feel.

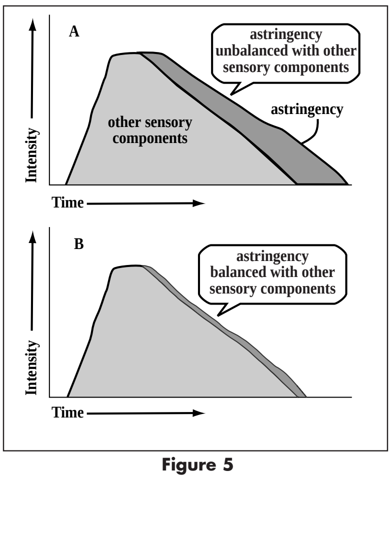

Figure 5

The bitterness and astringency responses that sensory scientists consider to be separate are ***not,*** in the opinion of winemakers. Again, to use winemaker terminology, under-ripe tannins would be considered to be tannins that have an excess of low molecular-weight tannins (the bitterness component), and those that are ripe have less.

Theory III: Intensity/Duration hypothesis

The third explanation for tannin quality is based on structural modifications of the tannins leading to modifications in their interaction with salivary protein. Tannin-protein complexes are held together by hydrophobic interactions and hydrogen bonds (see above).

Modifications of the tannin structure could lead to modifications in the ability of the tannin molecule to hydrophobically interact and hydrogen bond with salivary protein. If these changes result in changes in the duration of astringency relative to intensity (Figure 5), then this could be perceived as a qualitative change in astringency.

There is some evidence that seed tannins are oxidatively modified (see above), and oxidation would be expected to modify the tannin structure in this manner. Oxidation of the tannin molecule is expected to modify the A and B-ring portions of the tannin molecule, and create modifications of the hydrogen-bond donor sites, as well as the surfaces responsible for hydrophobic interactions, and would also make the tannin molecule less flexible.

It is predicted that, as a tannin molecule becomes increasingly oxidized, the corresponding protein-tannin complex becomes increasingly dependent on hydrophobic interactions for stability. If the interaction between tannin and protein is initiated by hydrophobic interactions, the complex between tannin and protein would form, but it is expected that the complex would be weaker because hydrophobic interactions are weaker than hydrogen bonding interactions.

It is unclear whether a soluble complex provides as much lubrication in the oral cavity as the uncomplexed protein (*i.e.:* not astringent), or if precipitation is necessary for lubrication to be lost (Figure 4). To use winemaker terminology, underripe tannins would be considered to be tannins that form stronger complexes with salivary proteins (due to higher proportion of hydrogen bonding and increased flexibility), and riper tannins would form weaker complexes.

Theories II and III could both be explained by oxidation and therefore, based on current predictions, both the size distribution and the three-dimensional structure are likely to be affected.

Conclusion

From the above three theories, improving the quality of perceived tannins in red wine begins with identifying whether the tannins are out of balance (Theory I), or whether their structure needs to be modified (Theories II and III). For some red wines, tannin quality could be improved by bringing the tannins into balance with other wine components, whereas, for other red wines, the structure of the tannins themselves may need modification.

Changing the structure of the tannins could take place in the vineyard through cultural practices or careful site selection. It could also take place in the winery by modifying maceration regimes or cellaring practices, although knowledge in this area is based on anecdotal evidence.

It is evident that, in addition to concentration, tannin structure could explain perceived differences in red wine tannin quality.

The task now is to determine the role that these theories play in red wine tannin quality. This requires sensory studies coupled with analytical methods capable of measuring the contribution of the three theories described. In addition, since the skin tannins are also present in red wine,[14] their contribution to quality also has to be considered. ■

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