White wine spoilage:
the impact of light

Background
The quality of white wines is determined by the chemical reactions that occur within the wine during its production. Some of these reactions are undesirable and will cause spoilage if steps are not taken to reduce their impact. Metal ions and organic acids are abundant in all wines, and, under certain conditions, can react with light or oxygen to negatively impact the wine colour or flavour.

One of the most concentrated, naturally occurring, organic acids in grapes and wine is tartaric acid. A particular fragment of tartrate known as glyoxylic acid has the ability to induce spoilage reactions in white wine. Glyoxylic acid can produce yellow coloured compounds which contribute to the browning of white wine. Sulfur dioxide, used as the main preservative in white wine, can bind to glyoxylic acid, reducing the concentration of preservative. As a result, the wine spoils more rapidly.

Iron in wine has long been associated with potential spoilage. The aeration of wine (i.e. adding of oxygen) will lead to iron conversion and produce a cloudy wine (iron casse). Modern vineyard and winemaking technologies (e.g. the use of stainless steel vats rather than ones made of iron or cast iron) have reduced the occurrence of iron casse.

The impact of light on the iron/tartrate/oxygen chemistry in white wine has not been well understood. Researchers at the National Wine and Grape Industry Centre have been studying this phenomenon using a series of experiments (see page 2). The outcomes from the research should assist in improving the shelf-life of white wine.

Glyoxylic acid and wine spoilage
Tartaric acid is a by-product of wine production. The ferric tartrate complex acts as a photochemical agent to adsorb the energy of incident light, and the energy is then utilised to fragment (i.e. break-up) the tartrate via oxidative reactions to form glyoxylic acid.

Example
A wine with 5 g/L tartaric acid requires a 1.5% conversion of the total tartaric acid to glyoxylic acid to fully deplete 30 mg/L free sulfur dioxide. For most wines, this would be near complete removal of the wines’ preservative.

When sulfur dioxide is absent, the glyoxylic acid can react with grape skin-derived phenolic compounds (catechins). The reaction with the catechins produces yellow coloured compounds called xanthylum cation pigments. These pigments can appear brown if found in high concentrations or if pulp-derived wine phenolic compounds are also present. Lightly pressed grapes extract fewer catechins. The discoloration is therefore more evident in white wines produced from heavier pressings.

Iron and wine spoilage
An increase in white wine discolouration or browning of the wine can also be linked to a reaction between iron and oxygen.

Iron (II) and iron (III)
Iron (II)/iron (III), usually in combination with other metals, has the ability to activate molecular oxygen, as well as catalyse the degradation of hydrogen peroxide (H₂O₂) to highly destructive hydroxyl radicals. The latter reaction was studied by Fenton in 1894, when it was found that tartaric acid was oxidised in the presence of hydrogen peroxide and iron (II) to form glyoxylic acid.

The source of iron in wine is varied and typically ranges from 2–20 mg/L, with an average around 5 mg/L. The iron can exist in two different redox forms—ferrous iron (II) and ferric iron (III).

The iron (III) is most commonly associated with tartrate. The ferric tartrate complex acts as a photochemical agent to adsorb the energy of incident light. This energy is then used to break-up the tartrate via oxidative reactions. The resulting tartrate fragment, glyoxylic acid, can then contribute to wine spoilage (see previous section Glyoxylic acid and wine spoilage).
Experiment 1

Factors influencing Glyoxylic Acid Production in White Wine

The aim of this experiment was to determine the factors influential in facilitating the production of glyoxylic acid in model white wine samples.

Treatments

The amount of glyoxylic acid produced from tartaric acid was determined in five different sample types exposed to UV-visible light. The light source was a 300 W xenon lamp. All samples (pH 3.2) that were exposed to the light were irradiated for 30 minutes at a temperature of 45°C. The control sample contained 12% (v/v) ethanol, ~3 g/L tartaric acid/potassium hydrogen tartrate, and 5 mg/L iron.

The treatments were:
1. Control sample
2. Sample minus iron
3. Sample with low oxygen
4. Sample not irradiated
5. Sample minus ethanol

Results

The results indicate that the presence of light or iron was necessary for glyoxylic acid to be produced from tartaric acid (Figure 1).

The production of glyoxylic acid was also reduced when the oxygen concentration in the sample was lowered. Oxygen is required by the photochemical process that causes tartaric acid to produce glyoxylic acid.

Experiment 2

Oxygen

The aim of this experiment was to determine the impact of oxygen on white wine colour development.

Treatments

The Chardonnay wine (Figure 2) was bottled in flint bottles with two levels of headspace and dissolved oxygen and then exposed to similar amounts of light at identical temperatures over 18 days.

Results

Wines with higher oxygen levels at bottling were much browner in colour than the equivalent wines without oxygen.

Wines with low oxygen had little development in colour over the irradiation period.

Oxygen concentrations appear to be a critical component for the photochemical colour development in white wine.
Experiment 3

Light
The results obtained in the two previous experiments highlight that white wine quality and shelf life are negatively affected by light exposure particularly in the presence of oxygen and iron (III) tartrate. Experiment 3 aimed to determine the type of light critical for the formation of glyoxylic acid from the iron tartrate solution.

Results
The wavelengths of light between 300–520 nm were the most efficient at generating the glyoxylic acid from iron tartrate (Figure 4). This wavelength included near UV light (300–380 nm) and some visible violet/blue light (380–520 nm). Lower concentrations of glyoxylic acid were formed when samples were exposed to the UV light (200–300 nm). The high energy UV light was most likely inducing different photochemical reactions including the production of hydrogen peroxide which is known to degrade glyoxylic acid.

Experiment 4

Bottle Colour
The aim of this experiment was to assess the proportion of light (across varying wavelengths) that different coloured wine bottles would allow into the solution inside of them.

Results
Experiment 3 showed that the most efficient glyoxylic acid production occurred at a wavelength range of 300–520 nm (Figure 4). None of...
the wine bottles in this experiment allowed light below 300 nm to reach the wine (Figure 5). All the bottles allowed at least some light through into the wine at wavelengths between 300–520 nm.

Light transmission above 300 nm (lowest to highest) of the bottle colours: amber, antique green, French green, flint, arctic blue

Complete protection of the wine from iron tartrate photochemistry is not possible regardless of bottle colour. However, the darker bottles would appear to be the most effective at limiting the transmission of light, and therefore the production of glyoxylic acid in the wine.

Experiment 5

Bottle Weight

This experiment aimed to assess the effect of bottle glass thickness (as measured by bottle weight) on light transmission. Flint and antique green bottles are readily available in both light (midsection 2 mm thick) and heavy (midsection 3 mm thick) weight bottles. Samples were irradiated from behind the glass and the glyoxylic acid concentrations were measured.

Results

There was a significant difference in the light transmission between the antique green light and heavy weight bottles (Figure 6). The heavy weight bottle had at least 30% less light transmitted than the light weight bottle. This difference in light transmission was consistent with the relative thickness of the bottles.

The flint bottles had higher glyoxylic levels compared with the antique green bottles. The heavy weight antique green bottle recorded less than half the glyoxylic acid concentration of the light weight antique green bottle (see Figure 7).
Outcomes of research
The research has shown that:

1. Iron (III) tartrate photochemistry can impact significantly on white wine quality. It may consume the main wine preservative, or produce undesirable brown colouration. The undesirable changes in wine quality and colour are greater with increased levels of oxygen.

2. Darker coloured bottles will adsorb more light and transmit less light to the wine. This may be particularly important for those wines designed for long storage periods before consumption.

3. Heavier/thicker dark bottles will adsorb more of the photoactive light than lighter/thinner dark bottles. Therefore wine stored in thicker, darker bottles has less photoactivity and a reduction in potential spoilage.

Figure 7  Glyoxylate acid concentration of sample wines in heavy and light flint and green bottles across wavelength range 200–800 nm

Further information

www.nwgic.org
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