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Grape and wine phenolics: Observations and recent findings

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Abstract

J.A. Kennedy. 2008. Grape and wine phenolics: Observations and recent findings. Cien. Inv. Agr. 35(2):107-120. What consumers taste in wine is the culmination of management practices from the vineyard to the glass. As researchers, in order to have control over the composition of wine at the time of consumption, it is important to understand how production practices affect wine chemistry. Because phenolic compounds are so important to the overall quality of wine, they are the subject of intense investigation throughout the world. This review is a summary of current knowledge and some recent findings that have taken place in this area.

Key words: Anthocyanins, proanthocyanidins, red wine, tannins, *Vitis vinifera*.

Introduction

Wine phenolics are important quality components that contribute to the color, taste, and feel of wines. Although phenolic compounds found in wine can also originate from microbial and oak sources, the majority of the phenolic constituents found in wine are grape-derived. In white wine, the most important phenolic compounds are the hydroxycinnamic acids and of minor quantities, the flavan-3-ol monomers. These compounds are important with regard to the visual quality of white wine.

In red wine, tannins and anthocyanins are the most important phenolic classes. Tannins contribute to the mouthfeel of wines but they also form pigmented polymers in association with the anthocyanins to provide the stable pigments required to give red wine its long-term color stability.

Winemakers inherently understand the importance of grape and wine phenolics to overall wine quality, yet increasingly, advances in grape and wine phenolic chemistry have made it difficult to remain current in our understanding. The complex nature of many recent findings has also made it at times difficult to apply the science in way that can be used practically. This review is a summary of our current state of understanding in this area with an emphasis on recent findings.

Grape phenolics

Compounds and distribution. The major phenolic compounds from a wine quality perspective are the hydroxycinnamic acids, anthocyanins, and tannins (*syn:* proanthocyanidins or condensed tannins) (Ribéreau-Gayon, 1965-1963, 1959, Figures 1-3). The identification of these compounds has been accomplished and their distribution in the grape berry has been well documented (Figure 4).

Biosynthesis, accumulation and management. The biosynthesis of grape phenolics has been a subject of intense investigation recently (Bogs *et al.,* 2007, 2005; Dixon *et al*., 2005; Xie *et al*., 2003; Winkel-Shirley, 2001; Boss *et al*., 1996). The biosynthesis of the phenolic compounds that are important to wine quality share a common pathway (Figure 5). While many of the genes in this pathway have been identified, portions of it remain speculative. In particular,

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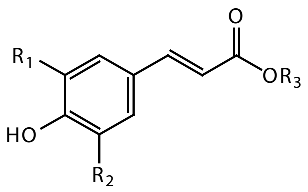
proanthocyanidin production in plants is still incompletely understood (Dixon *et al*., 2005). Despite this, recent advances have been made with regard to the factors that are involved in gene regulation (Bogs *et al*., 2007).

The concentration of grape phenolics increases throughout berry development. Beginning at fruit set and when expressed on a weight basis, tannins and hydroxycinnamic acids increase until véraison (Downey *et al*., 2003; Kennedy *et al*., 2001, 2000; De Frietas *et al*., 2000; Romeyer *et al*., 1983). Beginning at véraison, anthocyanins accumulate in the berry and increase during fruit ripening. There is evidence that suggests that anthocyanins can decline late in berry development (Kennedy *et al*., 2002).

It is accepted that phenolic compounds are important to the quality of wine and therefore a considerable amount of research has been directed towards the understanding of how vineyard management practices influence their concentration in grapes.



Hydroxycinnamic Acid	R_1	R_2
p-coumaric	H	H
caffeic	OH	H
ferulic	OCH_3	H
sinapic	OCH_3	OCH_3

R_3 esterification

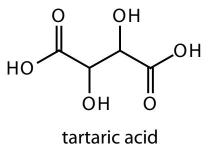
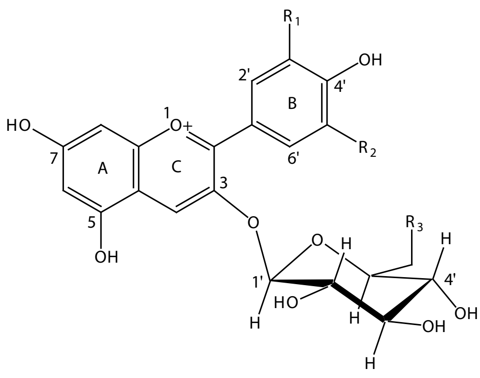


Figure 1. Hydroxycinnamic acids found in *Vitis vinifera*.



Anthocyanidin Moiety	R_1	R_2
cyanidin	OH	H
peonidin	OCH_3	H
delphinidin	OH	OH
petunidin	OCH_3	OH
malvidin	OCH_3	OCH_3

R_3 substituents:

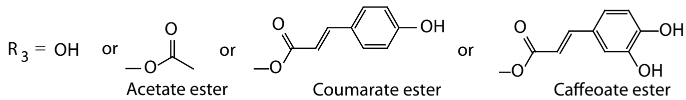
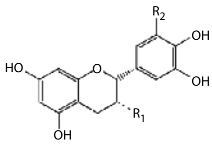
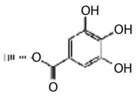


Figure 2. Anthocyanins found in *Vitis vinifera*.



Flavan-3-ol Monomer	R_1	R_2
(+)-catechin	OH	H
(-)-epicatechin	OH	H
(-)-epigallocatechin	OH	OH
(-)-epicatechin-3-*0*-gallate		H

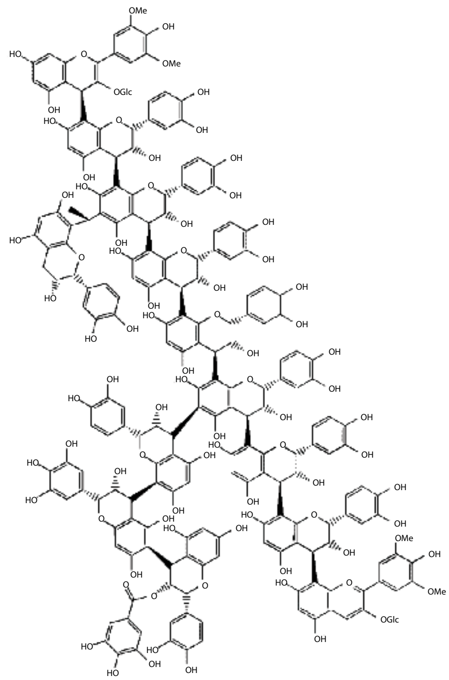


Figure 3. Flavan-3-ols found in grapes with an oligomer shown with various interflavonoid bonds as well as anthocyanin and ethylidene modifcations.

It is well established that phenolics vary with vintage (Cortell *et al*., 2007a, b; Pastor del Rio and Kennedy, 2006; Downey *et al*., 2003; Ribéreau-Gayon, 1972), and furthermore, that the cultural practice and environment around the developing fruit can effect composition (Pena-Neira *et al*., 2007; Smart *et al*., 1988). Fruit exposure influences phenolic production in the grape (Cortell and Kennedy, 2006; Downey *et al*., 2004; Bergqvist *et al*., 2001; Dokoozlian

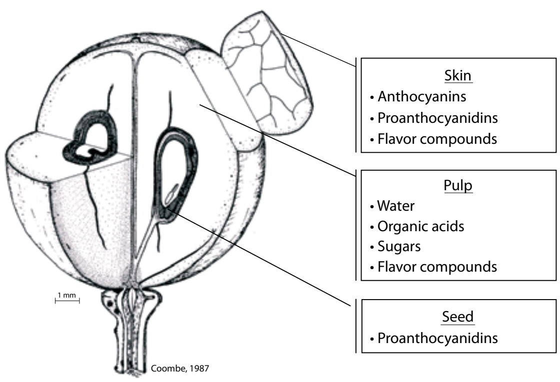


Figure 4. Distribution within the grape berry of compounds important to wine quality.

and Kliewer, 1996; Price *et al*., 1995; Gao and Cahoon, 1994; Kliewer and Torres, 1972; Kliewer, 1977). Research recently by Spayd *et al*. has shown that exposure differences can be due to temperature or light effects (Spayd *et al*., 2002). It is logical that the observed findings from commonly observed practices in vineyard management can be interpreted from changes in the exposure light/temperature environment around the fruit (Cortell *et al*., 2005; Kennedy *et al*., 2002, 2000; Ojeda *et al*., 2002; Mateus *et al*., 2001).

Phenolic extraction during wine production

Once grapes are harvested phenolic composition in the wine becomes dependent upon processing in the winery. With the exception of pulp-derived hydroxycinnamic acids, phenolics derived from the skin and seed tissue makes up the vast majority of the phenolic pool present in wine, with stem-derived phenolics making a minor component if included. Determining the total quantity of phenolic compounds therefore is under winemaker control.

Because anthocyanins are localized in the skin tissue of most grape cultivars, fermentation and maceration have a profound effect on the amount of anthocyanin present in the final wine. An extreme example of this would be the separation of the solid parts of the grape berry from the juice with little or know maceration resulting in a wine with little or no red color. Sparkling wines made from cv. Pinot noir grapes are an example of how little color can be extracted.

Clearly, because of the localization of anthocyanins within plant cell vacuoles, diffusion needs to be considered. Diffusion is simply the process by which a compound moves from a region of high concentration toward a region of lower concentration (i.e.: from the plant cell into the wine). Considering the generally observed extraction curves for anthocyanins (Ribéreau-Gayon and Milhé, 1970; Ribéreau-Gayon *et al*., 1970) and the effects that wine processing variables have on the rate of the compounds' extraction, the overall process is generally consistent with diffusion. Diffusion is dependent upon the following: 1. Temperature, 2. Molecular weight/size and type of molecule, 3. Concentration gradient, 4. Cell permeability, 5. Surface area over the concentration gradient, and 6. Composition of extraction medium (such as ethanol concentration).

In all instances but molecular size, these variables contribute positively to the rate of diffusion. Time, of course, is an important variable for overall extraction.

Previous research has shown that in any given fermentation, time and temperature are the two critical variables in determining the ultimate amount of anthocyanin present in wine (Aron and Kennedy, 2007; Zimman *et al*., 2002; Kovac *et al*., 1992; Mayen *et al*., 1994; Scudamore-Smith *et al*., 1990; Aubert and Poux, 1969; Ough and Amerine, 1961; Berg and Akiyoshi, 1956). For anthocyanins, higher temperatures reduce the time to maximum concentration, and increase the maximal amount. Besides the most obvious variables of time and temperature, the other variables undoubtedly also play a role in anthocyanin extraction. Determining their relative importance, however, is difficult because of the compound nature of their affects.

With regard to tannins, and in addition to the diffusion variables described above, winemakers have a general preference with regard to the origin of the tannin: skin versus seed. It is generally thought that skin-derived tannins are "riper" than those found in the seed, and if a more developed wine is preferred, then skin tannins are desired. One explanation for the improvement in tannin quality with respect to fruit maturity is that there is an increase in the proportion of skin-derived tannins. Using a recently developed analytical method (Peyrot des Gachons, and Kennedy, 2003), Pastor del Rio and Kennedy (2006) found that wine made from increasingly mature grapes results in an increase in the proportion of seed-derived tannins. This observation is inconsistent with general wine industry explanation for tannin quality improvement.

Additional research does suggest however that an increase in the proportion of skin tannin (and amount) provides some explanation for wine tannin quality improvement (Cortell *et*

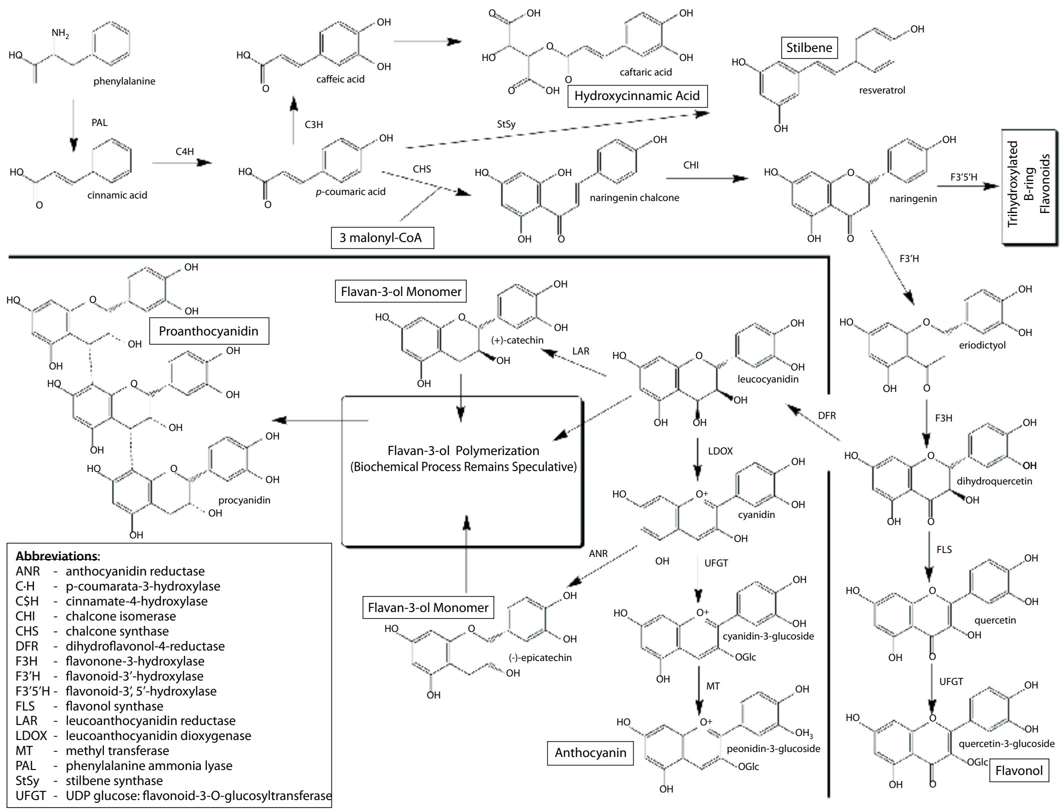


Figure 5. Phenylpropanoid biosynthetic pathway for the major phenolic classes found in wine.

al., 2005). Given this observation, and despite the evidence to date indicating that maturity does not increase skin tannin proportion, an improvement in tannin quality should be observed with an increase in the proportion of skin tannins found in wine. Skin tannins are generally extracted early in fermentation and as the maceration time increases, the rate at which seed tannin are extracted increases (Peyrot des Gachons and Kennedy, 2003). Tannin extraction will increase throughout fermentation (Ribéreau-Gayon *et al*., 1970) and therefore, at some point seed tannin dominates the tannins present in the wine. The trick from a winemaking perspective would be to optimize not only the quantity of tannin extracted, but also the proportion of skin and seed tannin.

In the final wine, the skin and seed tannin proportions are generally different than those found in the berry (Figure 6). In addition to grape maturity and maceration time, conditions in the vineyard (Cortell and Kennedy, 2006; Cortell *et al*., 2005) and the degree of berry crushing (unpublished data) have been found to influence the proportion of skin and seed tannin in wine. Understanding the consequence of tannin amount and composition from a perception standpoint is the long term key to understanding the best strategies for managing red wine quality both in the vineyard and in the winery.

The numbers indicated in this schematic (Figure 6) are based upon an actual experiment conducted on cv. Pinot Noir. Grape seed tannins exceed those found in the skin tissue and overall, a small portion of the overall quantity of tannins found in the grape is extracted during wine production. Finally, the maceration favored the extraction of skin tannins over seed tannins.

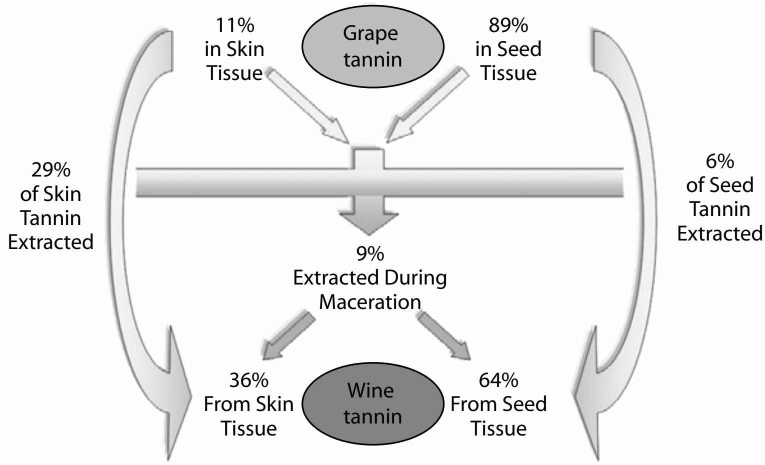


Figure 6. Schematic representation of skin and seed tannin extraction during maceration.

Wine aging

Once a wine is pressed, the concentration of grape phenolics is maximal, declining thereafter (Nagel and Wulf, 1979). In white wines, aging transforms lighter straw-colored wines into more deeply yellowed colors (Singleton and Kramling, 1976). In red wines, the initial blue-red color anthocyanins are transformed into brick-red pigments. The overall depth of red wine color can be quite persistent despite there being very little grape-derived anthocyanin remaining. It is this aspect of red wine color that has fascinated wine scientists for well over a century.

It is generally recognized in red wines that grape-derived anthocyanins become modified with other compounds found in wine. One recently identified example of a modified anthocyanin combines the yeast metabolite pyruvic acid with anthocyanins to form vitisin A (Fulcrand *et al*., 1998; Bakker and Timberlake, 1997). Vitisin A forms early after fermentation has completed (Schwarz *et al*., 2003) and has the familiar brick-red color of an older wine as opposed to a new wine which is dominated by absorption at 520 nm.

As wine ages, it is exposed to oxygen and the effects of oxidation (Waterhouse and Laurie, 2006). A product of wine oxidation is ethanal, which is an oxidation product of ethanol oxidation (Wildenradt and Singleton, 1974). Evidence for ethanal incorporation into red wine phenolic polymers has been recently observed and increases with age as a proportion of the total phenolic polymer (Drinkine *et al*., 2007a, b). It has been observed for some time that ethanal formation leads to a modification of red wine color (Bakker and Timberlake, 1997; Timberlake and Bridle, 1976; Trillat, 1908a-c).

The formation of the vitisin pyranoanthocyanins in wine has subsequently led to the identification of other reactive nucleophiles including hydroxycinnamic acids and ethanal-flavan-3-ol reaction products (He *et al*., 2006; Mateus *et al*., 2004, 2003; Benabdeljalil *et al*., 2000, Figure 7). In addition to ethanal mediated condensation reactions, recent work has shown that the oxidation of wine can result in the oxidation of glycerol to glyceraldehyde, another electrophilic species (Laurie and Waterhouse, 2006a, b).

The biggest challenge for wine scientists is characterizing the large molecular weight pigmented material present in red wine. Some time ago, structures were proposed for pigmented polymers and because of the prevalence of proanthocyanidins, these

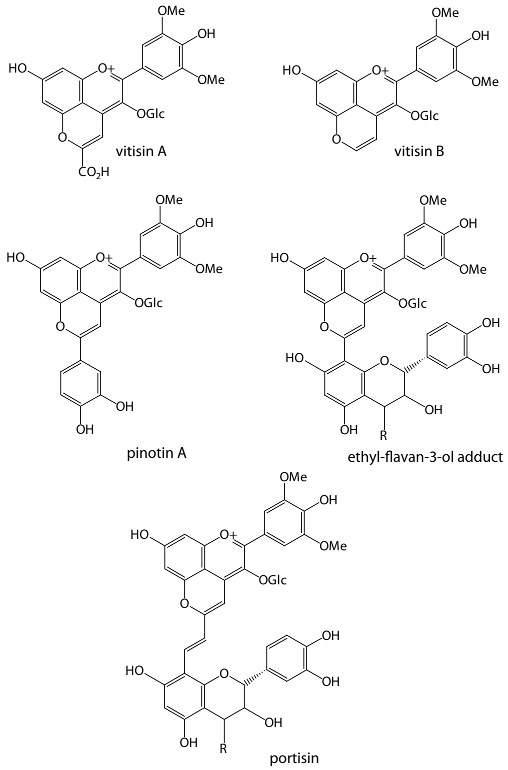


Figure 7. Examples of malvidin-3-O-glucoside-based pyranoanthocyanins that have been identified in red wine.

were speculated to involve anthocyanins and proanthocyanidins (Ribéreau-Gayon *et al*., 1983; Haslam, 1980; Somers, 1971; Jurd, 1969, 1967a, b). The accuracy of this speculation has been confirmed (Salas *et al*., 2004; Vivar-Quintana *et al*., 2002; Remy *et al*., 2000; Es-Safi *et al*., 1999, Figure 8), and this chemistry has been extended into higher molecular weight material (Hayasaka and Kennedy, 2003). It is interesting to note that pigmented polymers begin formation early in a wine's life (Eglinton *et al*., 2004).

Sensory properties of phenolics

The complexity of phenolic perception is apparent when you realize that wine phenolics can be sensed by sight, smell, taste, and touch. Of these, grape phenolics are generally regarded as non-volatile and therefore they cannot be smelled. Anthocyanins and hydroxycinnamic acids as mentioned above provide the visual component in wines. Flavan-3-ol monomers are bitter and thus have taste. The tannins or proanthocyanidins are astringent, and because of this complex perception, some discussion of this follows.

Tannins are compounds that seem to be designed by nature to be deterrents to herbivores and fungi. Tannins accomplish this because of their ability to bind strongly to proteins (Haslam, 1998). Brought back to wine, it is generally considered that we observe this as a loss of lubrication due to the tannins binding and precipitating our salivary proteins. To put it simply, tannins are astringent, terribly astringent (Gawel, 1998; Noble, 1994). Astringency is a tactile sensation and therefore, we *feel* it. This gives rise to the common term used to describe tannins in wine: mouthfeel.

Beyond astringency, tannins can also possess bitterness, which is a taste sensation and is brought about by the lowest molecular weight tannins (Kallithraka *et al*., 1997; Robichaud and Noble, 1990; Arnold *et al*., 1980). It is generally considered that too much bitterness in wine is not desirable and based upon the reduction in the lowest molecular weight tannins observed during berry maturation, this may provide a structural explanation for why tannin quality improves with fruit maturity.

Considering tannin perception in total, the astringency of tannins has a distinct temporal aspect to their perception (Ishikawa and Noble, 1995). When wines have and excess quantity of tannins, the astringency of the wine can linger beyond that of other components. This persistence is generally thought of as being undesirable.

Although bitterness and astringency is found in red wines, it is not a descriptor that is often used in a production setting. Instead, winemakers tend to describe tannins in terms that provide subquality information. Sensory scientists and chemists have spent a considerable amount of time trying to understand these more subtle aspects of tannin perception (Fernández *et al*., 2007; Lesschaeve and Noble, 2005; Vidal *et al*., 2004a, 2003; Gawel *et al*., 2001, 2000; Cheynier *et al*., 1998).

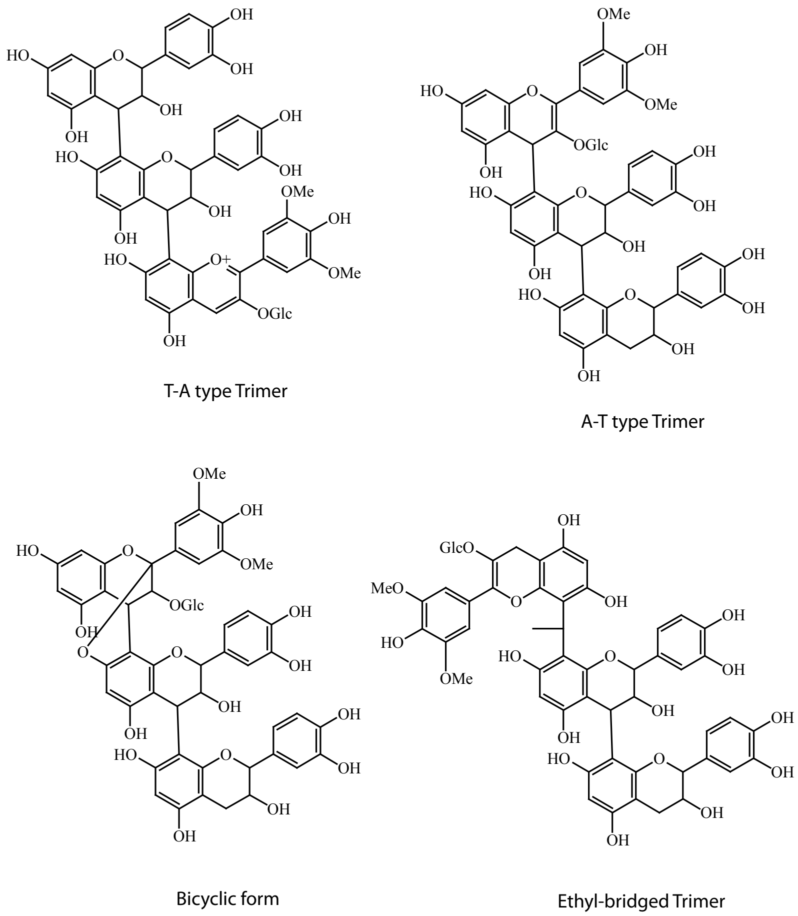


Figure 8. Examples of malvidin-3-O-glucoside proanthocyanidin derivatives.

From these investigations, it is clear that the perception of astringency in wine could be influenced by many components in wine including ethanol (Fischer and Noble, 1994), acidity (Peleg *et al.*, 1998; Fischer and Noble, 1994), viscosity (Smith *et al.*, 1996), simple sugars (Boselli *et al.*, 2004), polysaccharides (Vidal *et al.*, 2004b; Riou *et al.*, 2001) and anthocyanins (Vidal *et al.*, 2004b). Increasingly there are tools being developed in the winery that have an impact on tannin perception (Del Carmen-Llaudy *et al.*, 2006). It is difficult to convey how difficult these studies are to conduct because of the variation in human response to astringency and bitterness (Fischer *et al.*, 1994). Moreover, the complex interaction between tannins and other macromolecules found in wine (De Freitas *et al.*, 2003; Riou *et al.*, 2001; Saucier *et al.*, 1997a, b) indicates that fully understanding the nature of tannin perception will continue to be a challenging area of research.

Perhaps a good way of conceptualizing tannin perception and the relationship between tannin description and grape composition is to think about how different grape components influence our perception of tannins (Figure 9). Here tannins and acid are balanced with ethanol sugar and polysaccharides. As a winemaker, the goal is to balance these components in a red wine. Initially, when picked early, a wine would have a tendency to have excess tannins and acidity with a deficiency in polysaccharides, sugar and ethanol. As the fruit becomes more mature, the composition becomes more balanced and the descriptors become more positive. A winemaker has the ability to modulate wine descriptors by adjusting the balance accordingly. The figure as depicted is in line with research on tannins and perception.

From the research gathered to date, including the biosynthesis of tannins and the overall development of the berry, the picture that is emerging is that tannin changes in the grape do occur and their relative amounts in the skin and seed vary depending on grape production practice. Moreover, the changes that occur during berry maturation (Kennedy, 2002) that do not involve tannins are expected to result in changes that positively influence the quality of tannins.

The continued progress in grape and wine phenolic research in many ways will depend on the continuing development of analytical chemistry. The recent progress in our understanding can very much be related to analytical advances. Additional progress in analytical chemistry has been made recently and it is exciting to see that attention is being directed towards making analytical information easy to acquire and rapid (Fernández and Agosin, 2007; Mercurio *et al.*, 2007; Cozzolino *et al.*, 2006). These advances will likely lead to an improvement in grape and wine phenolic management.

Resumen

Lo que los consumidores prueban en el vino es la culminación de prácticas de manejo que parten en el viñedo y concluyen en la copa. Como investigadores, para tener un control sobre la composición del vino al momento del consumo, es importante comprender como afectan las prácticas de manejo la composición química del vino. Debido a que los compuestos fenólicos tienen tal importancia sobre la calidad final del vino, estos compuestos han sido objeto de una intensa investigación mundial. Esta revisión de literatura es un resumen del conocimiento actual y de algunos descubrimientos recientes que han ocurrido en esta área.

Palabras clave: Antocianinas, proto-antocianidinas, taninos, vinos tintos, *Vitis vinifera*.

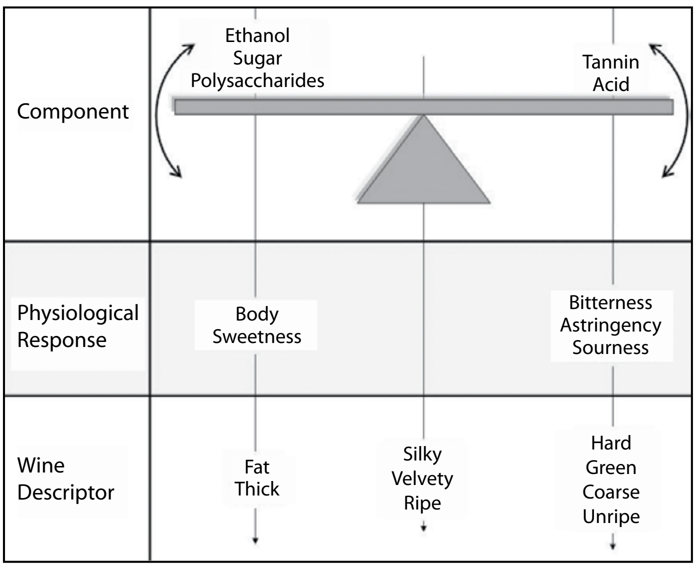


Figure 9. Schematic representation for the description of tannins based upon wine composition.

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