

## Grape and Wine Phenolics: A Refresher

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This presentation served as an introduction to the speakers who would follow and specifically clarified various terminology used in phenolics research. For example, "phenolics" and "polyphenolics" are equivalent terms to the research chemist or food scientist. Phenolics are secondary metabolites of plants, meaning they are not directly involved in the plant's survival. Phenolics are formed from the essential amino acid, phenylalanine, thru the phenylpropanoid biosynthetic pathway. Phenolic compounds constitute a very diverse group: more than 4,000 have been identified. These compounds have been linked to several functions in plants: protection from UV radiation, pigmentation (coloration), defense against invading pathogens (antifungal properties), nodule production, and attraction of pollinators and seed dispersers.

The phenolic content of wines is influenced by many factors, including grape cultivar, vineyard environment, vineyard management, and vinification technique, for example: fermentation temperature, yeast strain, processing enzymes, cap management, and alcohol concentration. While phenolics comprise only 1 to 5% of wine constituents (majority water and alcohol), they are important because of their contribution towards appearance (color), taste or mouthfeel (bitterness and astringency), and potential human health benefits. For example, resveratrol, a nonflavonoid phenolic compound found in grape skins and peanuts, recently has received significant attention—hype—in the popular press, as a potential key to prolonging life and to combating health problems due to obesity, with the grand caveat that its effects in humans, rather than yeast, worms, or rats, still are being sorted out by researchers.

All phenolic compounds are based on the primary chemical structure of hydroxybenzene, a phenol. Grape and wine phenolics can be divided into two groups: **nonflavonoids** and **flavonoids**. Nonflavonoids have C<sub>1</sub>C<sub>6</sub> or C<sub>3</sub>C<sub>6</sub> structures, meaning that either one carbon or three carbons are attached to the primary benzene ring (six carbons). More complex compounds are essentially substituted monomers or polymers of this basic structural layout. The majority of the **nonflavonoids** found in grapes are phenolic acids: **hydroxycinnamic acids** (found esterified

with tartaric acid; caftaric acid, coutaric acid, and fertaric acid); **hydroxybenzoic acids** (gallic acid, a hydrolysis product from grape or oak tannins); and **stilbenes** (resveratrol and piceid). Other nonflavonoids found in wine are from oak sources, or in other words, **oak tannins**, which are derivatives of ellagic acid (ellagitannin) and gallic acid (gallotannin). Oak tannins also are referred to as hydrolyzable tannins because they are easily hydrolyzed with weak acids or bases.

**Flavonoids** have a distinct  $C_6C_3C_6$  three-ring structure. There are three main classes of flavonoids: **flavanols**, also known as flavan-3-ols, which are the building blocks of grape tannins; **anthocyanins**, which impart color to the grapes and red wine; and **flavonols**. Grape tannins, which are polymers of flavanols, are known also as condensed tannins or proanthocyanidins. Proanthocyanidins contribute significantly to the complexity of wine taste and mouthfeel. Flavanol monomers and oligomers (links of two to four monomers) contribute to bitterness, and their polymers contribute to astringency in wine. There are five anthocyanidins (cyanidin, peonidin, delphinidin, petunidin, and malvidin) in grapes. Anthocyanin is a glycosylated anthocyanidin (sugar bound to the anthocyanidin moiety). Anthocyanins impart red/purple/black color in grapes. These base compounds also are found acylated (acid linked to the 6<sup>th</sup> position of the sugar) with acetic, coumaric and caffeic acids, making them more stable. At the pH of wine, about 10% of wine anthocyanins are in colored form. Finally, **flavonols** (kaempferol, quercetin, and myricetin) are present in grapes and wine as glycosides (sugar attached). Flavonols are important cofactors for color enhancement. They also act as a natural sunscreen in the skin of grape berries. The term **tannin** is derived from tanning, the preservation of animal hide as leather. As mentioned above, there are two sources of tannins in wine: grape-derived and oak-derived. Tannins protect wine against oxidation, stabilize wine color, and enhance mouthfeel.

In summary, phenolics in grapes and wines are a diverse group of compounds, with widely varying concentrations and composition in wine. Because phenolic compounds in wine constantly break and form new bonds, fewer than 50% of wine phenolics have been identified to date. The subject is a rich one for investigation by researchers and motivated winemakers alike.