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Grape and Wine Phenolics: History and Perspective

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Abstract: Given its rich history and tradition as well as its incredible complexity, wine has been the subject of a considerable amount of research. Grape and wine phenolics, because of their complexity and importance in wine quality, serves as a good example of how tradition and science have coevolved. This review summarizes early research on grape and wine phenolics and provides justification for continued research.

Key words: *Vitis vinifera*, grape, wine, phenolics

The development of grape and wine production methods in Western civilization has generally paralleled overall technological progress. Advances in production methods during the Egyptian and then the Greek and Roman periods (such as vine cultivation, pottery production, and winemaking practices) peaked around 200 to 400 AD and was followed by a period of 1200 to 1400 years during which progress in wine technology slowed and was generally restricted to monastic religious orders in western Europe (Allen 1961). The development of wine production methods began to accelerate in the eighteenth century, probably because of changes in trade relations in Europe, and led to the appearance of vintage, age-worthy wines (Allen 1961).

Given the inquisitiveness of humans and the importance of wine color, flavor, and astringency, the management of phenolic compounds predates their structural determination. The presence of vintage, age-worthy wines likely increased the awareness of the importance of grape and wine phenolics in wine quality. With the rapid advancement of science in Europe, it was natural that wine would become a research subject for many scientists. An early example of phenolic research (predating structure identification) was that by Pasteur, who recognized that oxygen played an important role in red wine development in general and color in particular (Pasteur 1866).

Grape and wine phenolic research per se is a recent occurrence, and through it the wine production world has realized the complexity of color, flavor, and astringency. The very perception of wine phenolics depends on many physical and chemical factors beyond the mere structure of the perceived phenolic itself. It is the drive to understand how these factors directly and indirectly affect phenolic perception in wine that continues to drive much of the research today.

A tremendous amount of chemical research on grape and wine phenolics has been published. At times, the bewildering array of compounds identified in grapes and wine may be daunting to wine production personnel. However, given the economic pressures on the industry, a scientific understanding of grape and wine phenolics is an increasingly important requirement for managing wine styles efficiently.

Phenolic Research Rationale

Generally, grape and wine phenolic research can be divided into three broad areas: development of phenolic compounds in the vineyard, extraction and modification of phenolic compounds during wine production, and fate of phenolic compounds during aging. To have intrinsic value to the wine industry, grape and wine phenolic research must identify and determine the concentration of specific phenolic compounds in wine, determine their sensory importance and interaction with other compounds, and identify the factors that lead to their presence in wine. In doing so, not only will the sensorially important compounds be identified, but strategies for their management will be developed. Historically, a considerable amount of research has focused on the elucidation of phenolic structures and on determining their concentrations in grapes and wine. Understanding in this area has paralleled developments in analytical chemistry. Without the ability to isolate and determine all phenolic structures in wine, researchers have theorized on the fate of phenolic compounds in wine and their sensory consequence.

To better understand and appreciate the phenolic research being conducted today, it is helpful to summarize the advances in phenolic chemistry that underpin virtually

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all modern research. The phenolic compounds that are responsible for the bulk of color and flavor/astringency in wine and that are initially produced in the grape will be summarized. The references in this paper are composed chiefly of research before 1985. By focusing on early research, the intention is to highlight that, in a broad sense, the questions that have historically motivated phenolic research are the same as those being asked today.

Grape Phenolics

The structures of all phenolic compounds are based upon a hydroxy-substituted benzene ring (Figure 1). Out of this basic element a veritable palate of phenolic compounds has been identified in grapes and wine, and the biosynthsesis of these compounds in the plant has been studied for some time (Harborne 1967, Hrazdina 1992, Winkel-Shirley 2001, Dixon et al. 2005). Understanding the biosynthesis of phenolic compounds is important if we are to efficiently manage their production in the plant and, by extension, in wine. The identification of phenolic compounds in grapes and wine began in the late nineteenth century and continues today. A summary of the concentration range of the sensorially important phenolic compounds in wine is given in Table 1 (Singleton 1992).

Nonflavonoids. Nonflavonoid phenolics are found in grapes and wine (Figures 2 and 3), but with the exception of hydroxycinnamic acids, they are present at low concentrations. Hydroxycinnamic acids are the major phenolic compounds in white wine and are important in white wine color. They are derived primarily from the pulp of the grape berry. Red wines also contain similar amounts of hydroxycinnamic acids.

Hydroxycinnamic acids were characterized in grapes and wine in the mid-twentieth century (Ribéreau-Gayon 1963). These compounds had previously been observed as free acids. It was later shown that free hydroxycinnamic acids are not present in grapes, but are esterified with tartaric acid (Ribéreau-Gayon 1965). Additional compounds were characterized (Baranowski and Nagel 1981, Cheynier et al. 1986) and were shown to be produced in the grape berry before veraison (Romeyer et al. 1983).

Flavonoid compounds. Flavonoid compounds make up a significant portion of the phenolic material in grapes and there are several classes that are discussed below, all of which have a similar skeleton (Figure 4).

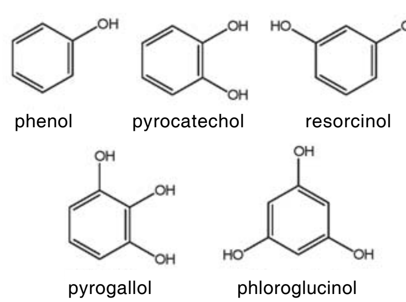


Figure 1 Structure of phenol and other low molecular weight phenolic compounds.

Table 1 Generalized concentration of various phenolic compounds present in wines (mg/L GAE) (modified from Singleton 1992).

Phenolic	White	Light Red	Full Red
Volatile	Trace	10	40
Hydroxycinnamic acids	150	200	200
Other nonflavonoids	25	40	60
Anthocyanins	0	200	400
Catechins	25	150	200
Polymeric catechins	0	600	900
Total	200	1200	1800

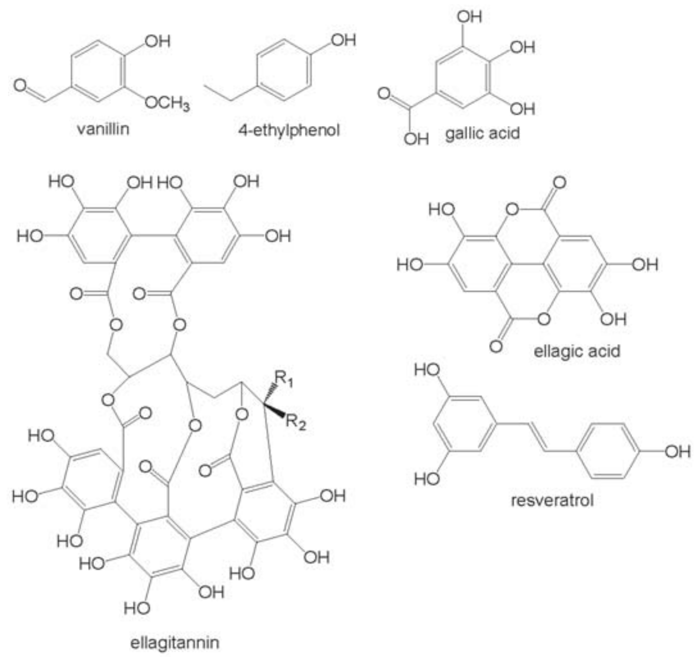


Figure 2 Examples of nonflavonoid phenolic compounds in wine.

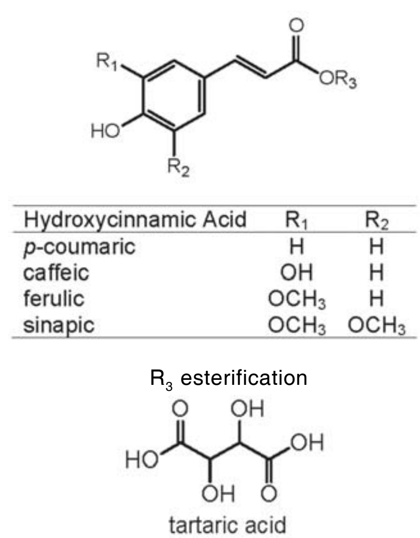


Figure 3 Structures of grape-derived hydroxycinnamic acids.

Anthocyanins. Anthocyanins are responsible for red wine color (Figure 5) and are restricted to the skin tissue in most grape varieties. Scientific investigation of red wine color predates the identification of anthocyanin structure (Pasteur 1866, Laborde 1908, Trillat 1908). The determination of the general anthocyanin structure occurred in the early part of the twentieth century (Willstätter and Everest 1913, Levy et al. 1931, Robinson and Robinson 1933).

Following the development of paper chromatography (Bate-Smith 1948), research on understanding grape and wine phenolics intensified. The structures for common anthocyanin in *Vitis vinifera* grapes and wine were determined in 1959, and malvidin-3-*O*-glucoside was found to be the major anthocyanin present along with its acylated forms (Ribéreau-Gayon 1959). Work by Ribéreau-Gayon also showed that anthocyanins in *Vitis vinifera* were different in structure than those found in non-*vinifera* species in that they were exclusively present as monoglucosides, whereas non-*vinifera* species also contained 3,5-diglucosides. Additional research on anthocyanin structure and distribution in *Vitis* sp. has added to our understanding of grape anthocyanins (Rankine et al. 1958, Puissant and Leon 1967, Fong et al. 1971).

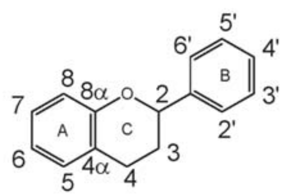
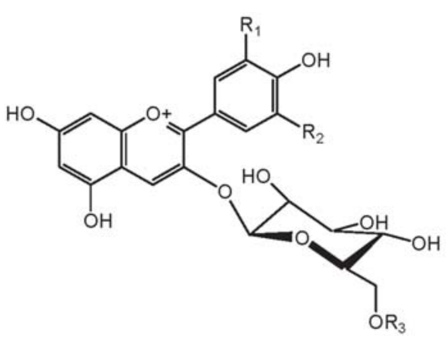


Figure 4 Flavonoid ring structure and numbering.



Anthocyanidin	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 esterification

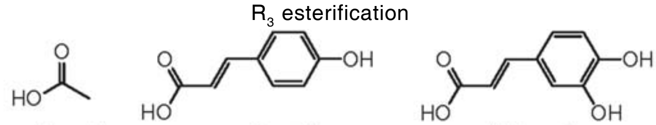
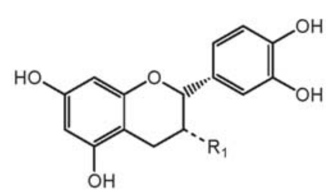


Figure 5 Structures of grape-derived anthocyanins.

Because of their unique color among grape and wine phenolics (which allows their study with less interference from other compounds), much more research on anthocyanin/color has been conducted than for other compounds. In addition to identifying anthocyanins in grapes and wine, studies have focused on their changes during berry maturation (Ribéreau-Gayon 1971, 1972, Pirie and Mullins 1977), the influence of cultural practices on their production (Kliewer and Torres 1972, Kliewer 1977, Wicks and Kliewer 1983), and their extraction into wine (Ribéreau-Gayon 1971, 1972). These studies have shown that anthocyanins are produced during fruit ripening, that their amount in the berry is clearly affected by vintage and overall growing conditions, and that their extraction during maceration peaks before the end of fermentation and then declines.

Flavan-3-ol monomers. Flavan-3-ol monomers (catechins) are responsible for bitterness in wine and may also have some associated astringency. These compounds were initially characterized in the 1920s (Freudenberg 1924) and later investigated in grapes and wine (Durmishidze 1955, Singleton et al. 1966, Singleton and Esau 1969). The major flavan-3-ol monomers found in grapes and wine include (+)-catechin, (-)-epicatechin, and (-)-epicatechin-3-*O*-gallate (Figure 6) (Su and Singleton 1969). Early work found these compounds to be particularly high in seed material (Singleton et al. 1966, Czochanska et al. 1979, Romeyer et al. 1986), and this work has also shown that flavan-3-ol monomers are produced before veraison and change during fruit ripening. The extraction of flavan-3-ol monomers has also been investigated during wine production (Singleton and Draper 1964, Meyer and Hernandez 1970, Oszmianski et al. 1986). It is generally agreed that much of the flavan-3-ol monomers originate from seed material and that longer extraction times, higher temperatures, and higher alcohol concentrations lead to an increase in wine flavan-3-ol monomer concentration.

Proanthocyanidins. Proanthocyanidins are a class of compounds that has been variously described as anthocyanogens, leucoanthocyanidins, flavan-3,4-diols, condensed



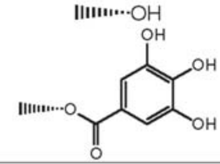
Flavan-3-ol Monomer	R_1
(+)-catechin	OH
(-)-epicatechin	OH
(-)-epicatechin-3-*O*-gallate	

Figure 6 Structures of grape-derived flavan-3-ol monomers and/or proanthocyanidin subunits.

tannins, and tannins. In current grape and wine literature, these compounds are generally called tannins or proanthocyanidins. Proanthocyanidins impart astringency to red wines and are extracted from the skin, seeds, and stems of the grape berry. These compounds were the last of the major phenolic compounds (based upon abundance) to be determined structurally (Figure 7) (Creasy and Swain 1965, Weinges et al. 1968), but their sensory properties have been studied much longer (Manceau 1895, Coudon and Pacottet 1901a,b, Laborde 1910). Since they are polymers of flavan-3-ol subunits, a very wide range in molecular weight is possible. Progress in fully understanding proanthocyanidin structure has been hindered because of limited subunit variation. Specific proanthocyanidins have however been identified (Czochanska et al. 1979, 1980, Foo and Porter 1980, 1981, Haslam 1980).

Early work on proanthocyanidins has generally focused on their development in fruit (Goldstein and Swain 1963, Joslyn and Goldstein 1964, Ribéreau-Gayon 1971, 1972, Czochanska et al. 1979, 1980, Lea et al. 1979, Foo and Porter 1980, 1981, Romeyer et al. 1986), varietal differences (Singleton et al. 1966, Bourzeix et al. 1986), and extraction during maceration (Berg and Akiyoshi 1956, Singleton and Draper 1964, Ribéreau-Gayon et al. 1970, Meyer and Hernandez 1970, Ribéreau-Gayon 1971, 1972, Oszmianski et al. 1986). In many of the early proanthocyanidin studies, analytical results were based upon colorimetric analyses of extracts without purification of material and/or elimination of interfering material. One striking difference between early results and more recent work is the development of methods that achieve this separation (Glories 1984b, Bourzeix et al. 1986, Oszmianski et al. 1986, Romeyer et al. 1986).

Reactivity of Phenolic Compounds in Wine

The major fruit-derived phenolic compounds of sensory importance have been identified and described above. Today, much research is focused on how these compounds are structurally modified during extraction and aging. There is interest in this topic because the sensory properties of phenolic compounds change during wine aging and winemakers would like to improve their ability to manage these changes. Numerous researchers have contributed to our current understanding in this area, and many of the mechanistic theories developed from early work remain valid. A brief summary of some of this work follows.

Of the compounds described above, anthocyanins can exist in several equilibrium forms in wine, with only the flavylium form appearing red in color (Figure 8). Only a small proportion of the anthocyanins in red wine are in the red flavylium form at wine pH (generally less than 10%), with most of the species existing as the hemiacetal product (Brouillard and Dubois 1977, Brouillard and Delaporte 1977, Glories 1984a). When sulfur dioxide is added to wine it combines with the flavylium form, resulting in an additional equilibrium between the colored form and the uncolored bisulfite adduct.

Phenolic compounds in wine can interact noncovalently with other components. One such noncovalent interaction is anthocyanin copigmentation (Asen et al. 1972), where interactions between anthocyanins and other molecules (cofactors) increase the proportion of the flavylium form of anthocyanin beyond what would be expected based upon

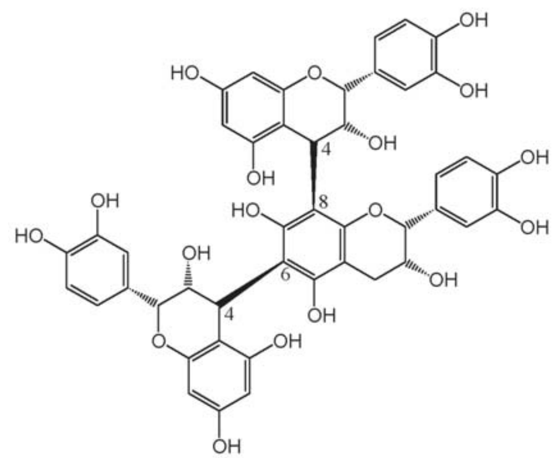


Figure 7 Generalized proanthocyanidin structure.

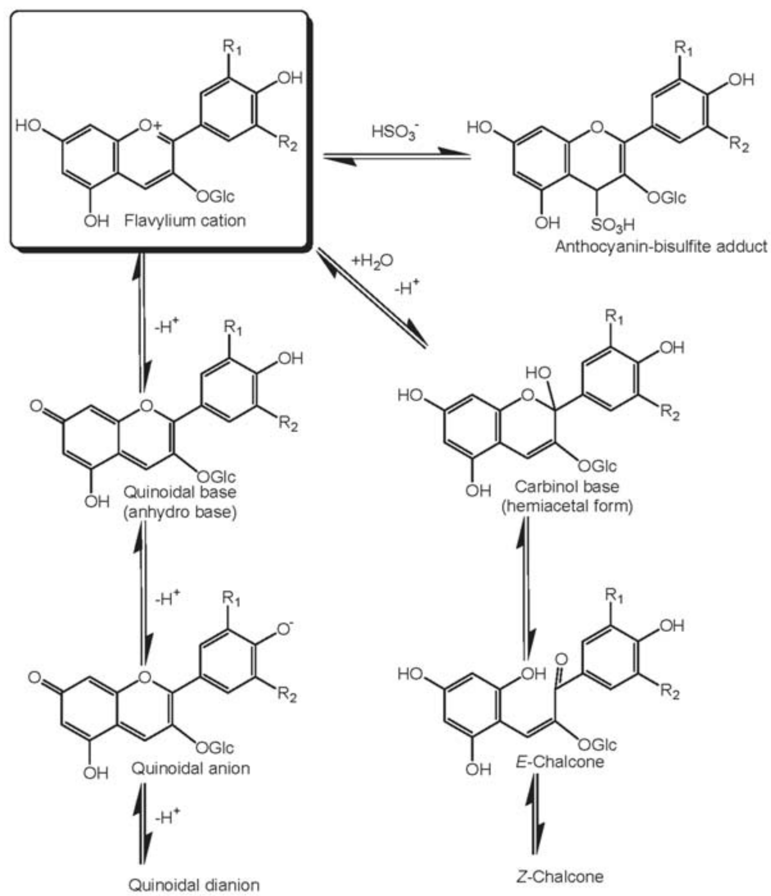


Figure 8 Anthocyanin equilibrium forms found in red wine.

wine pH. Increasing red wine color by optimizing copigmentation has been considered an option in wine production. Color losses during fermentation suggest that copigmentation is influenced by ethanol production (Somers and Evans 1979); because of this influence its full utility has not been determined.

Another noncovalent interaction that exists in wine is the formation of colloids involving tannins and other molecules. The formation of tannin colloids is of interest because colloids influence physical stability in wine and are considered important in astringency perception (Haslam and Lilley 1988). The existence of tannin colloids in wine has been known for some time (Ribéreau-Gayon 1933b). More recent work has explored protein-tannin interactions that have relevance from a sensory standpoint (Haslam 1981, Hagerman and Butler 1981, Porter and Woodruffe 1984).

In addition to the noncovalent interactions involving wine phenolics, interest has focused on the reactivity of phenolics once extracted into wine and their significance in wine quality. It can be argued that Pasteur's realization that oxygen is a key component in red wine color transformation may mark the beginning of grape and wine phenolic research (Pasteur 1866).

When examining the reactions of phenolic compounds in wine, it can be helpful to consider the processes that lead to the formation of reactive species. That is the essence of much of the mechanistic research being conducted today: identify the products and develop and test hypotheses for their formation. While it is beyond the scope of this paper to discuss mechanistic theory, it is probably sufficient to classify compounds in wine according to their electrophilic or nucleophilic nature (Figure 9).

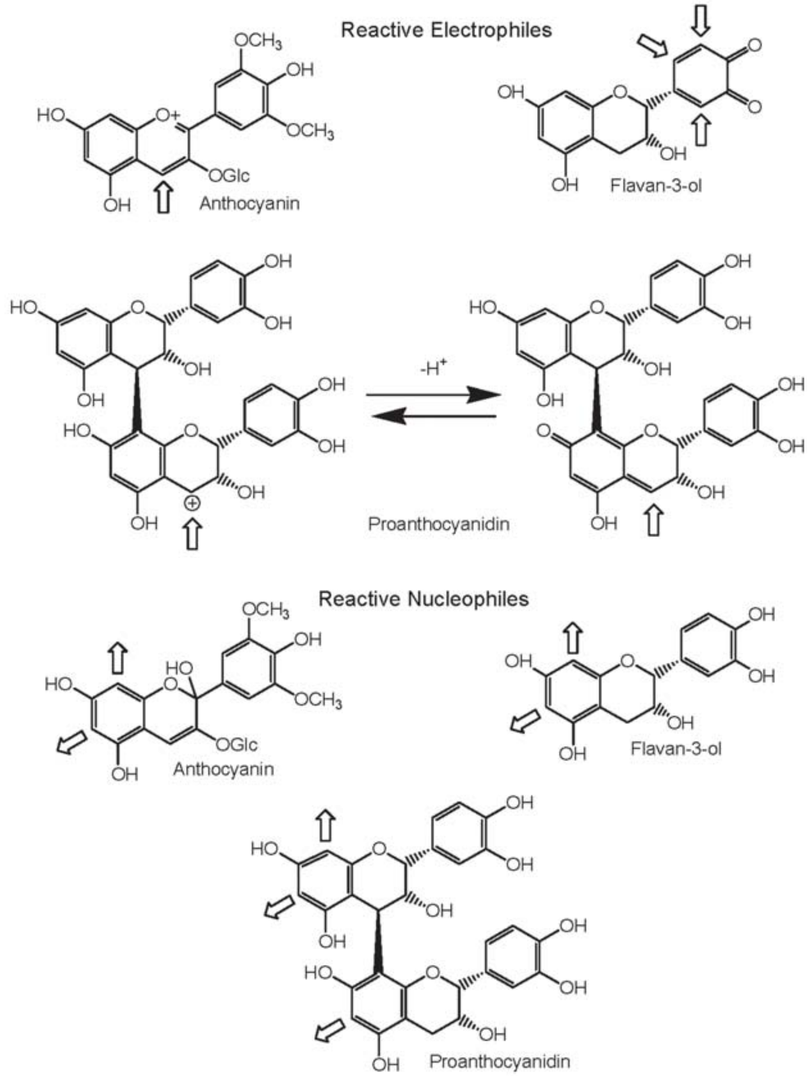


Figure 9 Examples of electrophilic and nucleophilic species found in wine; arrows indicate major reaction center.

A simplified definition of an electrophilic compound is one that is electron deficient and has a propensity to interact with reactive electron-rich species (nucleophiles). As an example, anthocyanins can act as both electrophiles and nucleophiles. The electrophilic flavylium form would be expected to interact with reactive nucleophiles; the reaction between anthocyanins and bisulfite anions described above can be explained in this way (Figure 8). Phenolic compounds react readily with oxidants because of the ease with which hydrogen atoms can be abstracted (Figure 10) (Taylor and Battersbey 1967). Because of this, oxidation gives rise to electron-deficient electrophilic species. Understandably, the role of oxidation in phenolic reactions has been a perennial theme in research since Pasteur (Trillat 1907, 1908, Ribéreau-Gayon 1933a, Rossi and Singleton 1966a, Wildenradt and Singleton 1974).

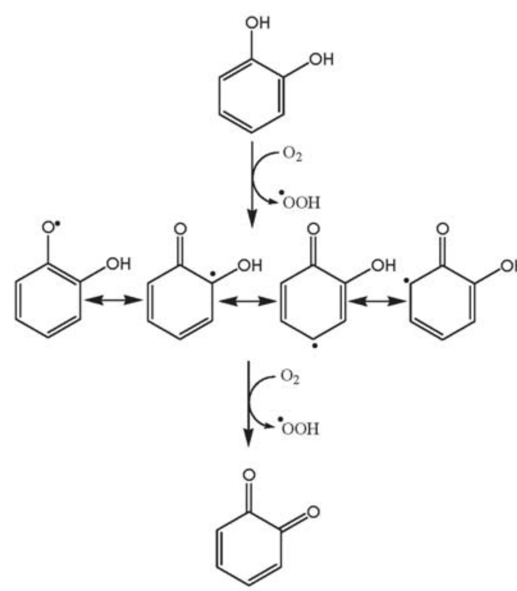


Figure 10 Generalized reaction sequence for the oxidation of an *o*-diphenolic compound.

Many phenolic compounds are also susceptible to acid-catalyzed degradation. Glycosides and gallic acid esters of phenolic compounds will slowly hydrolyze over time. Additionally, proanthocyanidins hydrolyze under the acid conditions that exist in wine, giving rise to electrophilic intermediates (Figure 11) (Laborde 1910, Haslam 1980, Hemingway and McGraw 1983). This electrophilic intermediate coupled with the nucleophilic flavonoid A-ring provides the dual reactivity properties of proanthocyanidins.

One of the major reactions that has fascinated wine scientists is the process by which red wine color becomes modified over time. The anthocyanins extracted into red wine are particularly unstable, and the majority are modified before bottling. However, the color of red wine persists. During wine aging, the UV-vis absorbance of wine at 620 nm initially increases proportionally and as a result the color appears red-blue. With time, the absorption at 420 nm increases and that of 520 and 620 nm decreases, and therefore the wine becomes red-orange. This familiar transformation of the red-blue color of new wines to the brick-red color of aged wines has been a persistent area of research (Mareca-Cortes and del Amon-Gili 1956, Sudraud 1958, Somers and Evans 1977, Glories 1984b).

Wine scientists have known for some time that the stable color in red wine is associated with polymeric material (Ribéreau-Gayon and Peynaud 1935, Somers 1966, 1968, 1971, Somers and Evans 1979), and various reaction mechanisms involving anthocyanins and flavan-3-ols have been envisioned (Figure 12) (Jurd 1967, 1969, Jurd and Waiss 1965, Jurd and Somers 1970, Timberlake and Bridle 1976, Haslam 1980, Baranowski and Nagel 1983, Bishop and Nagel 1984, Glories 1984b, Ribéreau-Gayon et al. 1983). The nature of this material is of interest not only because of the color stability that results from the transformation but also because of the potential for modifying the flavor/astringency of the wine. In large part, the mechanistic deductions developed before 1985 are still valid today, and the formation of many of the recently identified compounds from wine can be inferred using mechanisms developed some time ago.

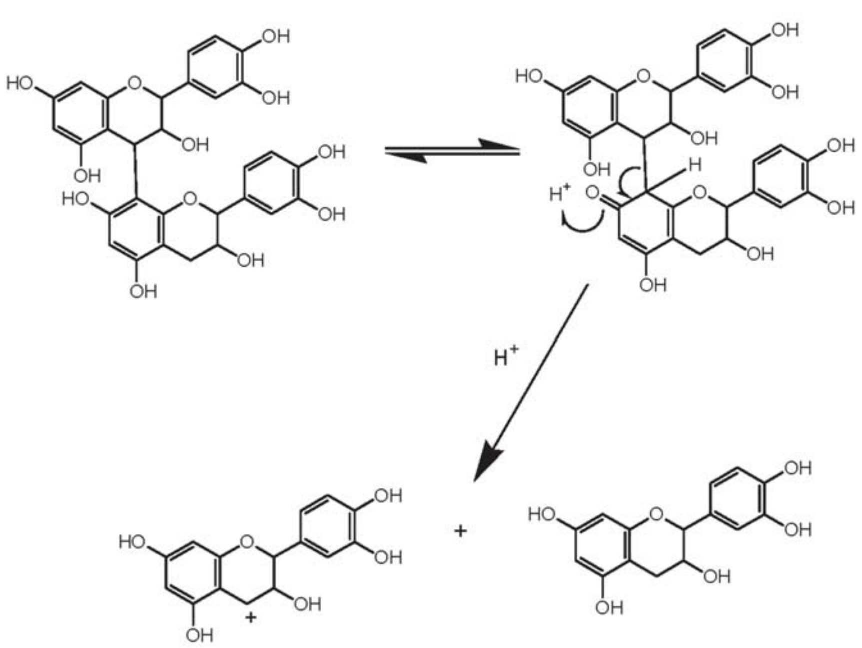


Figure 11 Reaction mechanism for the acid-catalyzed cleavage of proanthocyanidins.

Sensory Properties of Grape and Wine Phenolics

Phenolic compounds are critically important to the quality of all wines (Peynaud 1996), and determining the sensory significance of phenolic variation in wine presents the biggest challenge for wine phenolic research. This challenge is especially formidable because of the incredible structural diversity of phenolic compounds in wine and the associated sensory variation and because the perception of many phenolic compounds is influenced by other phenolic and nonphenolic material in wine (such as colloid formation and stability).

Color perception in red wines as discussed above can vary with respect to extraction, pH, and the age of the wine. Work by Somers and Evans (1974) indicated that the color of red wine influenced its preference. In white wines, the appearance of the wine is related to the amount of oxygen exposure (Singleton 1987).

Astringency of wine phenolics has also been studied (Rossi and Singleton 1966b, Delcour 1984, Joslyn and Goldstein 1964, Lea and Arnold 1978, Noble 1990, Robichaud and Noble 1990). The conclusion from this work is that flavan-3-ols can be both bitter and astringent, with bitterness being derived from lower molecular weight compounds and astringency from higher molecular weight material. From this, it can be concluded that bitterness tends to be associated with grape seed flavan-3-ols and more purely astringent flavan-3-ols are related to those from the skin.

The major questions that lie ahead involve the complex nature of wine perception. The overall impact of many recently identified wine pigments on wine color must be understood so management strategies can be optimized. And while astringency per se is not a highly desirable attribute in wine, astringency in the presence of other material giving rise to wine texture is desirable; consequently, the reactions leading to this quality are of interest to the wine industry. Understanding the complex relationship between proanthocyanidins and other wine components will require considerable work in analytical as well as the sensory sciences. The motivation for grape and wine phenolic research in the past was rooted in the interest to understand and improve their sensory properties, a motivation that remains today.

The Future

Wine history predates Western civilization itself, and it includes many symbols of a rich and storied past. Not surprisingly,

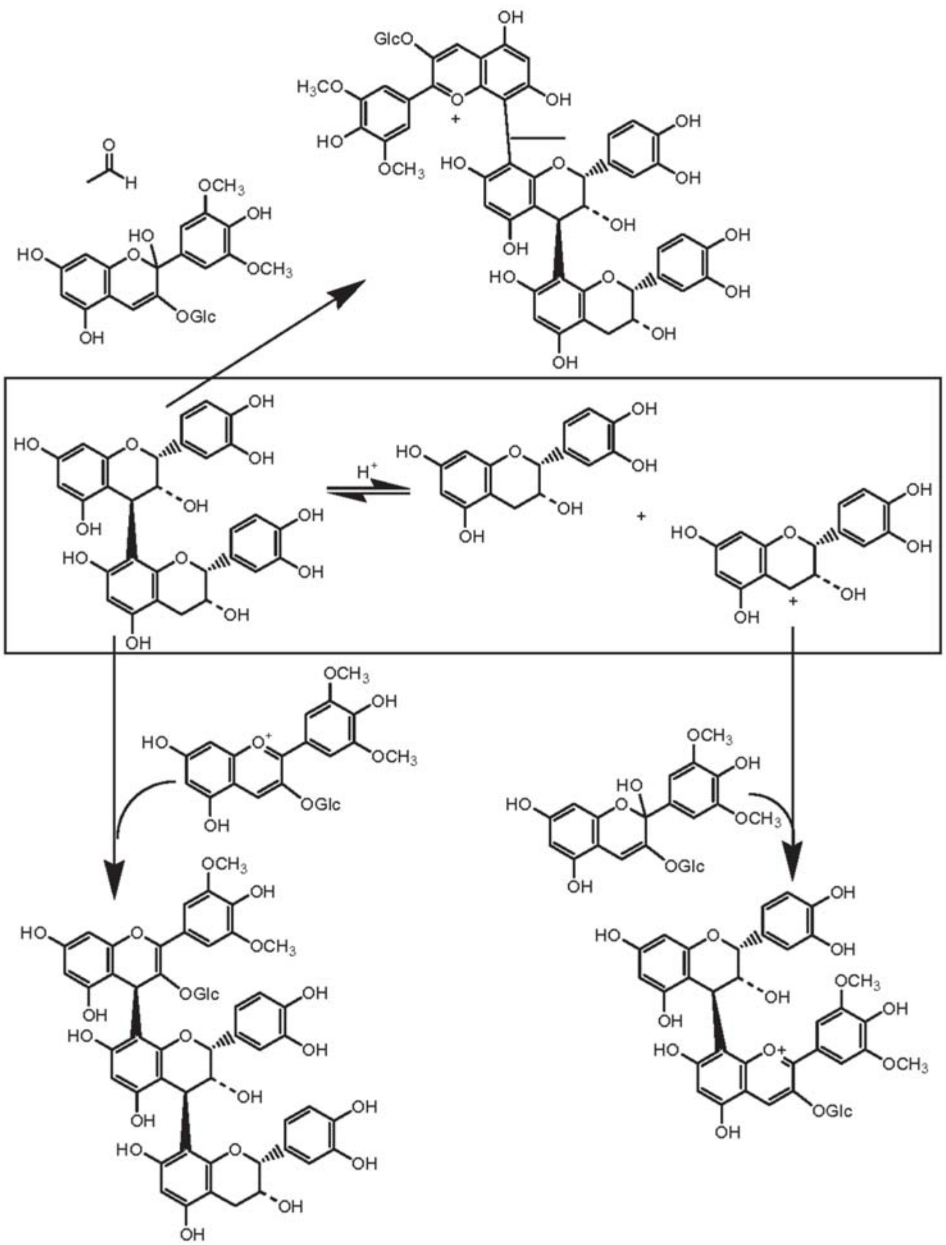


Figure 12 Reaction mechanisms for the formation of pigmented proanthocyanidins.

modern wine production is steeped in tradition. Despite the many advances in viticulture and enology, from a traditionalist's perspective, it often seems that the product of wine science is dull and uninteresting. In describing the perceived loss of nineteenth-century fine wine craftsmanship, the wine historian H. Warner Allen wrote:

> Great vintage wines must always need time and patience for their emergence and we live in an age of impatience which grudges time as waste of money on which the heart is set. No one can get rich quick by growing fine wine. Modern conditions, both profit and inclination, threaten something very like a return to the dark ages when the material means of maturing vintage wines were lacking. Now the means are available but the will to make them is dying out (Allen 1961).

A partial explanation for this was the encroachment of science in wine production. From a wine scientist's perspective, it can appear that progress in advancing wine quality is hampered by resistance to change.

Edwin Haslam, an eminent British phenolic chemist whose career contributed significantly to modern advances in phenolics and wine aging, wrote in 1998:

> Over the past three centuries Science has increasingly come to represent one of mankind's most formidable achievements. In areas as diverse as agriculture, materials and medicine its technological applications have transformed the lives of many throughout the world. Science conversely often exacts its own price, for benefits and risks are frequently found to be complementary aspects of the same technological advances; society has to judge between them. A popular misconception fostered by some writers and media pundits is that progress in Science, the accumulation of new and greater knowledge superseding previous discoveries, proceeds exponentially ever upwards and onwards. This is misleading. Science is a human endeavor and scientists are creative

beings. Science is therefore spiced with pride and prejudice; it is often subject to personal folly, wrong turns and cul-de-sacs. False dawns, unfortunately not always constrained to the confines of the laboratory, are legion (Haslam 1998).

The comparatively recent progress in grape and wine phenolics serves as a good example for how the wine industry is better served when science is allowed to prosper in the presence of craftsmanship. While technological gains in enology and viticulture can at times appear to be in direct conflict with the notion of wine quality, it is a mistake to believe that scientific advancement and the production of fine wines are mutually exclusive. In its purest form, scientific advancement is simply a product of the will to understand nature. The production of fine wine requires an understanding of general scientific principles in order to produce a wine that is consistently marketable. It must not be forgotten, however, that fine wine craftsmanship also requires an artistic approach to ensure that the individuality of a wine is preserved. In today's world the coexistence of these is essential.

History teaches us that change is a constant and it is wise to move with it as best as we can. Today, wine industries are being created in parts of the world that have little in the way of wine history, and the rapidity with which these regions have become producers of high-quality wines is impressive. The increase in competition and the overall economics of the wine industry dictates that a successful industry is one that follows the mantra put forth by the Australian Society of Viticulture and Oenology: "Be well informed, think laterally and always question established practices" (Rankine 2001). There is no question that grape and wine phenolic research will continue to address the challenges that remain (Boulton 2001) and those to come because there are regions and countries that implicitly understand the following: the industry of wine production is very competitive; all of the marketing in the world cannot compensate for a mediocre wine; and mediocre wine is quickly forgotten.

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