

Biochemistry of natural wine making essay

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Wine is of great importance in our society today, and has been so for thousands of years.

Grapes have been cultivated for wine production in the Near East since 4000BC, and in Egypt since 2500BC. They were spread from the Black Sea to Spain by the Greek Empire, into Germany by the Romans and to the New World by Columbus. Wine has had religious significance as both an offering and a sacrament since Biblical times, and this has helped its development. Today an enormous variety of wines are available, made from more than 5000 varieties of a single species of grape: *Vitis vinifera*.

In the production of all these wines, chemistry is important, and as some of the complexities of wine chemistry have begun to be understood chemists have been able to contribute greatly to the improvement of wine quality. Wine making, or vinification, is the production of wine, starting with selection of the grapes or other produce and ending with bottling the finished wine. Although most wine is made from grapes, it may also be made from other fruit or non-toxic plant material. The basic fermentation process whereby alcohol is produced from the sugar in grapes is very simple, but its chemistry is still not completely understood. As this knowledge increases, winemakers are being helped to improve the quality of their wine. The composition of grapes is of great importance in determining the quality of the wine produced. Many compounds are carried over from the grape juice into the wine, and other compounds undergo reactions to form the compounds distinctive to wine.

It was once common to ameliorate the wine produced with a variety of chemical treatments, but now this is frowned upon. In this new climate, using high quality grapes is essential to producing high quality wines, and grape composition is more important than ever. In general, grapes consist of clear juice (80%), skins (8%), seeds (4.5%), pulp (4.

5%) and stems (3%). The skins, seeds, pulp and stems are collectively known as 'pomace'. Another way of looking at grape composition is in terms of chemical components.

However, it is important to realize that the quantity of a given ingredient is not directly related to its importance. For example, vitamins are very important for yeast growth and for fermentation. The major constituents of grapes are carbohydrates, organic acid, phenolic, nitrogenous compound, minerals (ash), vitamins and aroma compound.

The first major constituent is carbohydrates. Carbohydrates are molecules of the general formula $C_x(H_2O)_x$, and sugars are a sub-group of carbohydrates. They consist of up to 10 'monosaccharides' – carbohydrates that cannot be broken down into two new carbohydrates. Usually these do not consist of more than seven carbons. Sugars are sweet-tasting, water soluble and good energy sources. Higher carbohydrates generally have structural functions. The most important sugars in grape juice are the two six-carbon sugars glucose and fructose.

These are the sugars that make the juice sweet and are fermented to alcohol by the yeast. In addition, small quantities of pentoses (five carbon sugars) and pectins (galacturonic acid polymers) are found. The pectins have no
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great importance in the juice itself, but if they are not broken down they can create haziness in the wine. The second major constituent are organic acids. Three main organic acids occur in grapes: malic, tartaric and citric acid. Of these, tartaric acid is rare in fruits but the others occur widely. A fourth acid, succinic acid, is formed from yeast metabolism and so is found in wine but not in grapes. The acids give the juice its acidity, and act as an effective buffer to maintain the pH at around 3.2 - 3.4.

3. They are also important contributors to the flavour balance of the juice and wine, providing the sharp acidity. The third major constituent are phenolics. The term 'phenolics' refers to a large group of compounds containing at least one phenol group. These compounds contribute to the astringency / bitterness of the grapes and wine and are responsible for most of the color. There are six main classes of phenolics found in grapes: catechins, procyanidins, anthocyanins, flavonols, hydroxycinnamates and hydroxybenzoates. The difference between red and white wines is due to the different types of phenolics in the two beverages.

The simple phenolics - the hydroxycinnamates and hydroxybenzoates - occur in the flesh of the berry and so occur in both red and white wines. The other more complex phenolics, known collectively as flavanoids, occur in the skin, seeds and stems and so occur mostly in red wines. The procyanidins are also known as condensed (or non-hydrolysable) tannins, and it is these that give wine most of its astringency.

A further group of tannins, the hydrolysable tannins, are found in wine that has spent time in oak barrels. These tannins are also astringent, and are

complex esters of glucose and gallic acid. Anthocyanins are the commonest source of colour not only in grapes but in all flowering plants. Their color depends on the number of hydroxyl groups on the molecule and can range from orange through red to purple. The fourth major constituent are aroma compounds.

The basic flavor of a wine is formed from the balance of sugars, acids, phenolics, and ethanol, but the character of the wine is provided by the volatile aroma compounds. Over 1000 of these volatiles have been identified in wines from around the world, all present at low, almost trace, levels. The most important volatiles in the grape are the monoterpenes, present even in aromatic varieties such as the Riesling at concentrations no higher than 4mg kg⁻¹. These give a range of odors ranging from floral / fruity to resinous / solvent effects. Examples of the most important monoterpenes are Citronell, α -Terpineol, Citronell and β -Terpineol.

The monoterpenes exist in both the free volatile form and as bound glycosides. The glycosides are not volatile and so do not contribute to the aroma. They are slowly hydrolyzed in the acid conditions of the wine and contribute volatiles as the wine ages. During processing and aging of the wine these monoterpenes are also converted to other more complex volatiles such as TDN and vitispirane. The terpenes are not the only contributors to the grape aroma. The yeast also contributes volatiles both from its own metabolism and by modification of compounds in the grape juice. This results in the formation of the fusel oils (alcohols) such as 3-methyl butanol and 2, 3-butandiol. Volatile phenols such as vinyl phenols are also produced by decarboxylation of the hydroxycinnamates.

Other contributors to the wine aroma are esters such as ethyl acetate and hexyl acetate (formed from interactions between the alcohols and acetic acid), furans such as furfuryl alcohol (formed from the decomposition of sugars) and vanillin (extracted from the oak barrels). The fifth major constituent are nitrogenous compounds. There are many sources of nitrogen in grapes (e. g. DNA, enzymes, inorganic nitrogen etc.) but the most common of these are amino acids.

As free acids they are important building blocks for yeast during fermentation. In addition, many enzymes retain. Their catalytic activity in grape juice. Two groups of enzymes of significance are the pectinases ("pectolytic" enzymes which hydrolyze pectins, preventing them from forming a haze in the wine) and the phenol oxidases (which cause browning reactions to occur in the juice unless they are inhibited by dissolved SO₂). The sixth major constituent is vitamins. These are present in very low levels. However, although grapes are not a very good source of vitamin C they do contain some vitamins in large enough concentrations to be useful in human nutrition. Some of the main vitamins found in grapes are inositol (500 000 g/l), nicotinamide (3 260 g/l), pantothenate (820 g/l), pyridoxine (420 g/l), riboflavin (21g/l), cobalamine (B12) (0.

05 g/l). The last major constituents is minerals. The minerals in grapes are those found in the soil in which the grape vine was growing, so mineral content varies greatly from vineyard to vineyard.

In general, minerals make up 0. 4% of the weight of the grapes. The most important minerals are magnesium and potassium, which are important in

fermentation, and phosphate, which is necessary for yeast growth. Aside from this major constituents, grapes is also composed of aldehyde and water. In wine making there is a certain process undertaken. The first process is harvesting. As the grapes ripen the concentration of sugars and aroma compounds rises and the concentration of acids falls.

The aim at harvest is to pick the grapes at their optimum composition. This depends on the type of wine to be produced. For example, sparkling wine requires a higher acidity than still table wine. The development of the grapes is followed by taking samples of the grapes at regular intervals from a few weeks before the expected optimum levels will be reached. The samples are analyzed for pH , acid (by titration with sodium hydroxide), sugar (by refractive index or chemical reduction of copper salts) and flavor compounds. When optimum levels are reached, the grapes are harvested. The second is crushing and destemming.

Sulphur dioxide (5 - 10% solution of metabisulphite) is usually added to the grape bunches as they are fed into the crusher/destemmer. The stems are removed as the bunches pass through a perforated rotating cylinder in which the grapes fall through the perforations while the stems are separated out by beaters. The berries are then passed through rollers and crushed. The SO₂ inhibits the growth of wild microorganisms and prevents oxidative browning of the juice. Molecular SO₂ is the active biocide, but in solution this is in equilibrium with inactive HSO₃⁻-% At wine pH only 2 - of the SO₂ exists in the molecular form, but this is usually sufficient to give the required protection. Wherever possible during the manufacturing process the juice is kept under

a blanket of CO₂ to exclude air, and if necessary more SO₂ is added to maintain the level of molecular SO₂ at a minimum of 80ppm.

The third is juice preparation. The free-run juice is separated from the crushed berries, which are pressed by gentle squeezing to obtain a high quality juice. The juice is allowed to settle overnight or is centrifuged to clarify it. If necessary pectolytic enzymes are added to remove haze. Finally, the pulp is then squeezed almost dry.

This final juice is of low quality and is used for cask wine or fermented for distillation into alcohol for sherry or port production. The fourth is fermentation. Fermentation is begun by inoculating the juice with the chosen wine yeast. This yeast catalyzes a series of reactions that result in the conversion of glucose and fructose to ethanol: $C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$

The driving-force behind this reaction is the release of energy stored in the sugars to make it available to other biological processes. In aerobic conditions, the reaction can proceed further and convert the ethanol to H₂O and CO₂, releasing all of the energy present in the original sugars. This process is undesirable in wine production, so fermentation is usually carried out under a blanket of CO₂ to exclude oxygen and hence maximize alcohol production. The chain of biochemical reactions involved are glycolysis and alcohol fermentation as shown in the diagram 1. Depending on the conditions, various intermediates in the fermentation process can be converted into other products.

The yield of ethanol is affected by such factors as temperature, extent of agitation, sugar concentration, acidity, strain of yeast and yeast activity. The

lower the temperature the higher the alcohol yield due to a more complete fermentation (better sugar utilization) and less loss of alcohol entrained with CO₂. While it may be important to maximize the yield of ethanol it is equally important that this is never achieved with complete efficiency.

The various byproducts of yeast metabolism formed by this inefficiency contribute to wine's distinctive flavor and aroma and prevent it from simply being alcoholic grape juice. The juice used to be fermented in wax-lined concrete or plastic vats, but now stainless steel is used for all wines except for certain high-quality ones that are fermented in wood. Wooden barrels are the container of choice for chardonnay, sauvignon blanc and pinot noir as the wood is smoked during processing, forming additional flavor compounds (particularly tannins) which are leached into the wine, giving it further complexity. The last is purification. In former times, after fermentation was complete, the wine was heavily treated to alter the pH, composition etc. to give it a desirable flavor, appearance etc.

Very few such measures are used today, but those that are retained are outlined briefly below. Proteins and tannins that are suspended in colloidal form in the wine are precipitated out with substances such as gelatin or adsorbed to the surface of substances such as bentonite. This process is called fining. The wine is often also clarified in a process called racking. Wine is often also cold stabilized (left at 0 to -3°C for 10 – 14 days) to crystalline out any potassium bitartrate. These treatments are only usually necessary in white wine as red wine fines and clarifies itself by forming deposits of proteins, tannins and tartrates during the aging process, although sometimes proteinaceous fining agents are added to modify tannin levels

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and structures. The wine is continually racked off this precipitate, such that by the end of the aging process all it needs is simple filtration before bottling and sale.

As more and more research is done into the constituents of the wine and the way they are formed, two areas in particular stand out. First is the idea that regular consumption of wine in moderation is good for you. Statistical studies have shown that wine drinkers are less prone to heart disease, cancer and other diseases. This may be explained by the fact that wine drinkers tend to have a healthier lifestyle and are in groups which are less at risk to these diseases. It may be that there are certain chemicals that combat certain conditions, for example the antioxidant resveratrol which may reduce cholesterol and the risk of Alzheimer's disease. These chemicals can, of course, be found in other food and drink without the damaging presence of alcohol. Then there is the development of the scientific study of the process of wine making, and the technology to improve it. There are many who would desire to depend on the natural processes of grapes and fermentation.

Others have studied the chemicals which make up wine, seeking to determine those that cause the flavor, aroma and appearance of wine so that these can be manipulated in the production process. This tension will continue as the desire to make money affects the love of natural processes.