

Ascorbic Acid – Friend or Foe?

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Richard grew up in an Australian wine producing region and went on to study microbiology and winemaking at university. After starting his career in brewing, he joined Penfolds Wines in 1979. Penfolds became a part of Australia's largest and most successful wine company of the time, Southcorp Wines. Richard held senior management positions within Southcorp at a time when the Australian wine industry became a global leader for innovation and quality. In 2001, Richard left Southcorp Wines to establish Scorpex Wine Services, specialising in technical and strategic consulting to the global wine industry. Scorpex is now involved in a wide range of activities with suppliers, wine companies and wine industry customers around the globe.

Ascorbic acid is a molecule that is naturally present in many foods. It is also known as vitamin C. Ascorbic acid has important properties for human health. Humans cannot synthesize vitamin C. A deficiency of vitamin C in the diet causes scurvy.

Ascorbic acid acts as an antioxidant by reducing oxygen. A relatively stable oxidized form of ascorbic acid, dehydroascorbic acid, is formed by the reaction, along with hydrogen peroxide.

The optical isomer of vitamin C, erythorbic acid, also acts as an antioxidant. However, it has very little vitamin C activity.

Ascorbic acid was first isolated from natural sources in 1928, and first synthesized in 1933. Ascorbic acid is naturally present in grapes, but the levels are low (below 10 mg/L).

Additions of ascorbic acid to wine were first allowed in the USA in 1957. Early studies considered the use of ascorbic acid as a complete or partial substitute for sulfur dioxide. It was soon realized that ascorbic acid could not be used as a complete replacement for SO₂, for the following reasons:

1. Ascorbic acid does not have antimicrobial properties.
2. Ascorbic acid will not bind to residual aldehyde in wine.
3. Ascorbic acid has no impact on oxidative enzymes.
4. The reaction of ascorbic acid with oxygen produces an oxidative species.

After this initial research, most researchers recommended that ascorbic acid be used in conjunction with sulfur dioxide, not as a replacement. Investigations showed that oxygen reacts with ascorbic acid much more rapidly than with SO₂. The oxidative species produced by the reaction between oxygen and ascorbic acid, hydrogen peroxide, can then react quickly with SO₂.

The introduction of ascorbic acid as an intermediate in the reaction between oxygen and SO₂ in wine was considered to be beneficial. Oxygen could be scavenged quickly by ascorbic acid. The by-product of this reaction could then be mopped up by SO₂ present in the wine. It was considered that this gave fresher wines with more fruit character.

Without ascorbic acid, oxygen can react with easily oxidized phenolic compounds. This is not usually an issue with red wines, where some oxidative modification of the phenol content after fermentation is desirable. In white wines, however, phenol oxidation can lead to increased color formation.

Over the years, ascorbic acid has become popular in some countries for use during white wine production. However, use of this material is by no means universal. In Australia, ascorbic acid additions were widely adopted when reductive white winemaking techniques became popular in the 1980s. Use of ascorbic acid was seen to contribute to the production of clean, fresh, fruit-driven wines made from varieties such as Riesling, Semillon and Sauvignon Blanc. Ascorbic acid was also widely used in Chardonnay.

It was also found that ascorbic acid had the valuable property of preventing pinking in white wines. Pinking is an issue that appears sporadically in Australian white wine, apparently associated with seasonal conditions, grape variety, juice expression techniques, the amount of oxygen exposure given to juice prior to fermentation and the amount of oxygen exposure given to finished wine. The bag in box pack popular in Australia (just under 50% of domestic wine sales by volume are sold in this package format) allows oxygen ingress after packaging. Susceptible white wine can form a considerable amount of pink color after a short time in a bag in box pack. Ascorbic acid use in white wine packaged in bag in box, often made from varieties such as Colombard, Thompson's Seedless and Muscat, or pressings of higher value varieties, is almost universal.

More recently, ascorbic acid has been found to delay the formation of atypical aging character (ATA). ATA is as yet unknown in Australia. It is not yet clear if this is due to Australian irrigation practices, climatic conditions (although one of the apparent trigger conditions, drought, is certainly not unknown in Australia) or winemaking techniques. Mechanisms associated with ascorbic acid impact on ATA are not well understood.

While the use of ascorbic acid by Australian winemakers became widespread, there was little published research that confirmed its effectiveness. Older German literature questioned the benefits of its use. To resolve these questions, the Australian Wine Research Institute (AWRI) undertook a study to review the impacts of ascorbic acid usage on the color of white wines and model wine solutions. The results were published in the Australian Journal of Grape and Wine Research in 1998 (Peng et al 1998).

The major findings of this study were:

1. Soon after its addition, ascorbic acid decreased the brown color of white wines.
2. With time, the samples with added ascorbic acid developed more browning than samples without added ascorbic acid.
3. Under a variety of accelerated (45°C, air in the headsapce) or prolonged storage conditions, the browning of model wines and white wines was invariably enhanced by ascorbic acid addition.

4. This enhancement took place whether or not SO₂ was present.

The researchers concluded that the addition of SO₂ alone, rather than ascorbic acid alone or SO₂ plus ascorbic acid, appears to be the most effective and least expensive way of protecting white wine from browning during bottle conservation.

The outcomes of this study caused a good deal of discussion in the Australian wine industry. Many winemakers quickly reviewed their use of ascorbic acid. By the 2000 vintage in Australia, ascorbic acid use in many products had ceased.

Unfortunately, this vintage also saw the widespread occurrence of pinking issues in Australian white wines. Winemakers had been lulled into a sense of security by years of ascorbic acid use. Little routine testing of white wines for pinking potential was being carried out prior to packaging. A painful lesson was learned when consumers started to find blush wine in bag in box packs.

Further discussion took place on ascorbic acid use. The results of the AWRI study were reviewed. Some industry members were convinced that ascorbic acid addition was indeed beneficial in preventing the development of darker color in white wines. Further work showed some very interesting conclusions.

In the study reported in 1998, browning was measured by the conventional method of measuring absorbance of clarified samples at 420 nanometres in a spectrophotometer. Measurement of absorbance at other wavelengths and evaluation of the samples by eye had not been carried out.

The AWRI undertook a study after 2000 to review the impacts of added oxygen on white wine color. Quantities of oxygen were accurately added to samples of the same wine in glass bottles. The bottles were sealed and kept in an anaerobic environment. After a period of storage, the color of the wine in the unopened bottles was assessed by measuring absorbance at 420 nm in a specially adapted spectrophotometer. Wine color was also assessed by eye.

In general, it was found that the absorbance at 420 nm correlated well with the apparent “brownness” of wine samples when evaluated by eye. However, an interesting phenomenon was noted. As part of the trial, additions of oxygen had been made to samples of the same wine with and without added ascorbic acid. After 15 months of storage, the absorbance at 420 nm of each sample was measured. 60 panellists were then asked to pick the more brown sample from two bottles of the same wine, one with and one without added ascorbic acid, to which the same amount of oxygen had been added. It was found that the correlation between brown color and absorbance at 420 nm for wines with and without ascorbic acid was not strong.

Evaluation of these samples showed that:

1. Wines perceived as browner by eye did not always have a higher absorbance at 420 nm.
2. Wines with added ascorbic acid were judged to be less brown by eye in all cases.

These results led to a review of the absorption shown by samples of the same wine with and without ascorbic acid at different light wavelengths. It was found that ascorbic acid caused a slight increase in absorbance at 420 nm, associated with yellow color. However, absorbance at light wavelengths between 500 and 600 nm, associated with colors such as orange, was higher for wine without ascorbic acid. The cumulative effects of the absorbance at the higher wavelengths outweighed the effects of the absorbance at 420 nm, making the wines without ascorbic browner to the eye.

This work called into question the findings of Peng et al reported in 1998. Although the absorbance at 420nm of wines with ascorbic acid was higher, the overall color intensity developed in wines with ascorbic acid additions was lower.

No evaluation of the impacts of the presence or absence of ascorbic acid on aroma and flavor had been carried out in this trial. The differences in color behavior between wines with and without ascorbic acid had been unearthed as a sideline finding during the study of the effects of oxidation on samples artificially dosed with oxygen. What effects does ascorbic acid have on flavor and aroma? Do the differences in color happen in real commercial situations? Fortunately, a trial had been started in the late 1990s that would provide samples that could enable these questions to be answered.

The trial involved the bottling and storing of two wines, a Riesling and a wooded Chardonnay, with several variables:

1. With and without ascorbic acid (100 mg/L for the Riesling, 75 mg/L for the Chardonnay).
2. Bottles sealed with different closures – screw cap (with metal liner), natural cork, synthetic closure.
3. Bottle storage orientation – upright and inverted.

Assessments were carried out over five years of storage. Color was estimated by measuring absorbance at 420 nm, determining CIELAB values and by visual inspection.

The overall conclusions from this study concerning the influence of ascorbic acid on the composition, color and flavor properties of the wines were:

1. After three and five years storage, the concentration of SO₂ was either not different or slightly higher in the wines to which ascorbic acid had been added.

2. The color intensity and brownness of the Chardonnay wines without added ascorbic acid was higher than the wines to which ascorbic acid had been added. There was no significant difference between brownness and overall color intensity for the Riesling wines with and without ascorbic acid, although the Riesling wines with added ascorbic acid were generally higher in yellow color.
3. For both wines, at storage times of three years and more, ascorbic acid additions resulted in either no difference in aroma or wines with less oxidized and/or more fruity and fresh aromas compared with wines without ascorbic acid addition, even if all the added ascorbic acid had been depleted in the samples. When wine had been exposed to relatively high levels of oxygen (e.g. in bottles sealed with the synthetic closure), this effect was more evident.

In this trial, the addition of ascorbic acid at bottling was never detrimental, and in some cases was protective against oxidative spoilage of wines. At no time during the trial were the wines with ascorbic acid addition perceived as more oxidized than those without addition.

The researchers also reported that A420 measurements did not always appear to correlate with the brown scores obtained by visual assessment or color measures obtained by CIELAB when wines with and without ascorbic acid were compared together. In some cases, ascorbic acid addition reduced the score for oxidized aroma. Ascorbic acid addition never caused an increase in oxidized aroma.

Bottles without ascorbic acid scored higher for oxidized character at the same A420 reading. This information reinforces the point that the use of A420 measurement to give an estimate of the degree of oxidation in a wine to which ascorbic acid has been added in comparison with a sample of the same wine to which ascorbic acid has not been added may not give valid results.

Conclusions:

Ascorbic acid is known to be beneficial in protecting white wines against pinking, and may well contribute to the delay of ATA formation. Research has now shown that the addition of ascorbic acid reduces the amount of brown color and oxidized character produced in some wine during bottle maturation. In other wines, there appears to be little positive impact, but no negative impact is likely to occur. This information should give winemakers confidence to use ascorbic acid in white wine.

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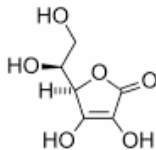
Skouroumounis GK, Kwiatkowski MJ, Francis IL, Oakey H, Capone DL, Peng Z, Duncan B, Sefton MA, Waters EJ (2005) The influence of ascorbic acid on the composition, colour and flavor properties of a Riesling and a wooded Chardonnay wine during 5 years' storage. *Australian Journal of Grape and Wine Research* **11**, 355-368

ASCORBIC ACID FRIEND OR FOE?

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New York Wine Industry Workshop
7 April 2006

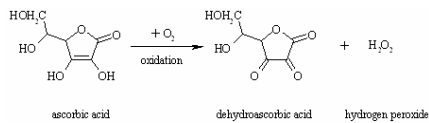
Ascorbic Acid:

- Ascorbic acid – vitamin C
- Optical isomer – erythorbic acid
- Permitted in wine since the 1950s



Ascorbic Acid:

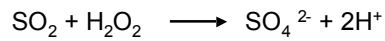
- **Reducing agent** – gives up protons (hydrogen) in reaction with oxygen



Reaction produces hydrogen peroxide

Antioxidant Properties:

- Hydrogen peroxide will react with other oxidizable materials
- Sulfur dioxide can fulfil this role



- End products of the overall reaction between oxygen, ascorbic acid and SO_2 are benign

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Impact On Rate of Reaction:

- Ascorbic acid as an intermediary **enhances the overall rate of reaction** between oxygen and sulfur dioxide
- Rapid reaction minimises interaction of oxygen with other wine components – phenols, aroma molecules
- Ascorbic acid is not a replacement for SO_2

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What Ascorbic Acid Can't Do....

- No antimicrobial properties
- No aldehyde binding properties
- Does not denature oxidative enzymes
- Cannot act alone as a protective antioxidant

Complementary adjunct to sulfur dioxide, not a substitute.....

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Benefits – Ascorbic Acid:

- Used only in white and rosé wines
- Prevents pinking, slows browning
- Converts oxidised phenols e.g. quinones to non-colored forms
- Delays oxidised aroma formation
- Delays formation of ATA characters in some, but not all, susceptible wines.....

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Questions – Ascorbic Acid Use

- Popular in Australia, use not so widespread in other countries
- Some debate in the literature on effectiveness
- Bottled wine oxidation issues in Australia led to a review of ascorbic acid use
- AWRI Oxidation research program



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AWRI Study – Peng et al (1998)

- Compared the effectiveness of combinations of ascorbic acid and SO₂ in preventing browning of white wines and model wines
- Accelerated (high temperature, air in headspace), short term and prolonged storage conditions
- Browning – measured absorbance at 420 nm
- Flavor and aroma impacts not studied

Peng et al (1998) The effect of ascorbic acid on oxidative browning of white wines and model wines AJGWR Vol 4 #3 127-135

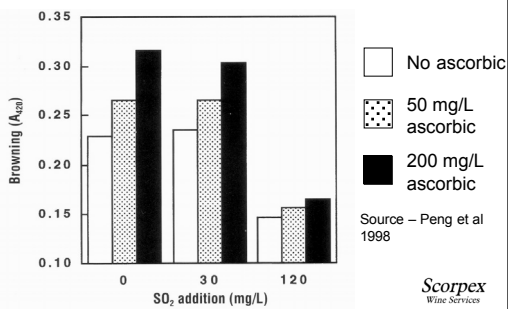
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Peng et al – Conclusions:

1. Soon after its addition, ascorbic acid **decreased** the brown color of white wines
2. With time, browning in the samples **with** added ascorbic acid was **greater** than in samples **without** added ascorbic acid
3. Under accelerated or prolonged storage conditions, the browning of model wines and white wines was invariably **enhanced** by ascorbic acid addition

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Effect of ascorbic acid on browning of a Colombar wine after 5 years of storage



Peng et al – Conclusions:

- The addition of SO₂ alone, rather than ascorbic acid alone or SO₂ plus ascorbic acid, appears to be the most effective way of protecting white wine

Take home message:

Ascorbic acid is a foe, not a friend

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Industry Reaction:

- Ascorbic acid use discontinued by some winemakers
- Pinking issues – 2000 vintage
- Continuing debate
- Further AWRI work started to provide more information.....

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Further AWRI Study:

- Oxygen added to wine in controlled amounts
- Absorbance at 420 nm measured after 15 months
- Samples also evaluated by eye
- Study included samples of the same wine with and without ascorbic acid addition

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Visual Evaluation and OD 420 nm:

mls/L O ₂	0	0	3.5	3.5	7	7
OD 420 nm	0.211	0.192	0.236	0.209	0.245	0.248
	+ ascorbate		+ ascorbate		+ ascorbate	
Number of panellists who picked this wine as browner	0	60	14	46	0	60

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New Information:

- Wines perceived as browner by eye did not always have a higher absorbance at 420 nm
- Wines with added ascorbic acid were judged to be less brown by eye in all cases

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Ascorbic Acid Effects:

- Ascorbic acid inhibits the formation of yellow and orange pigments that absorb light at wavelengths higher than 420 nm
- A420 nm is not a reliable measure of browning when comparing the oxidative status of wines with and without added ascorbic acid

Peng et al (1998) conclusions were based on A420 measurements.....

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Further Study.....

- Trial set up to investigate white wine development over five years

Variables:

- **Wine** – Chardonnay (oaked) and Riesling, with and without ascorbic acid (addition to give 100 mg/L)
- **Closures** – screw cap, cork, synthetic
- **Storage orientation** – upright and inverted

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Further Study.....

Wine impacts assessed by:

- A420
- CIELab – values L*, a* and b*, _E
- Evaluation by eye
 - Yellow, orange, brown, green – assisted by Pantone color strips.
 - Overall color intensity
- Wine analysis (SO₂)
- Sensory evaluation - aroma

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Results:

Skouroumounis, G.K., Kwiatkowski, M.J., Francis, I.L., Oakey, H., Capone, D.L., Peng, Z., Duncan, B., Sefton, M.A., Waters, E.J. (2005)

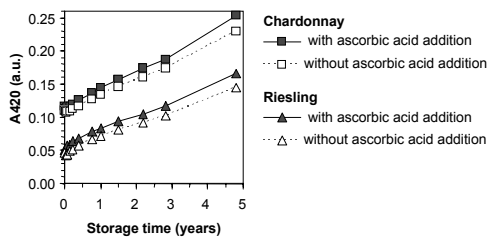
The influence of ascorbic acid on the composition, colour and flavour properties of a Riesling and wooded Chardonnay wine during five years' storage

Australian Journal of Grape and Wine Research, 11, 355-368

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A420 nm:

A420 is higher when ascorbic acid is added



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Skouroumounis et al (2005) AJGWR Vol 11 #3 355-368

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CIELab:

- Wines with ascorbic acid were higher in **yellow** but lower in **red** than wines without ascorbic acid
- **E** values exceeded 1 for all ascorbic/non-ascorbic pairs at 5 years
 - Indicates detectable visual difference

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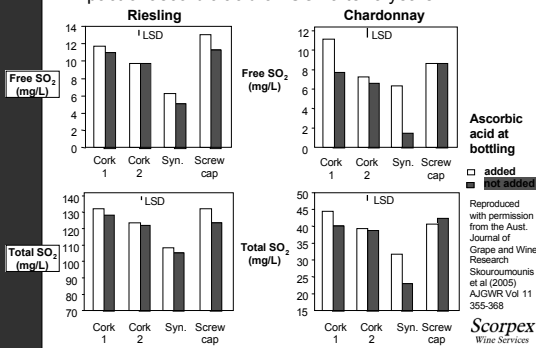
Visual:

- Paired comparison at 2 years:
- Chardonnay without ascorbic acid consistently selected as more brown
 - Riesling...no consistent trend
- Descriptive analysis at 2.5 years:
- Chardonnay – ascorbic acid gave lower brown, lower orange and higher yellow
 - Riesling - ascorbic acid gave higher yellow

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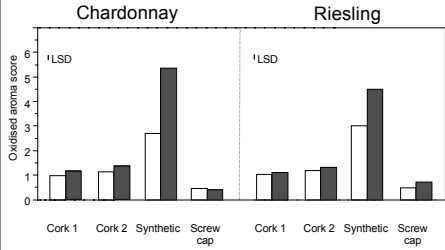
Analysis:

Impact of ascorbic acid on SO₂ after 3 years



Sensory:

Impact of ascorbic acid on oxidized score at 3 years



Ascorbic acid at bottling: added not added

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Conclusions:

- The addition of ascorbic acid resulted in wines either **not different** or **less oxidized** than wines with no addition.
- At no time were the wines with ascorbic acid addition found to be more oxidized than those without addition

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Bottom Line:

- Ascorbic acid addition is likely to be beneficial in controlling pinking and ATA
- Ascorbic acid does not promote oxidative change - it either has little effect or inhibits oxidative impact
- **Results of this work indicate that ascorbic acid can be used with confidence**

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Practical Use of Ascorbic Acid

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Grapes and Juice:

Ascorbic acid can be used on grapes and in juice.....

BUT

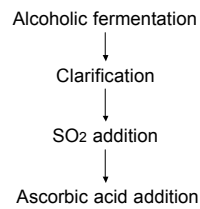
Make sure that free SO₂ is also present when active fermentation is not removing oxygen

Ascorbic acid without SO₂ has been used to promote hyperoxidation of juice....

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After Fermentation:

Ascorbic acid is often added directly after alcoholic fermentation...but make sure that sufficient SO₂ is added first.



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During Storage:

- Monitor ascorbic acid levels – iodine or DCPIP titration sufficient
- Sensitive indicator of oxygen contact
 - if ascorbic acid is depleted, oxygen contact has occurred
- Top up concentration to target level if necessary
- Watch SO₂ levels.....

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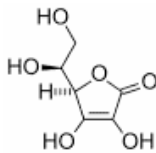
Pre and Post Bottling:

- Top up ascorbic acid concentrations to target levels
- 75-100 ppm standard often used
- Post-bottling ascorbate analysis can be valuable in reviewing
 - Oxygen pick up at bottling
 - Oxygen transfer through the closure or pack e.g. bag in box

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Ascorbic Acid – Friend or Foe?

When used wisely, ascorbic acid can often be a friend.....and not a foe.



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