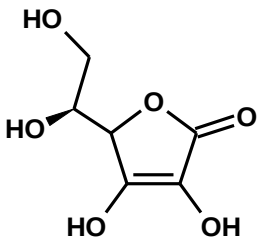
Wine Chemical Dictionary

Edited
Dr Eric Wilkes

Contents

Ascorbic Acid

Structure



Molecular Weight
176.13
Melting Point 192 ºC
Density 1.65 g/cm^3 (solid)
Acidity di-protic, pK_{a1} 4.2, pK_{a2} 11.6
Allowable Additive Yes
Legal Limits Yes*
EU 300 mg/l
Norway 150 mg/l
Switzerland 150mg/l
Typical quantity in wine
10-150 ppm

Analytical Methods
DCIP or Iodine titration
HPLC reverse phase

*2001 figures

Ascorbic acid (AA) has been used as an antioxidant in wine for many years (as well as in other food stuffs). It can be added as its naturally occurring form L-ascorbic acid (vitamin C) or as the optical isomer erythorbic acid. Its main roles are to prevent oxidative browning and pinking and to add freshness to a wines profile. In recent times however it efficacy in white wines has been called into question with some studies showing that in certain circumstances it can act as an oxidant and accelerate the browning. Other recent studies however have shown that wines stored long term (5 years) with AA, reasonable levels of SO_2 and good DO control appear fresher and younger than wines stored without AA. This just tends to highlight the complicated chemistry involved and that ascorbic acid must be used with a degree of caution.

Ascorbic acid is an effective oxygen scavenger reacting with O_2 (which would otherwise react with phenolics to produce browning) around 1700 times more quickly than SO_2. However the products of the sacrificial oxidation of AA (among them H_2O_2) further react to produce compounds which, it would appear can accelerate oxidative effects once the levels of AA have dropped low enough that it is no long effective as an antioxidant. SO_2 here seems to play a role in scavenging these side products delaying the onset of browning. However, since SO_2 is not as effective an anti oxidant as AA, the by-product catalysed browning proceeds in a competitive manner with the SO_2 at most playing a delaying role. To add to the complexity of the situation, any excess free copper or iron also seems to catalyse the browning caused by these compounds. Despite this most authors agree if wine is packaged with sufficient SO_2 and good DO control (including ensuring that O_2 transmission through the closure is limited) that the AA levels will not decline to the point where these secondary adducts will play a role in the reasonably expected lifetime of a white wine.

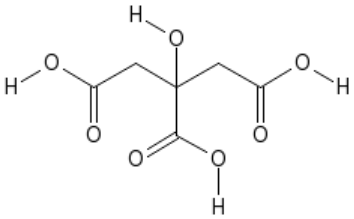
As a rough guide each 1 ppm of dissolved oxygen will require 6 ppm of AA which in turn will need 4 ppm of SO_2 to scavenge reaction products. However it needs to be remembered that the levels and effectiveness of both the SO_2 and ascorbic acid will be influenced by the phenolics in the wine. Typical levels of 100ppm ascorbic and >30ppm free SO_2 would appear to offer beneficial effects, especially in wines that have been properly managed for DO, have secure seals (screw caps) and are destined for long term storage.

References

Wessel du Toit, www.newworldwinemaker.com
G.R. Scollary, Factors Determining Wine Oxidation Final report to WDC, 31 May 2002
G. Skouroumonis et al., Australian Wine Research Institute, pers. Com
Godden et al., AWRI Technical Review, no. 129 December 2000

Citric Acid

Structure



Molecular Weight 192.13
Acidity tri-protic pKa_1 3.15, pKa_2 4.76, pKa_3 6.40
Allowable Additive Yes
Legal Limits 1 g/L (EU)
Typical quantity in wine 0.1 to 0.5 g/l

Analytical Methods
Enzymatic/spectroscopic analysis, HPLC

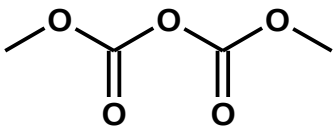
Citric acid is a naturally occurring organic acid. It is a relatively minor acid in wines typically found at levels of less than 0.5 g/l. Unlike tartaric acid its salts with potassium and calcium in alcoholic solution are relatively soluble. For this reason it often used to acidify wine without the risk of forming cold unstable precipitates. As a general rough guide 1kg of citric in 10,000 l of wine gives around a 0.15 increase in TA. It will also have a greater impact on pH than will tartaric due to its tri-protic nature, however the exact changes are hard to predict and should always be determined by trials. However large additions of citric acid can lead to unwanted organoleptic changes including the development of citrus characters.

Additions of citric acid to juice are not normally recommended as it may delay the onset of fermentation by inhibition of the EMP pathway enzymes. Also, wine spoilage organisms (especially lactic acid bacteria) can readily convert citric acid to acetic.

References
Zoecklein etal., Production Wine Analysis, 1990
Rankine, Making Good Wine,1989

DMDC, Dimethyl Dicarbonate (Velcorin)

Structure



Molecular Weight 134.09
Melting point 18 ºC
Boiling Point 172 ºC
Density 1.25 g/ ml (liquid)
Allowable Additive Yes
Legal Limits 200mg/l (in wine)
Typical quantity in wine NA

Analytical Methods
GC-FID indirectly by measuring methanol produced.

DMDC or Velcorin® is a sterilant used in a range of beverages including wine. One of the main reasons for its use (other than its effectiveness) is that it reacts completely with water to form methanol and CO_2 (both of which are naturally occurring in wine). It does react with ethanol to form ethyl methyl carbonate, but the reaction with water appears to happen preferentially. This reaction is temperature dependent and is complete within hours of addition and as such the wine is safe to drink soon after packaging.. As it is considered a sterilant, rather than a preservative, and breaks down completely in wine there is no requirement to label for it. Velcorin is permitted in Australia, USA and Europe (among other markets) but is not permitted in Japan.

DMDC is thought to kill microorganisms by inhibiting the enzymes acetate kinase and L-glutamic acid decarboxylase. It has also been proposed that methoxycarbonylation of the histidine part of the enzymes alcohol dehydrogenase and glyceraldehyde 3-phosphate dehydrogenase by DMDC inhibits these essential enzymes also. DMDC is more active against yeast than bacteria and mould, and its effectiveness is diminished with increased organism loading.

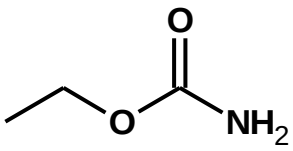
In Australia DMDC is added at the time of bottling with a limit of addition of 200mg/l to wine (250 mg/L for other beverages). Velcorin is only added via specialised dosing systems and hence is not used in the cellar, although bulk container filling is a potential application. In the US some wineries dose to wine before packaging, however this does restrict the amount that can be added later in the process as the 200 mg/l limit applies to the life time of the wine. Because of the speed of the reaction with water it is not practical to test for DMDC itself but rather the changes in methanol level in the wine are monitored to ensure consistent additions and that methanol levels are within acceptable limits.

References

Alison Soden, Group Microbiologist, Fosters Group
Product information from Lanxess International (formerly Bayer)
Wikipedia

Ethyl Carbamate

Structure



Molecular Weight 89.09
Boiling Point 185˚C
Allowable Additive no
Legal Limits Yes, country dependant
US* 15 ppb, 60 ppb (fortifieds)
Typical quantity in wine
12 to 15 ppb

Analytical Methods
GCMS

*As of 2005

Ethyl carbamate (also known as urethane) is formed from a reaction between ethanol and urea. It has become an issue in recent years as a possible carcinogen and a number of countries have flagged the possibility of legal limits being applied. The urea precursor is the result of the yeast metabolism of arginine (an amino acid) and cannot be eliminated. The formation of ethyl carbamate, while it cannot be eliminated, increases exponentially with heat and the quantities formed can be controlled by good storage practice and the avoidance higher temperatures. Ough etal (1993) showed that for wines with over 5mg/l urea storage temperatures greater than 25 ºC should be avoided.

Limiting the amount of the urea precursor produced is the main way of controlling ethyl carbamate. In the vineyard vines displaying excess vigour or those that are heavily fertilised tend to be higher in arginine resulting in ferments which produce more urea. Some yeast show a lower tendency to produce urea from arginine and it is an active area of research (and promotion) by a number of suppliers. Many yeasts tend to produce urea in the first part of the fermentation cycle and then to metabolise it in the later stages so ferments which are stopped before sugar fermentation is completed can have higher levels of urea. Citrulline which is another precursor of ethyl carbamate is produced by some forms of lactic acid bacteria and the levels available can be dependant the type of bacteria used for malolactic fermentation. There is some conjecture that some indigenous or wild malo bacteria lead to higher levels of formation and as such some authors recommend avoiding the use spontaneous secondary ferments as a way of limiting ethyl carbamate production.

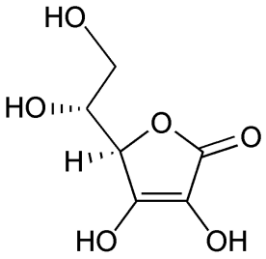
Because the quantity of ethyl carbamate changes with time and storage it has become quite common practice in some discussions by regulatory and academic bodies to refer to potential ethyl carbamate which is essentially a measure of available urea in the wine. As such there is a possibility that wine in the future may be regulated by urea content. While there are urease enzymes available to treat wines with high urea contents, their effectiveness in wine conditions is extremely limited.

References

www.fst.vt.edu/extension/enology
Ethyl Carbamate Preventative Action Manual, US Food and Drug Administration, 1997

Erythorbic Acid

Structure



Molecular Weight 176.13
Acidity diprotic, pK_{a1} 4.2, pK_{a2} 11.6
Allowable Additive Yes
Legal Limits
Typical quantity in wine
NA

Analytical Methods
DCIP or Iodine titration (does not discriminate from ascorbic)
HPLC reverse phase (can separate erythorbic and ascorbic)

Erythorbic acid is an optical isomer of ascorbic acid (it differs in the organisation of the -OH and –H on the first carbon in the aliphatic chain after heterocyclic ring). It was traditionally used as an ascorbic acid replacement (i.e. to add freshness and as an antioxidant) in wine for cost reasons however modern production methods means that there is little advantage.

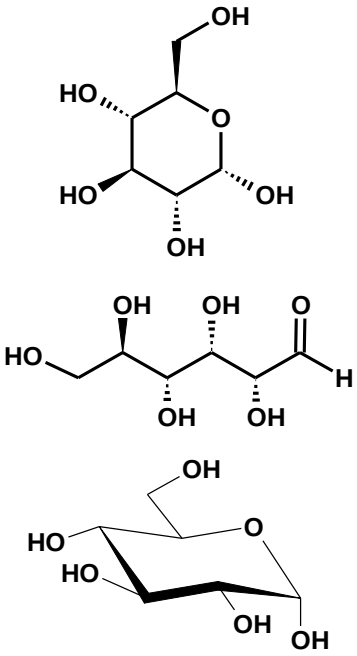
Chemically in most ways it acts in a manner similar to ascorbic acid except it has no vitamin C effect. Some current research in model wine systems suggests that samples with erythorbic acid suffered less oxidative browning however the erythorbic acid itself was consumed more quickly than ascorbic acid in equivalent systems. It is difficult to determine if a similar effect will be apparent in the much more complex situation of real wines other than to say that there may be some differences in duration of their effectiveness.

In general the same regulations and conditions with regards to ascorbic acid apply, along with the warnings that sufficient SO_2 be available when used to ensure that the by-products of its antioxidant function do not lead to browning and organoleptic deterioration.

References
Barril etal., Australian Grapegrower & Winemaker, October 2006
SGE Technical Note, www.sge.com

Glucose

Structure



D-Glucose

Molecular Weight 180.16
Melting point
146℃ (α-D)
Density 1.54g/cm3
Allowable Additive Yes, but only as juice or juice concentrate in Aus.
Legal Limits NA
Typical quantity in wine
NA

Analytical Methods
HPLC
Enzymatic spectroscopic

Glucose with fructose is one of the two main grape sugars and is one of the most important carbohydrates in biology. It is one of the classes of sugar called hexoses because of the six carbons of its backbone. It is one of the primary products of photosynthesis with only the D-form, also called dextrose, being biologically active. It differs from fructose by the location of the carbonyl or double bonded oxygen at the end of the carbon chain. This arrangement leads to glucose being able to form a six member ring known as the hemiacetal or pyranose form. This arrangement is in equilibrium with its straight chain isomeric form; however the vast majority is in the ring form in solution. When it forms the cyclic hemiacetal it gives rise to two other isomers, the α and β forms, defined by the location of the $–CH_2OH$ in relation to the –OH group nearest the ring oxygen. The α and β forms freely interconvert in solution, reaching a stable ratio of around1:2.

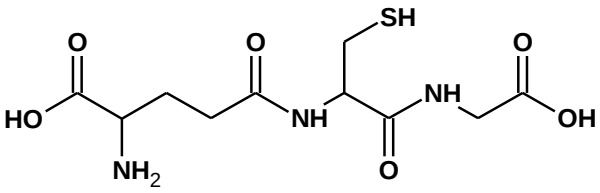
In mature grapes it is found at concentrations in the region of 100g/kg. The ratio of glucose to fructose in mature grapes tends to be close to 1 but this can vary greatly depending on conditions. It has been reported that in general cooler growing seasons can see a bias towards glucose in grapes. Glucose is directly metabolised by yeast during fermentation to produce ethanol. Many yeast strains show a preference for the metabolism of glucose over fructose leading to glucose in musts being depleted before fructose. As a result dry wines show very little residual glucose. Wines which have been sweetened with juice or juice concentrate will have near equal quantities of glucose and fructose, while wines which have had fermentation stopped before completion will have a preponderance of fructose.

Glucose is only about half as sweet as fructose however it is nearly twice as sweet as the pentoses, the next most common sugars in wine. It can be converted to gluconic acid by the action of some moulds, notably *botrytis*, and acetic acid bacteria. *Botrytis cineria* can also lead to the formation of glucans which are high molecular weight polymers of glucose which can cause difficulties in filtration/clarification and fermentation. Glucose is also involved in many reactions with wine phenolics, notably malvidin glucoside and related pigment polymers.

References
Zoecklein etal., Production Wine Analysis, 1990
Rankine, Making Good Wine,1989
Wikipedia

Glutathione

Structure



Molecular Weight 307.33
Acidity ND
Allowable Additive NA
Legal Limits NA
Typical quantity in wine

Analytical Methods
HPLC and LCMS

Glutathione (GSH) is a tripeptide antioxidant which is widely found in both animal and plant systems and plays a role in the protection of cells from free radical toxins. It is produced both in the grape vine (and is present in must) and by yeast towards the end of fermentation. It is synthesised in vines and yeasts from the amino acids l-cysteine, L-glutamate and glycine. Increased levels of FAN (free amino nitrogen) in juices seems to increase the available GSH at the end of primary ferment above that naturally carried forward from the must.

Especially in white wine its antioxidant effects appear to be important in the stabilization of aroma compounds and the longevity of wines. It has been suggested (enology notes #129) that its presence in lees explains some of their protective effect in barrel aging of white wines towards oxidative effects. It may also be involved in the ascorbic acid cycle in wines as it plays a role in the regeneration of ascorbate from its oxidised form dehydroascorbate in living systems.

Free copper in either juice or wine has the potential to inactivate glutathione. Hence excess copper in wine will reduce the long term freshness of the wine and its longevity. Minimising excess free copper at all stages of production, that is copper which is not being tied up and precipitated out by unwanted volatile sulphur compounds, can have major positive impacts on wine quality especially in respect to storage both in tank and bottle.

References
Enology notes 129
Wikopedia
PDR Health, www.pdrhealth.com

Gum Arabic

Molecular Weight NA
Melting point Variable
Boiling Point NA
Density Variable
Allowable Additive Yes (except Japan)
Legal Limits 250 ppm (US)
Typical addition in wine 20-1000 ppm

Analytical Methods
NA

Gum Arabic is a natural gum harvested from certain species of acacia tree in sub-Saharan Africa. It is a complex mixture of saccharides and glycoproteins which varies greatly from product to product, and occasionally from batch to batch. It can come as it solid or in a purified form in solution. It is used in a wide range of food and pharmaceutical applications including beverages, candies, gums and wines.

The major application of Gum Arabic in wines has been in the stabilization of colour in young red and rose wines. It appears to achieve this through the formation of a protective colloids which prevents the precipitation of wine pigments. It can also be used to modify the organoleptic qualities by softening astringent tannins and acids and broadening the perceived palate and body of the wine. The strength and effectiveness of any given Gum Arabic product varies depending on its chemical makeup and as such it must be used in conjunction with extensive fining trials. Like all natural products there can be significant variations from batch to batch.

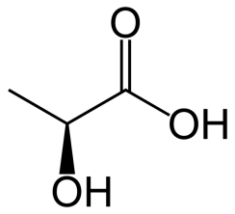
There is also reasonable evidence that it is effective at preventing cold instability in wines. Once again it would appear to achieve this by forming a coating or attaching to the nucleation sites thus inhibiting further crystal growth and precipitation, leaving the crystal precursors in colloidal suspension.

Traditionally Gum Arabic has had to be added immediately prior to bottling post filtration. The filtration process tended to remove the colloids from solution destroying the protective characteristic of the additive, actively stripping any colour retained by the colloid and at the same time irreversibly blocking the filters. The potential benefits of this additive and its widespread use has led to many European bottling operations offering Gum Arabic as a standard in line addition post filtration using metered pumps. There are now a number of highly purified Gum Arabic solutions available on the market which it is claimed do not effect filtration. These effectively work by not forming colloids of sufficient size to be removed by filtration and hence while they remain effective palate modifiers they do not appear to be as effective at colour and cold stabilization. This is however disputed by some manufacturers.

References
Enology notes #86, www.fst.vt.edu

Lactic Acid

Structure



Molecular Weight 90.08
Acidity mono-protic pKa_1 3.86
Allowable Additive yes
Legal Limits none
Typical quantity in wine 0.2 to 5 g/l

Analytical Methods
Enzymatic/spectroscopic analysis, HPLC

Lactic acid is the bi-product of malolactic fermentation through the conversion of malic acid. Because it is formed from the naturally occurring L-Malic it is only present in wine as L-lactic. It is considered milder tasting than malic acid and as such malolactic fermentation has a pronounced organoleptic effect.

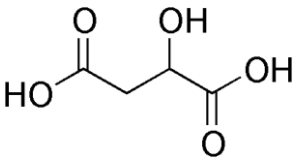
The conversion of malic acid to lactic involves the conversion of a di-protic acid to a mono-protic acid and hence can result in significant reduction in titratable acidity and increases in pH of as much as 0.2 units.

Malic acid does not usually form insoluble salts in wine and so is not associated with cold instability. As a result it is occasionally used for acid adjustments, occasionally to avoid the harsher effect of citric acid. Typical addition rates are in the region 0.1 to 0.2 g/l and are usually done as a final adjustment before packaging. Lactic acid is a minor interferent in VA by steam distillation, however as usually only ~2% is distilled across it is generally considered insignificant.

References
Zoecklein etal., Production Wine Analysis, 1990

Malic Acid

Structure



Molecular Weight 134.09
Acidity di-protic pKa_1 3.46, pKa_2 5.10
Allowable Additive Yes
Legal Limits none (however there are limits on titratable acidity)
Typical quantity in wine 0 to 3 g/l

Analytical Methods
Enzymatic/spectroscopic analysis, HPLC reverse phase

Malic acid is a tart tasting organic acid naturally found in a number of fruits including apples and grapes. In biological systems it is only ever found as the L-isomer. In grapes it can be found in levels varying from 1 to 8 g/l and is considered to be the most tart or sour of the common grape acids (lactic→citri→tataric→malic). In red wines and some whites it generally undergoes bacterial malolactic or secondary fermentation. In this process it is decarboxylated to produce L-lactic acid and CO_2. Since this in involves going from a di-protic to a mono-protic acid malolactic fermentation results in a decrease in titratable acidity and an increase in pH of up to 0.2 units. As such wines with high malic acid contents may need to be acid adjusted to retain suitable acid balance. As with all acids in wine the taste threshold can be a function of the alcohol content and the presence of sugars and phenolics. All of these tend to raise the threshold for the detection of acids.

Malic acid does not tend to be used as often as tartaric for acid adjustment of wines for a number of reasons. Firstly it can be metabolised by a number of organisms (especially *oenococcus oeni*) hence its addition to wine can add microbiological instability. It is also a weaker acid than tartaric and hence its addition to wine does not have as big an impact on pH. At normal temperatures the common salts of malic acid (malates) are soluable so its addition does not usually contribute to cold instability and cold stabilization does not remove any naturally occurring malic acid. Also, because of its relatively high pKa, during deacidification it is tartaric and not malic acid which is neutralised leading to changes in acid profile.

References
Zoecklein etal., Production Wine Analysis, 1990
Rankine, Making Good Wine,1989

Metatartaric Acid

Molecular Weight
variable length polymer
Acidity variable
Allowable Additive Yes
Legal Limits 100 ppm (EU)
Typical Addition in wine
50 to 100 ppm

Analytical Methods
NA

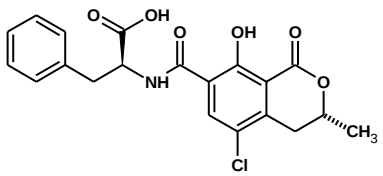
Metatartaric acid is the hemipolylactide of tartaric acid and is produced by heating tartaric acid under controlled conditions. It forms a stable white solid and is usually used to improve the cold stability of wines, especially in the presence of high levels of calcium which may precipitate as calcium tartrate in bottle despite traditional cold stabilization methods.

In wine it hydrolyses with time to tartaric acid and it is believed to inhibit crystal gown be coating the surface of the nucleating crystals. While its initial efficacy is unquestioned it rapidly looses its effect as it hydrolyses, the speed of which is temperature dependant. In wine stored at ambient temperatures the metatartaric can be gone in as little as 3 months while in refrigerated conditions it can still be detected after 12 months. However for fast turnover products the protection offered can be significant.

References
Zoecklein etal., Production Wine Analysis, 1990

Ochratoxin A

Structure



Molecular Weight 403.81
Allowable Additive no
Legal Limits Yes, country dependant
EU 2 ppb (2005)

Typical quantity in wine
0.01-3.4 ppb (EU)

Analytical Methods
HPLC

Ochratoxin A (OTA) is a mycotoxin produced by certain moulds as a secondary metabolite and is recognised as a carcinogen (Class 2B). It is a problem in cereals, beer, coffee and cocoa as well as wine. This toxicity has led to a number of nations, notably the EU, regulating the maximum allowable in various foods and beverages.

Its main route into wine is through the growth of mould on fruit, especially towards maturity. The main mould on grapes contributing to the formation of OTA is Aspergillus; however some forms of Penicillium also are found on grapes and can lead to OTA formation. In general the mould Aspergillus can only form on damaged or bruised fruit and cannot penetrate the unbroken skin of berries. OTA producing moulds can also be found on raisined fruit. Due to the difficulty most moulds have growing in wine its formation does not appear to be a problem post vinification.

The prevalence of OTA appears to be greater in the EU (especially in warmer regions around the Mediterranean) than in Australia however surveys have found it present in some Australian wines in small quantities. This may be due to a combination of factors including viticultural practices and environment. Once formed it is a relatively stable compound however the process of vinification can significantly reduce the amount found in the wine compared to that found in the must. Studies have shown that the final concentration of OTA after fermentation is independent of initial concentration; however a figure 8.1% retention has been reported.

Normal winemaking practices appear have little impact on OTA levels with the exception of carbon fining at levels up 0.3g/l which could remove up to 72% of the OTA present, but at some organoleptic cost. The best measure would appear to be preventative by rejection of unsound fruit.

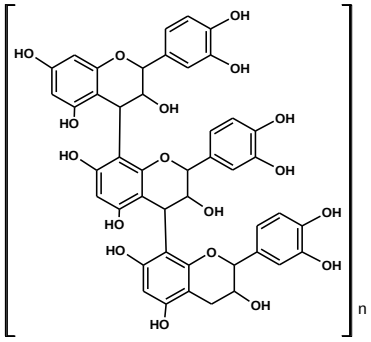
There are a number of screening test kits now available to determine the presence of OTA at problematic levels. Positive results from such kits usually need to be confirmed by HPLC. While very stable in wine OTA can be degraded to the still problematic OTB (non-chlorinated derivative) and OTC (the ethyl ester).

References

Rousseau, Ochratoxins in Wine Current Knowledge, vinidea.net, Wine Internet Journal, 2004, N. 5
Gambuti etal., Am. J. Vitic 56:2, 2005
Ferandes etal., Am. J. Vitic 58:1, 2007

Procyanidins

Structure



Typical procyanadin

Molecular Weight
variable but usually 500 to 700 in grapes
Allowable Additive NA
Legal Limits NA
Typical quantity in wine
180 +/- 100 mg/l

Analytical Methods
HPLC?

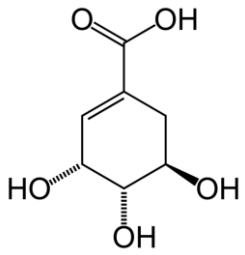
Procyanidins (also known as proanthocyanidins, oligomeric procyanidins and leucoanthocyanin) are condensed tannins naturally occurring in grape skins and seeds. They are generally polymers formed from monomeric flavonoids such as flavanols (e.g. catechin) or flavan-3,4-diols. Generally in grapes they are found as dimers and trimers however they tend to be involved in the formation of much larger polymers in red wine aging (resulting in tannins with 8 to 14 flavonoid units and molecular weights over 2000).

Recently their consumption has been extensively linked with certain health benefits such as reduced chances of cardiovascular disease and certain cancers. Earlier research had attributed these effects from red wine to resveratrol however the quantities found in wine have since been considered to be too low to have a significant effect. However as one of the major polyphenols found in red wine procyanidins exist in sufficient quantities to have a beneficial affect at reasonable rates of consumption.

Research has shown that some old world wineries using more traditional fermentation techniques (extended ferments on skins and inclusion of pressings) can have as much as 4 times the quantity of procyanidins as new world wines. There is also evidence that grapes grown at higher altitude have higher levels (probably due to the higher UV levels catalysing greater production in the grape). This suggests that these wines will have greater health benefits per given consumption rate than their less traditionally made counterparts. However the techniques of vinification have very significant organoleptic impacts as do the higher levels of condensed tannins.

Shikimic Acid

Structure



Molecular Weight
1174.15
Chemical Name
(3R,4S,5R)-3,4,5-trihydroxy-1-cyclohexenecarboxylic acid
Acidity mono-protic
pKa_1 ?
Allowable Additive
naturally occurring

Analytical Methods
HPLC

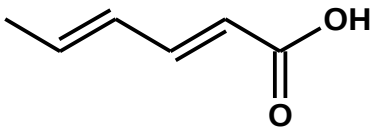
Legal Limits NA
Typical quantity in wine 20 to 120 mg/l

Shikimic acid is a naturally occurring substance which is an important intermediate or precursor in the biosynthesis of some aromatic the amino acids phenylalanine and tyrosine, indole and its derivatives, many alkaloids, tannins and lignin. It is found in significant quantities in star anise and is used as a precursor in the production of Tamiflu.

There is some suggestion that it can be used to identify the country that a wine has come from as for any given variety there seems to be significant variation in the amount present based on origin. However a large amount of work still needs to be done to define the impact of vintage, viticultural and vinification practices on overall levels. Also the variation between varietals from a given region can be significant meaning that blending can also obscure its usefulness for defining regionality.

Sorbic Acid

Structure



Molecular Weight 112.12 (potassium salt 150.22)
Acidity mono-protic pKa 4.8
Allowable Additive Yes
Legal Limits 200 mg/l (Aus, dependant on total SO_2 present, see text)
Typical quantity in wine NA

Analytical Methods
Steam distillation/UV analysis
HPLC

Sorbic acid (not to be confused with ascorbic acid) is a naturally occurring fungistat which is widely used in both the food and beverage industries to control yeasts and moulds. In wine if used correctly it can be effective against yeasts but it has little impact on lactic acid or acetic bacteria. It does not appear to kill yeast but rather inhibits their growth and reproduction. As such it is usually used in conjunction with SO_2 and cannot be used as a replacement. There is some evidence that the presence of sorbic acid reduces the effectiveness of SO_2 to combat bacteria due to intermolecular interactions and as such when used SO_2 levels should be maintained at above minimum rates. Sorbic acid is also ineffectual against wines with a high yeast loading (>100 CFU/ml) and should only be used on clean or filtered wines. While sorbic acid is more persistent than SO_2 (ie it is not volatile) it can be oxidised in solution to compounds which have an unfavourable organoleptic signatures. Over time sorbic acid can react with ethanol to give ethyl sorbate (celery-pineapple taint) or, in the presence of lactic acid bacteria, a geranium like taint. As such it not usually recommended for use in wines to be stored for long periods or with high DO's. The thresholds for the pure compound have been described as low as 50 to 150 mg/l.

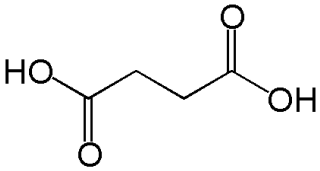
The effectiveness of sorbic acid is controlled by factors including free SO_2 level, % alcohol, concentration and yeast count. As it seems the un-ionised molecule is the active form lower pHs give a much greater effect with it doubling between pH 3.5 and 3.1. Lower alcohols also have a negative effect. One study showed that the concentration needed to inhibit growth in a 14% alcohol wine was 50 mg/l as opposed to 150 mg/l in a wine at 11% alcohol.

In Australia the legal amount of sorbic acid in wine is a function of the total SO_2 concentration. e.g. if a dry wine has a total SO_2 of 150 mg/l (60% of the maximum) then you can only add 40 % of the allowable amount of sorbic acid (i.e. 40% of 200, 80 mg/l). Due to its low solubility sorbic acid is usually added in the form of potassium sorbate. The required amount of sorbic acid should be multiplied by 1.34 to get the required amount of potassium sorbate to be added. It is usually dissolved in water before addition to ensure its effective dispersion in wine.

References
Zoecklein etal., Production Wine Analysis

Succinic Acid

Structure



Molecular Weight 118.1
Acidity di-protic pKa_1 4.21, pKa_2 5.64
Allowable Additive NA
Legal Limits NA
Typical quantity in wine
Whites 0.1~1.6 g/l (mean 0.6)
Reds 0 to 2.6 g/l (mean 1.2)

Analytical Methods
HPLC

Succinic acid is most abundant in grapes immediately post fruit set but drops rapidly to trace amounts as fruit matures. The majority of succinic acid found in wines is the by-product of alcoholic fermentation. It is considered to have a salty taste component compared to the other major wine acids and does impart a distinctive organoleptic character.

Different yeast types vary greatly in the ability to produce succinic acid and fermentation conditions can also have a major impact on its production. In general higher pH and sugar conditions can lead to greater formation of succinic acid as can higher fermentation temperatures (depending on yeast type). There is also some evidence that seasonal variations in grape constituents (including nitrogen availability and type) can lead to variations in its production.

It and its salts are much more soluble in alcoholic solution and so ferments producing large quantities of the acid can reverse the normal trend seen during fermentation with TA increasing (normally the precipitation of bitartrates leads to a decrease in TA during fermentation). Once formed it is biologically stable and is not usually degraded by bacterial action. Its solubility also means that cold stabilization has little impact on its level in a given wine leading to a higher retained TA in wines with relatively large quantites. Because of its smaller molecular weight 1g of succinic equates to 1.3g/l of tartaric in a normal TA titration however its larger pK_a means it is a weaker acid and hence leads to a higher pH per given amount.

Sugar

Allowable Additive
Country dependant
Legal Limits
Country dependant
Typical quantity in wine
0-2 g/l (dry wine)

Analytical Methods
-Reducing Sugar Methods (Rebelein, Lane-Eynon)
-Enzymatic / spectrophotmetric (glucose and fructose)
-HPLC

Wine is itself the product of the fermentation of the two main grape sugars, glucose and fructose. These two sugars are by far the most abundant to be found in must being present in quantities in the region of 100 g/l each, depending on the fruit and its ripeness. They represent around 95% of the total dissolved solids which gives the typical Baume or Brix reading used to describe grape ripeness. They usually occur in near equal amounts in must, but climatic and varietal differences can lead to large variations with glucose / fructose ratios varying from 0.71 to 1.45 reported. In general, cooler seasons tend to favour glucose while warmer seasons favour fructose. The next most abundant sugar is the disaccharide sucrose, which is the familiar cane or table sugar. It is present in quantities in the region of 2 to 10 g/l. A range of polysaccharides such as pectins and dextrans as well as pentose monosaccharides such as arabinose and rhamnose are also found in grapes.

Typical wine yeast is only capable of metabolising the hexose monosaccharide sugars glucose and fructose. However yeast produces invertase enzymes that hydrolyse sucrose to its component glucose and fructose allowing it to be metabolised. Typically conversion rates of sugar to ethanol of 0.51 to.55% by weight are quoted for fermentation. The pentoses are not metabolised and remain in the wine after fermentation at levels of 0.4 to 2 g/l. However they are reducing sugars and contribute to the non-zero value that is found in dry wines when measured by reducing sugar methods.

Yeast has a preference to metabolise glucose over fructose which can lead to a G/F ratio of 0.25 towards the end of ferment. The degree of this imbalance can be strongly dependant on yeast type and ferment conditions, and can be implicated in slow and stuck ferments. As fructose is twice as sweet as glucose,1.73 compared to 0.74 on a scale where sucrose is 1, this preference explains why wine stopped before it is dry appears sweeter than those which have grape concentrate or juice added, which contains equal amounts of glucose and fructose. The pentoses, the next major sugars, only have a relative sweetness of 0.4 and as such contribute very little to perceived sweetness.

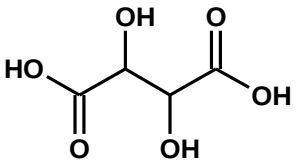
In Australia only juice or juice concentrate can be added to raise sugar levels in must or sweeten wines. The exception is in sparkling wine production where sucrose can be added prior to secondary fermentation. Under acidic wine conditions the sucrose rapidly begins to hydrolyse to glucose and fructose and over time disappears from the wine. However before analysis such wines must be inverted by either heat/acid hydrolysis or enzymatic inversion to ensure that a hydrolysis endpoint has been reached as neither typical G/F enzymatic kits nor reducing sugar methods measure sucrose.

References

Zoecklein etal., Production Wine Analysis, 1990
Rankine, Making Good Wine,1989
Adrian Coulter, AWRI, pers. Com

Tartaric Acid

Structure



Molecular Weight 150.1
Acidity di-protic pKa_1 3.04, pKa_2 2.98
Allowable Additive Yes
Legal Limits none (however limits do exist for maximum titratable acidity)
Typical quantity in wine 1-6 g/l

Analytical Methods
HPLC

Tartaric acid is (along with malic acid) is one of the two major organic acids found in grape juice and subsequently wine. It is naturally present as L-(+) tartaric acid in grapes. Unlike malic it is not further converted during the secondary fermentation process and hence much of wine pH chemistry revolves around its concentration. It is a stronger acid than malic acid (ie, greater pH change for a given addition) and is relatively non-metabolizable.

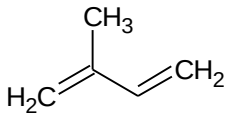
Tartaric is often added to musts and ferments to adjust pH. One of the advantages is that if the pH of the resulting wine is less than 3.65* cold stabilization and the subsequent loss of KHT (potassium bitatrate) will result in a further decrease in pH. Hence lower pHs may be achieved without higher TA's. Above pH 3.65 generally KHT precipitation will result in an increase in pH. The mixed isomer form of tartaric (DL-Tartaric or racemic tartaric) is occasionally used as a wine additive to precipitate CaT from wine to help cold stability. This is achieved because the D form of CaT is slightly less soluble and can be preferentially forced out of solution. However great care need to be taken as if sufficient Ca is not removed later precipitation can occur in bottle.

Tartaric acid exists in wine not just as its acid form but also as its salts KHT and CaT. These have only a limited solubility in alcoholic solution. Due to the crystallization inhibiting abilities of a number of wine components (phenols, proteins, sulphates, tannins etc) most wine are supersaturated to tartrate salts. As such additions of tartaric acid to cold stabilized wines should be avoided as it can result in increases in tartrate instability, especially in the presence of high calcium levels.

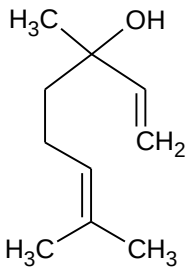
* Note this is an approximate value and will vary to some degree depending on the alcohol concentration in the wine and temperature.

Terpenes

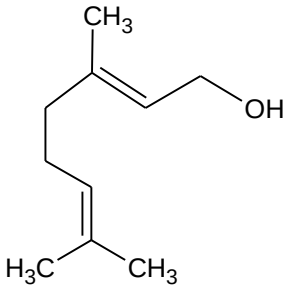
Molecular Weight
variable
Allowable Additive NA
Legal Limits none
Typical quantity in wine
0 to 6 ppm



Isoprene



Linalool



Geraniol

Terpenes are a group of naturally occurring plant hydrocarbons which can be considered to be derived bio-synthetically from collections of the sub-unit isoprene. They have the generalised formula of $(C_5H_8)_n$. This basic structural unit is open to many biosynthetic additions and rearrangements. They occur in many natural plant products such as oils, resins and distilled products such as turpentine. They are the primary constituent in many essential oils.

In wine volatile terpenes can play an important role in wine aroma chemistry, especially in Muscat and some aromatic white varieties. They are present in grapes and can undergo structural changes during vinification and maturation to change their impact on the organoleptic charter of the wine.

The major class of terpene found in wines are the monoterpenes which are made up of two isopropene groups (n=2). Two important examples of these are linalool and geraniol.

Another group of terpenes found in wine (but to a much lesser extent) are the sesquiterpenes (n=3).

The mono terpenes can be broken into a number of sub classes. The *volatile* monoterpenes which tend to be characterised by only a single hydroxyl group are the active aroma terpenes. The *polyols* are monoterpenes with more than one hydroxyl group and are hence too polar to be volatile. The monoterpene glycosides are covalently bonded to a glucose unit and are also too polar to be volatile. In general the two non-volatile forms are in the vast majority in most wines however acid and enzymatic hydrolysis reactions may convert them to the volatile form in certain circumstances during vinification and maturation.