White Wine Oxidation: Ascorbic acid, Sulfur Dioxide and Colour Formation

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National Wine and Grape Industry Centre is a Partnership between
Charles Sturt University, NSW Department of Primary Industries and NSW Wine Industry Association

Talk Outline

Oxygen and ……

- White Wine Quality
- Bottled White Wine
- Phenolic compounds, Sulfur dioxide and Ascorbic acid (Colour formation)
- Shelf-life
- Future Plans

Oxygen and White Wine Quality

Oxygen and White Wine

- Undesirable characters
  - Colour

COLOUR PRECURSORS $\xrightarrow{O_2}$ YELLOW/RED PIGMENTS

  - Aroma

AROMA PRECURSORS $\xrightarrow{O_2}$ OXIDATIVE AROMA

  - Taste

Bottled White Wine

Oxygen available to wine during aging

- Dissolved oxygen
- Head space oxygen
- Oxygen permeation through closure

(Oxygen Transmission Rate (OTR))

Bottled White Wine

Dissolved and Head Space Oxygen

Measurement using Presens: Luminescence measure of oxygen

- Winery 1
  - Dissolved oxygen 0.2 mg/L
  - Head space oxygen 0.5 mL (0.9 mg/L)
- Winery 2
  - Dissolved oxygen 0.8 mg/L
  - Head space oxygen 1.2 mL (2.3 mg/L)
- Winery 3
  - Dissolved oxygen 0.1 mg/L
  - Head space oxygen 2.2 mL (4.1 mg/L)

O'Brien et al. 2009 Wine Industry Journal 24(1) 24

Bottled White Wine

Permeation through closure (OTR)

- Synthetic closures
  - 30-45 µL/day for first month*
  - 6-13 µL/day afterwards
- Cork closures
  - 25-40 µL/day for the first month*
  - 2-6 µL/day remainder of first year
  - 0.1-2 µL/day next two years
- Screw cap
  - < 1 µL/day after day 2

Measurement using colorimetric measurements of Indigo Carmine solution in wine bottle

*Consequence of bottling Process

Lopes et al. 2007
J Ag Food Chem
55 5167-5170

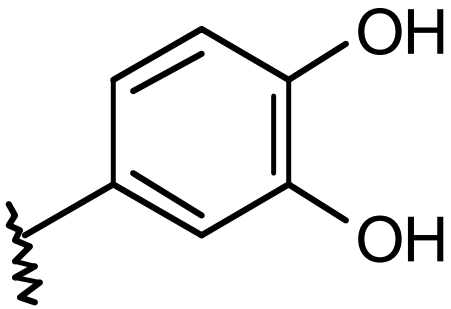
Oxygen and Phenolic Compounds

COMPLEX REACTION DEPICTED BY SIMPLE EQUATION

Oxygen

O_2

\+



Phenol

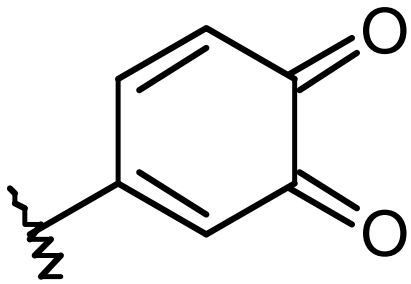
Metal ions

Reactive Intermediates

Hydrogen Peroxide

H_2O_2

\+



ortho-Quinone

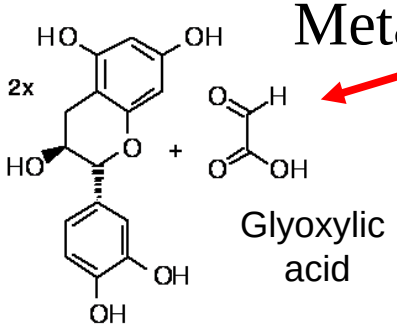
Oxidative pigment - example

Tartaric acid

Metals

+

Hydrogen peroxide



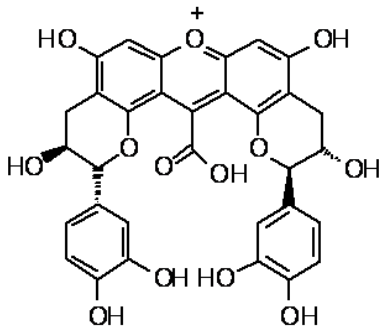
Glyoxylic acid

1 **2**

(+)-Catechin

skins and seeds

Oxidation



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Xanthylium cation

Yellow Pigment

Oxygen and Sulfur Dioxide

Hydrogen Peroxide

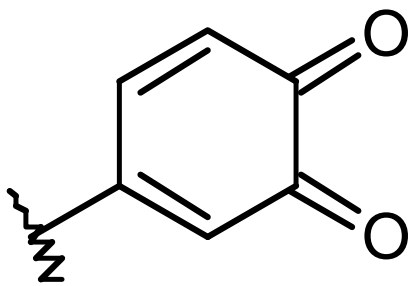
H_2O_2

HSO_3^-

Bisulfite

Sulfuric acid

H_2SO_4

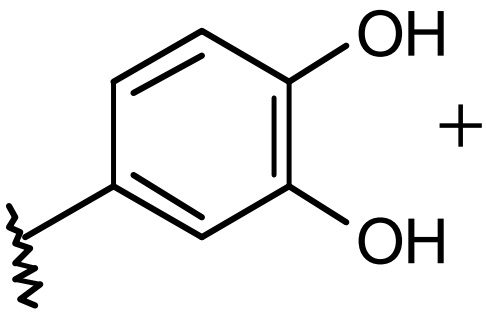


ortho-Quinone

HSO_3^-

Bisulfite

H_3O^+



+ H_2SO_4

Phenol

Oxygen and Sulfur Dioxide

Theoretically:

- 1 molecule of oxygen consumes

2 molecules of sulfur dioxide

- 1 mg/L oxygen (31.3 µM) consumes

4 mg/L sulfur dioxide (62.5 µM)

- Experimentally:

oxygen : sulfur dioxide = 1:2

Danilewicz et al. (2008) Am J Enol. Vitic. 59:2 128

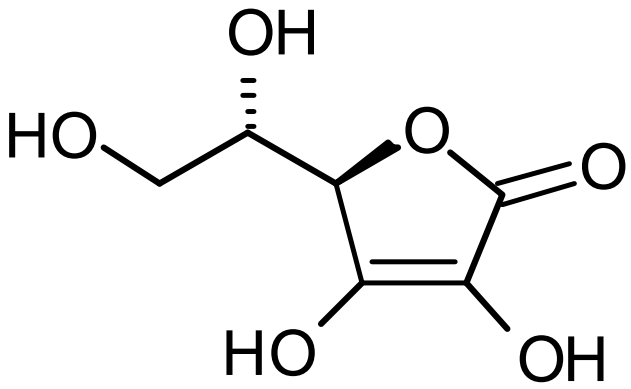
Oxygen and Ascorbic Acid

More efficient than SO_2 at scavenging oxygen ‘directly’

Oxygen

O_2

\+



Ascorbic acid

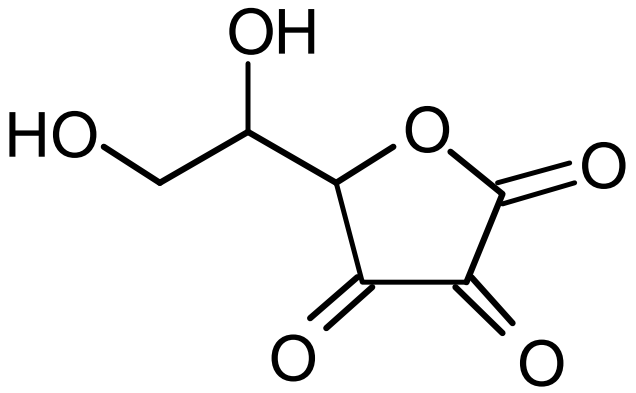
Metal ions

Reactive Intermediates

Hydrogen Peroxide

H_2O_2

\+



Dehydroascorbic acid

Oxygen and Ascorbic acid

Hydrogen Peroxide

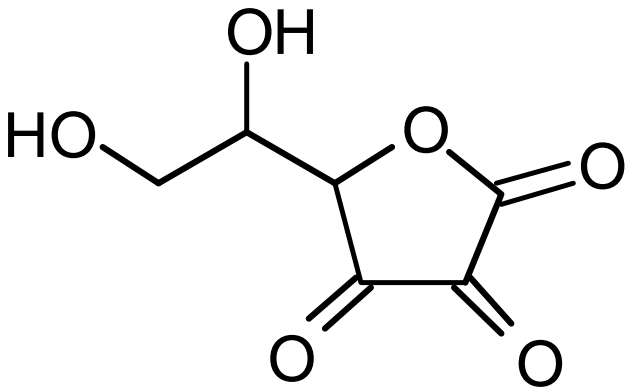
H_2O_2

HSO_3^-

Bisulfite

Sulfuric acid

H_2SO_4



HSO_3^-

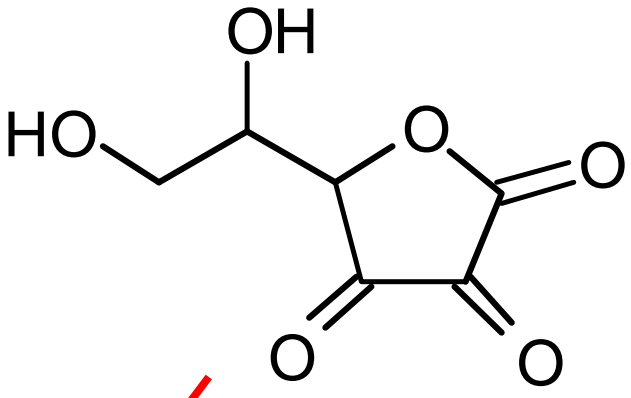
Bisulfite

H_3O^+

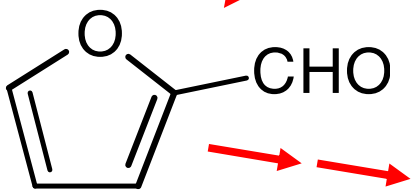
?

Dehydroascorbic acid

Fate of Dehydroascorbic Acid



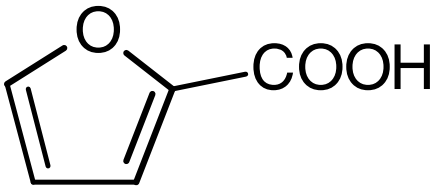
Intermediate product



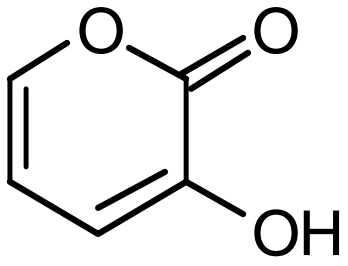
Furfural

Main products

Terminal products



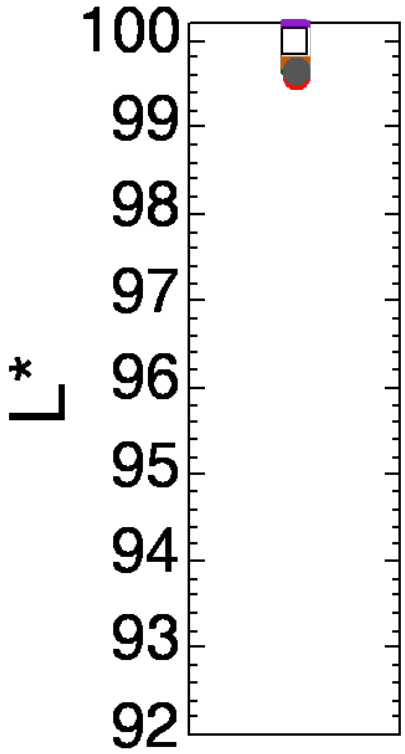
Furonic acid

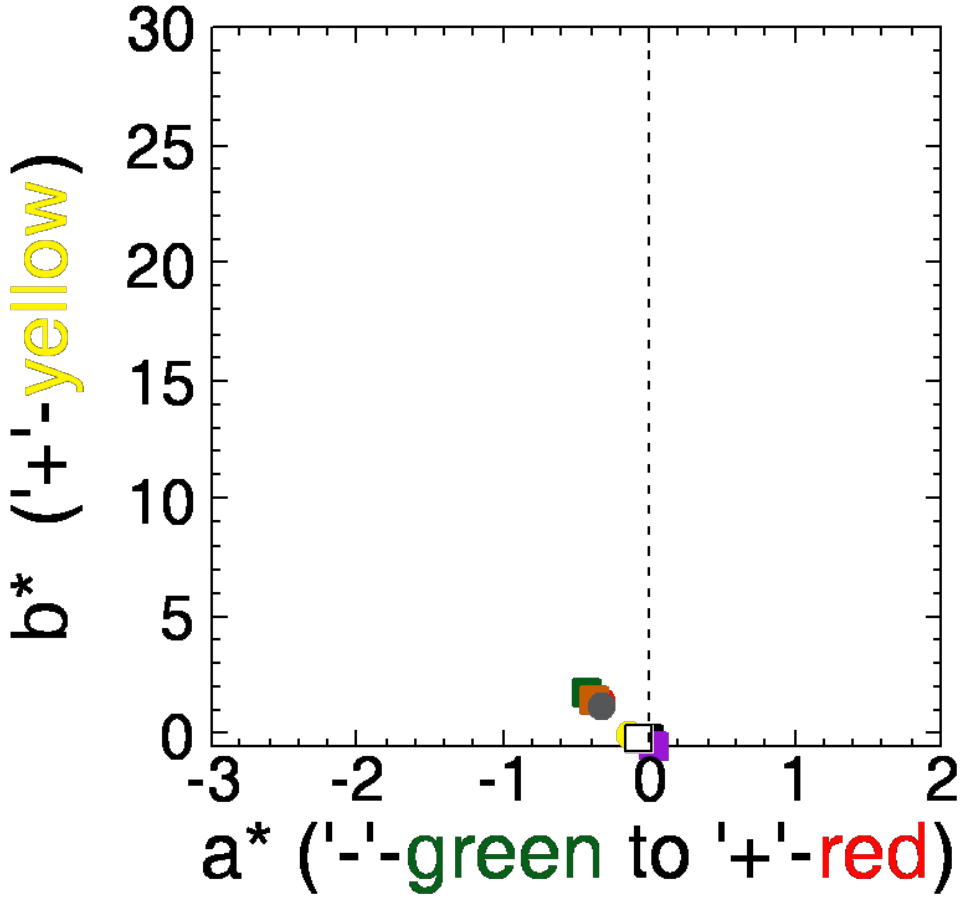


3-hydroxy-2-pyrone

Ascorbic acid and Phenolic Compounds

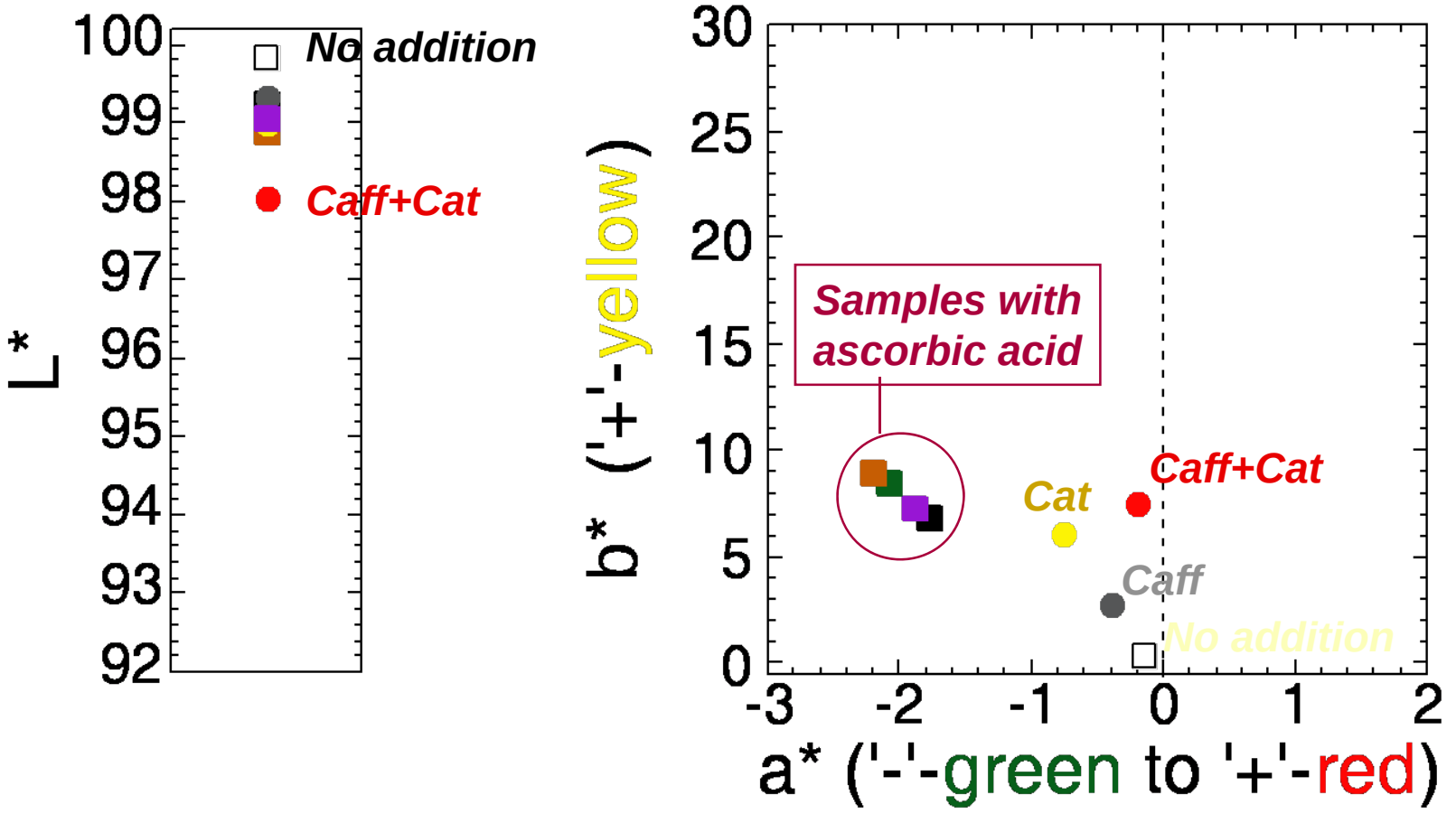
CIELab analysis - Day 0





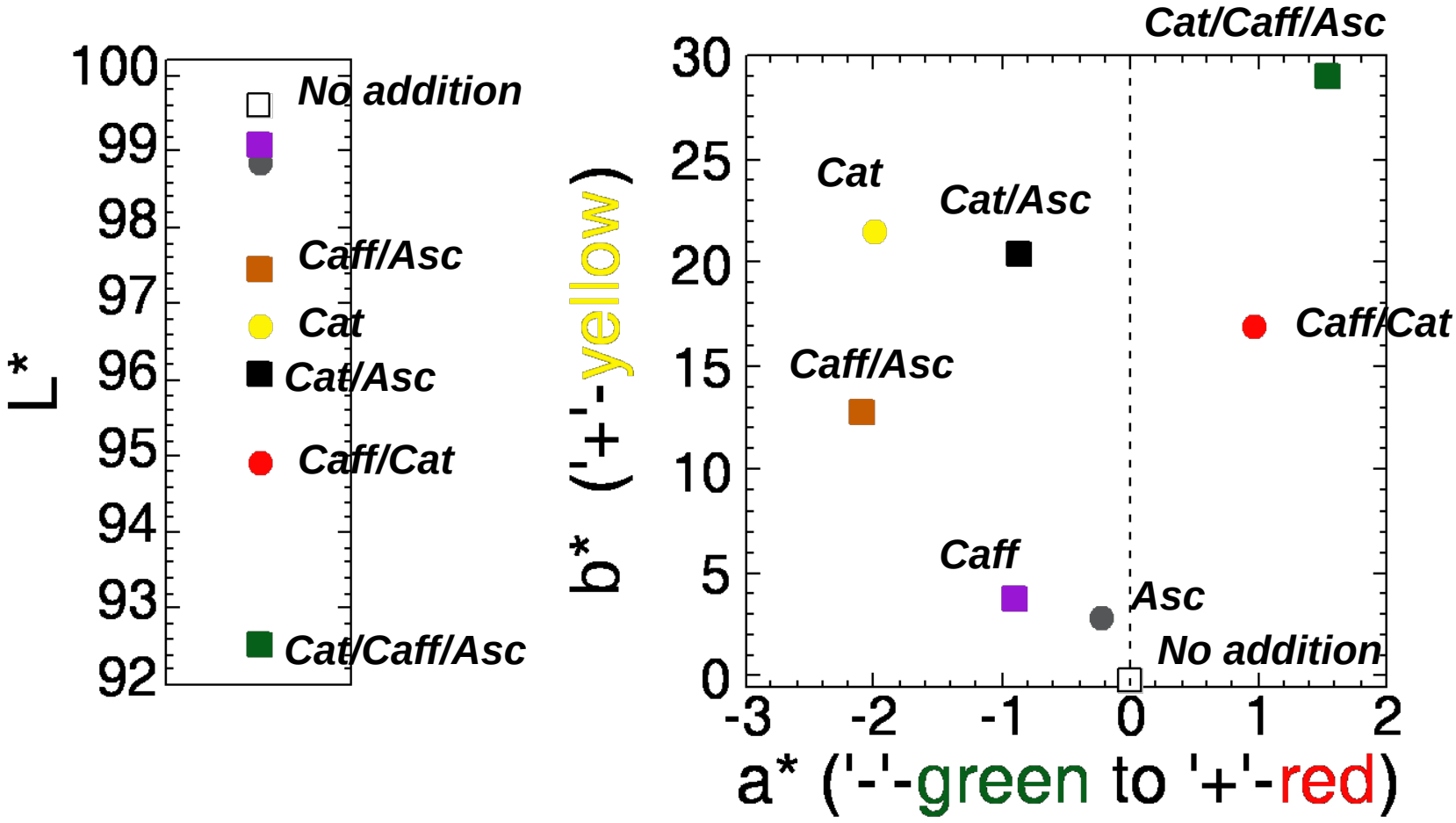
Ascorbic acid and Phenolic Compounds

CIELab analysis - Day 8

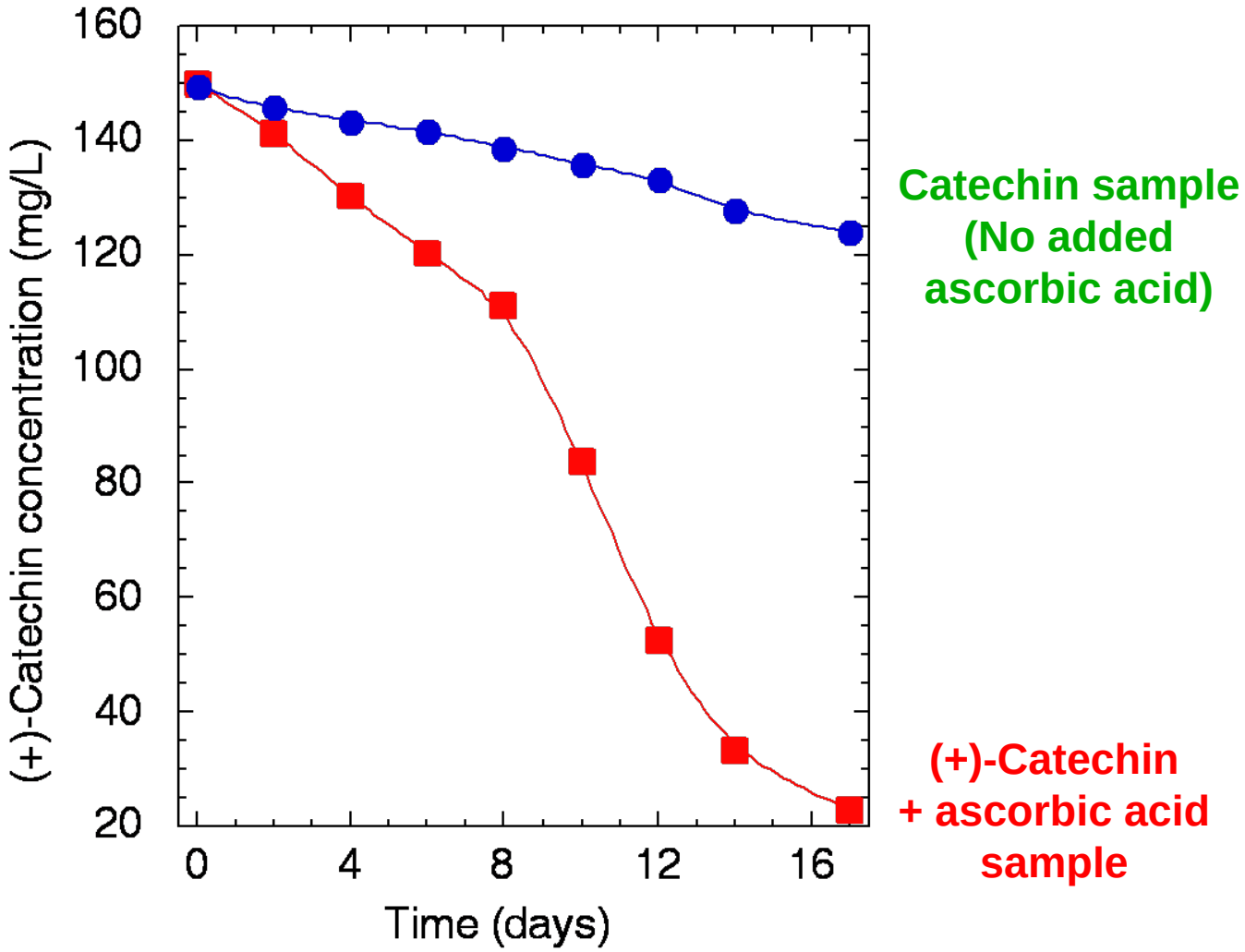


Ascorbic acid and Phenolic Compounds

CIELab analysis - Day 17

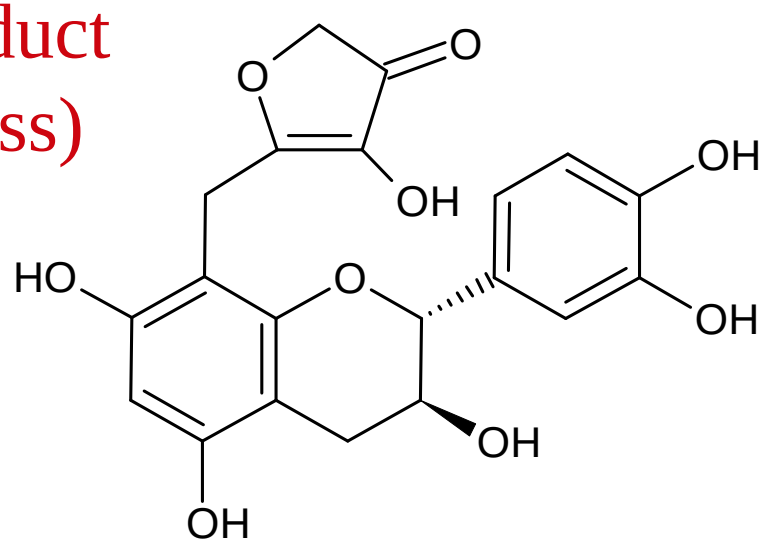


Ascorbic acid and Catechin



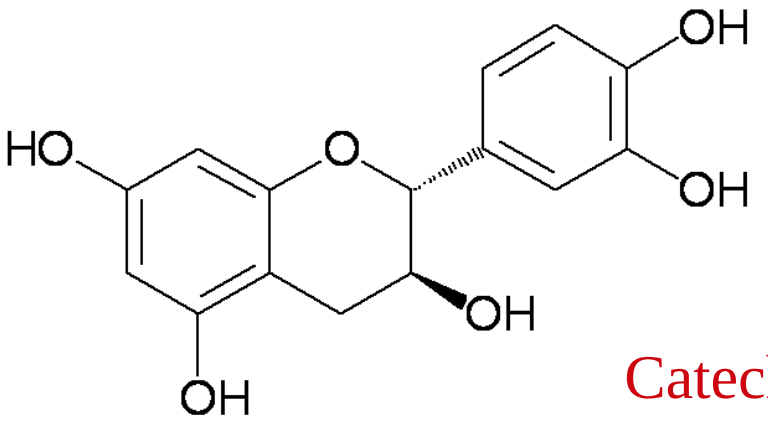
Ascorbic acid and Catechin

Main product
(colourless)



Xylosone

Dehydroascorbic acid



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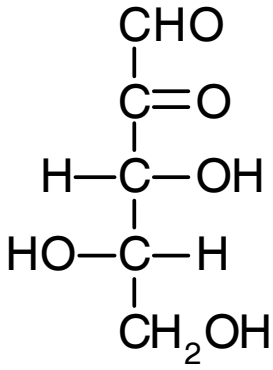
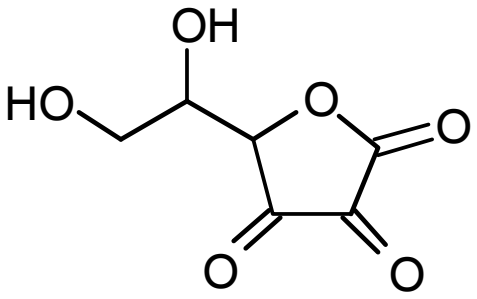
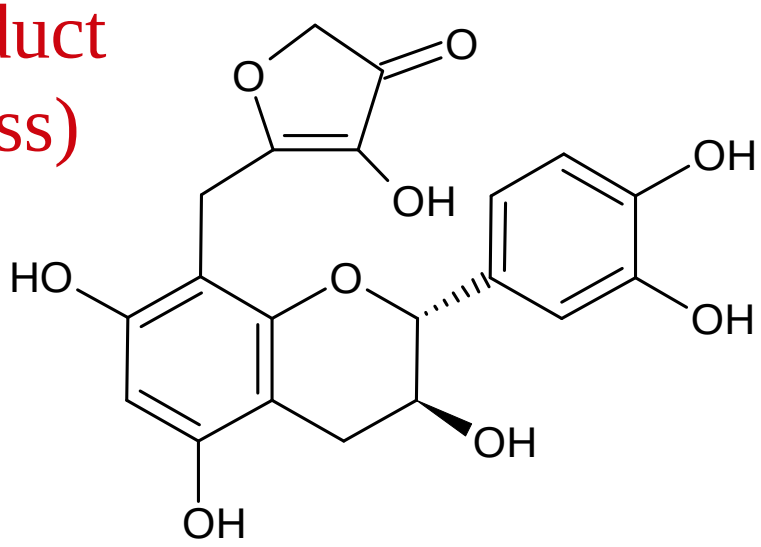




Catechin

Ascorbic acid and Catechin

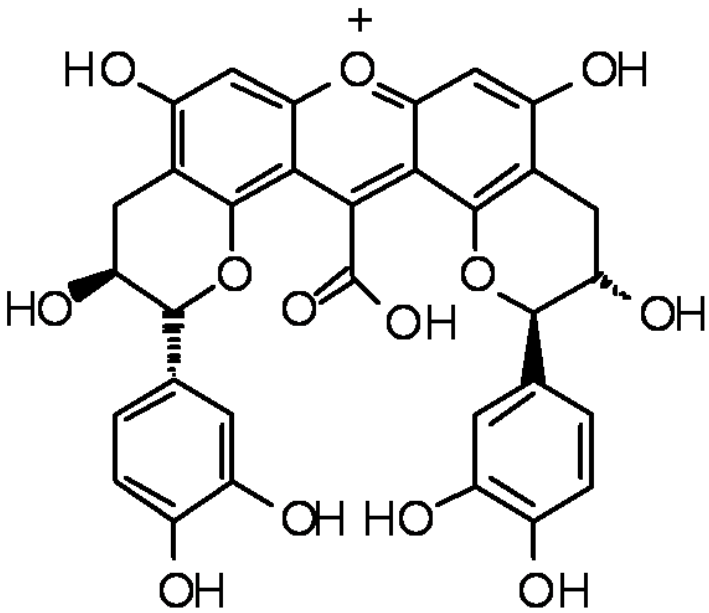
Main product
(colourless)



Pigment precursor

O_2

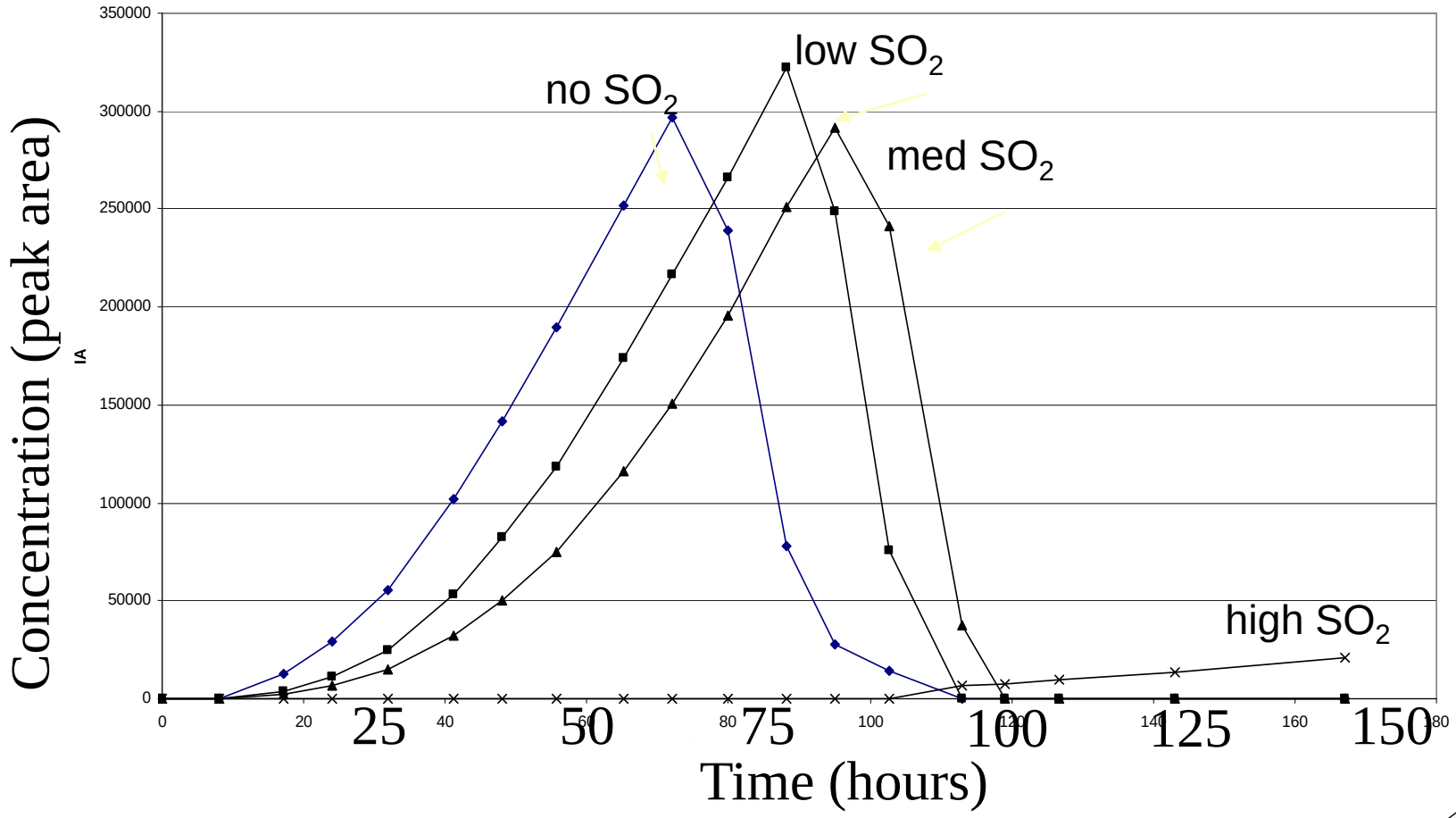
Catechin



Yellow Pigment

On depletion of ascorbic acid

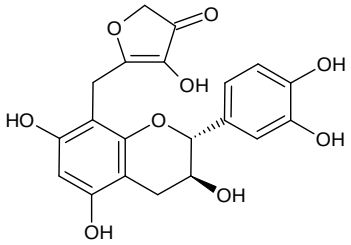
Pigment precursor concentration: Effect of sulfur dioxide concentration



Low SO_2 (45 mg/L) - depleted before 24 hours

Med SO_2 (90 mg/L) - depleted before 48 hours

High SO_2 (900 mg/L) - still present at 180 hours



Xylosone and Sulfur Dioxide

- Dissociation constant for xylosone and sulfur dioxide = 1.4×10^{-3} (pH 3.3)*
- Considerably weaker binder than acetaldehyde (1.5×10^{-6})

- xylosone : sulfur dioxide = 4:1
- 1 mg/L xylosone : 0.1 mg/L sulfur dioxide

* Burroughs and Sparks 1973 J Sci Food Agric 24 187

Oxygen and Ascorbic acid

Experimentally:

ascorbic acid : sulfur dioxide = 1:1.7

Therefore

- 1 molecule of oxygen consumes

1 molecule of ascorbic acid and

1.7 molecules of sulfur dioxide

- 1.0 mg/L oxygen (31.3 μM) consumes

5.5 mg/L ascorbic acid (31.3 μM) and

3.4 mg/L sulfur dioxide (53.2 μM)

Bradshaw et al. (2004) J Sci Food Agric 84 318

Winery 3 - Shelf life - Rough Calculations*
at bottling - 100 mg/L ascorbic acid
- 30 mg/L free sulfur dioxide

- Dissolved oxygen 0.1 mg/L
- Head space oxygen 2.2 mL (4.1 mg/L)
- 4.2 mg/L O_2 could eventually consume
  - 23 mg/L ascorbic acid
  - 14 mg/L sulfur dioxide
- Remaining
  - 77 mg/L ascorbic acid
  - 16 mg/L sulfur dioxide

* Many assumptions

Winery 3 - Shelf life - Rough Calculations*

After bottling - 77 mg/L ascorbic acid

- 16 mg/L free sulfur dioxide

- If 10 mg/L free sulfur dioxide is critical level

- Synthetic closure (OTR) ~10µL O_2/day
  - equates to 14 µg O_2 /day
  - consumption of 76 µg/L SO_2 /day
  - ~80 days to fall under 10 mg/L free sulfur dioxide

* Many assumptions

Winery 3 - Shelf life - Rough Calculations*

After bottling - 77 mg/L ascorbic acid

- 16 mg/L free sulfur dioxide

- If 10 mg/L free sulfur dioxide is critical level

- Crown seal (OTR) <1 µL O_2/day
  - equates to 1.4 µg/L O_2 /day
  - consumption of 5.6 µg/L SO_2 /day
  - 1070 days to fall under 10 mg/L free sulfur dioxide (3 years)

* Many assumptions

Future Work

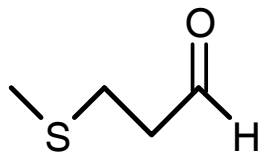
- Oxidation aroma/colour and Semillon

- Link to vineyard practises - some amino acids are precursors to oxidative aromas

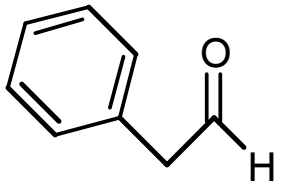
- Efficiency of ascorbic acid/sulfur dioxide to prevent production of oxidation aromas compared to sulfur dioxide alone

Cullere et al. 2007 J Ag Food Chem 55 867

a

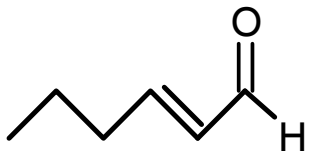


Methional



Phenylacetaldehyde

Compounds associated with oxidative spoilage aroma

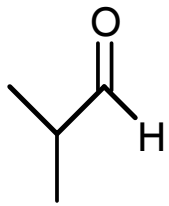


(E)-2-hexenal

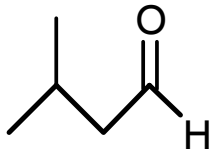
(E)-2-octenal

(E)-2-alkenals

b



methylpropanal



3-methylbutanal

branched aliphatic aldehydes

Compounds associated with masking oxidative spoilage aroma (Red wine only)

Conclusions

- New techniques may eventually allow more accurate predictors of wine shelf life.
- Ascorbic acid degradation better understood.
- Its ability to produce pigments in the absence of sulfur dioxide is understood.

Wine Oxidation Group

- Geoffrey Scollary
- Célia Barril
- Paul Prenzler
- Leigh Schmidtke
- Visiting research students
  - Jochen Vestner