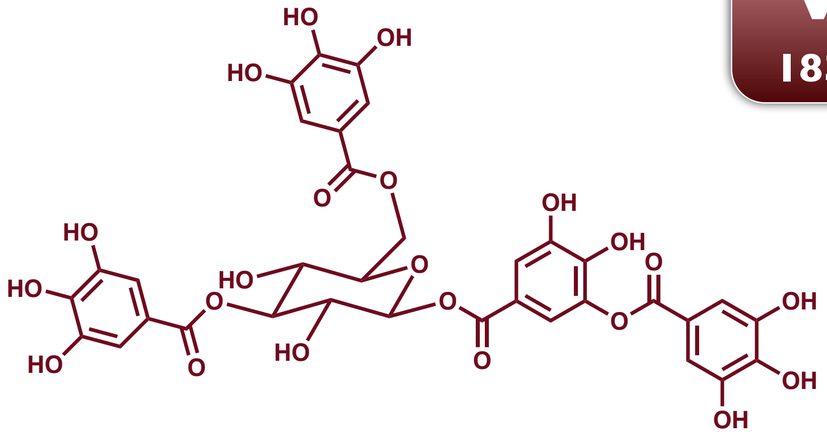
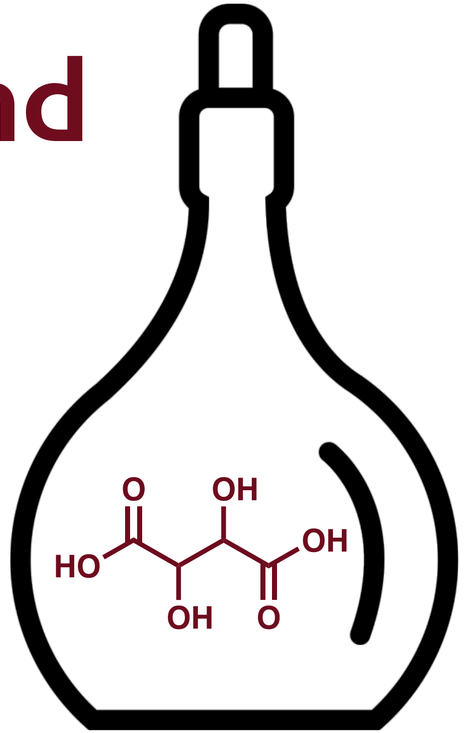
Message in a Bottle: The Chemistry of Grapes and





Greg Cook
4e Winery

Montana Grape and Winery Association Conference
6 April 2018

4e winery Mapleton, North Dakota

What is Wine?

- "Wine is a living liquid containing no preservatives. Its life cycle comprises youth, maturity, old age and death. When not treated with reasonable respect it will sicken and die."

  ~ *Julia Child*

TTB Definition for tax purposes

- The term "wine" means "any class and type of product that is . .
- (A) is made on a bonded wine premises from grapes, other fruits or agricultural products;
- (B) contains not less than 0.5 percent alcohol by volume and not more than 24 percent alcohol by volume, including all dilutions and mixtures thereof by whatever process produced; and
- (C) is for nonindustrial use."

How Wine is Made (from grapes)

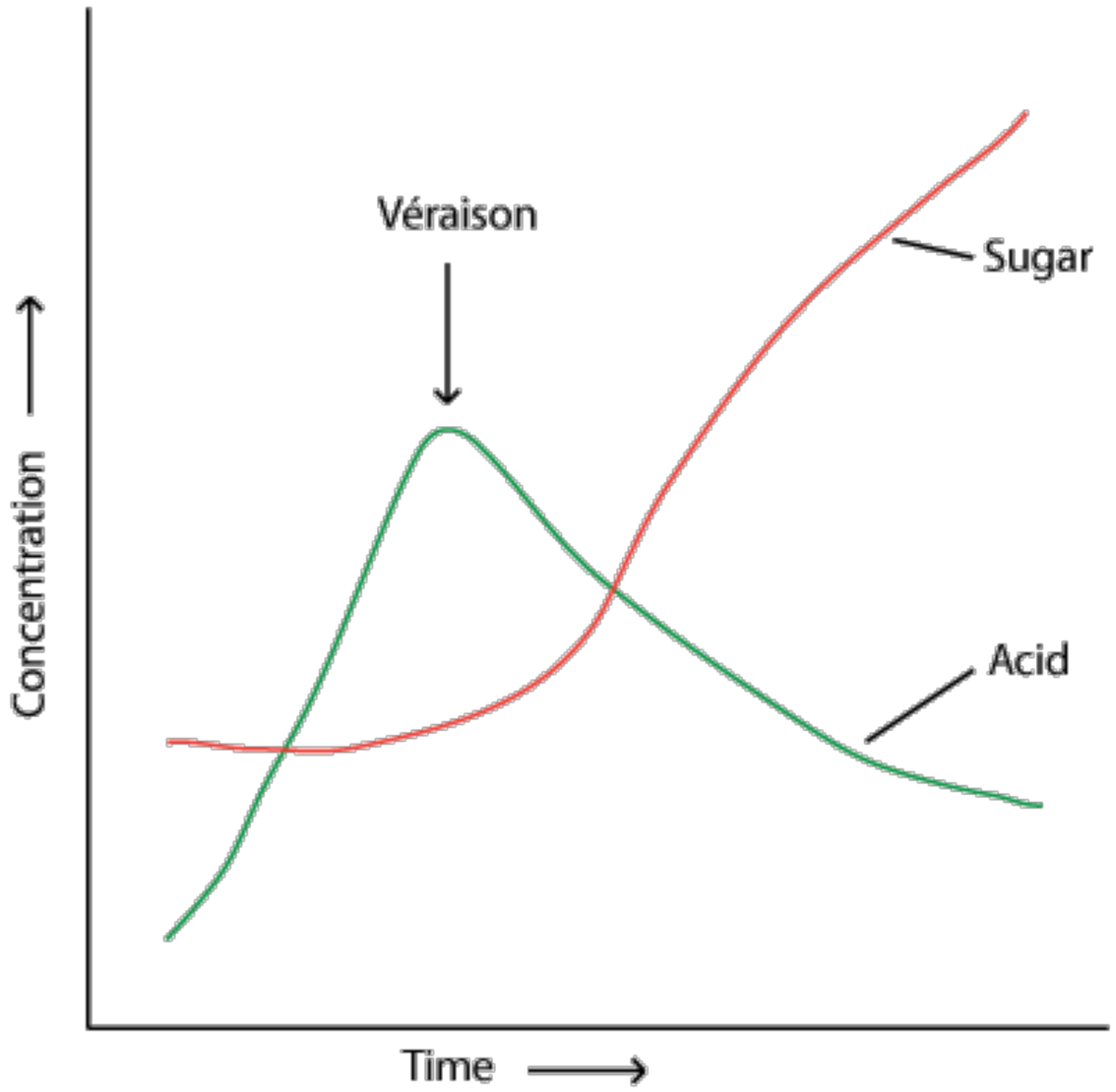
- Grapes are grown
- Grapes are crushed
- White wines - juice is pressed away from skins
- Red wines - fermented with the skins
- Yeast is added to the must
- Fermentation ensues converting sugar to alcohol
- ML fermentation may be done converting malic to lactic acid
- After fermentation wine is allowed to clear
- Wine is aged, often in oak barrels, and bottled

Components of grapes

- 70-80% Water
- 18-30% Sugars
- 0.3-1.5% Acids
- ~1% Proteins/Amino Acids
- ~1% Esters, Polyphenols, Vitamins, Minerals, Flavonoids, Tannins

Grape Ripening

- After veraison, sugars rise and acids fall.
- Tannins, colors and flavor molecules also rise and fall throughout ripening.



Changes in sugar and acid levels as a grape berry grows

Anatomy of a Grape

Stems, Seeds
Astringent
Tannins

Skins
Anthocyanins
Quercetin
Resveratrol
Tannins
Catechins

Pulp
Sugars
Acids
Water

The Critical Chemistry

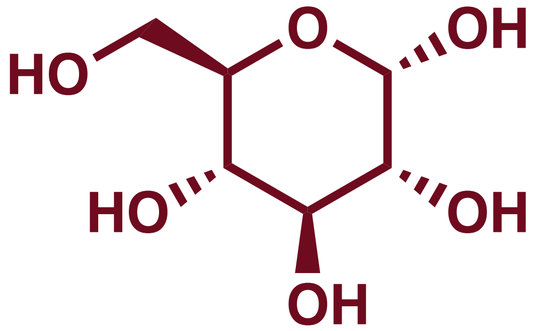
- $C_6H_{12}O_6 \xrightarrow{\text{yeast}} 2\ C_2H_5OH + 2\ CO_2$

  (sugar) (ethanol)

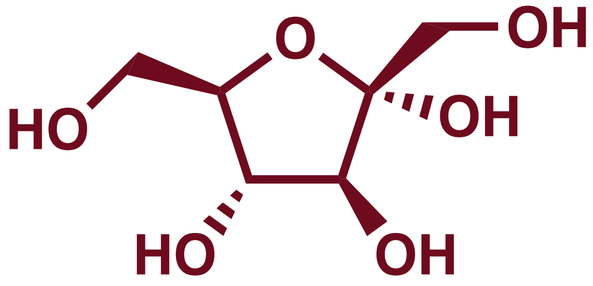
- Sugar level in grapes = °Brix
  - 1° Brix = 1% sugar ⟶ 0.55% ethanol

Fermentable sugars

- At harvest glucose and fructose levels are about even
- Over-ripened grapes have more fructose
- Fructose tastes about 2x's as sweet as glucose
- Glucose is the first sugar metabolized by yeast
- Non-fermentable sugars may be present - Arabinose, Rhamnose, Xylose



D-glucose



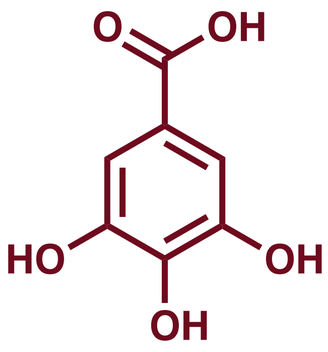
D-fructose

Tannins

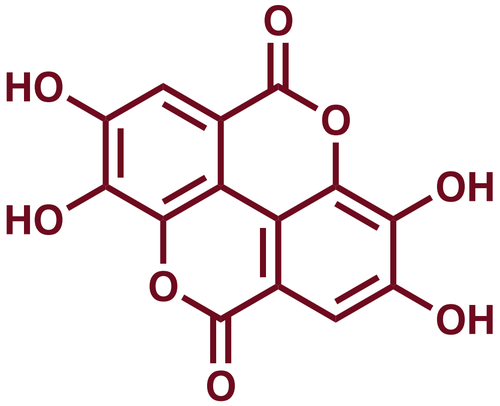
- Plant Polyphenols - astringent and bitter flavors, antioxidants
- The term *tannin* derived from wood tannins used to tan animal hides into leather
  - now refers to any large polyphenolic compounds that can bind to proteins
- In grapes found in the skins, seeds and stems
- Two main kinds in grapes - hydolyzable and non-hydrolyzable (condensed)
- Polymerize over time and drop out, softening a wine

Hydrolyzable Tannins

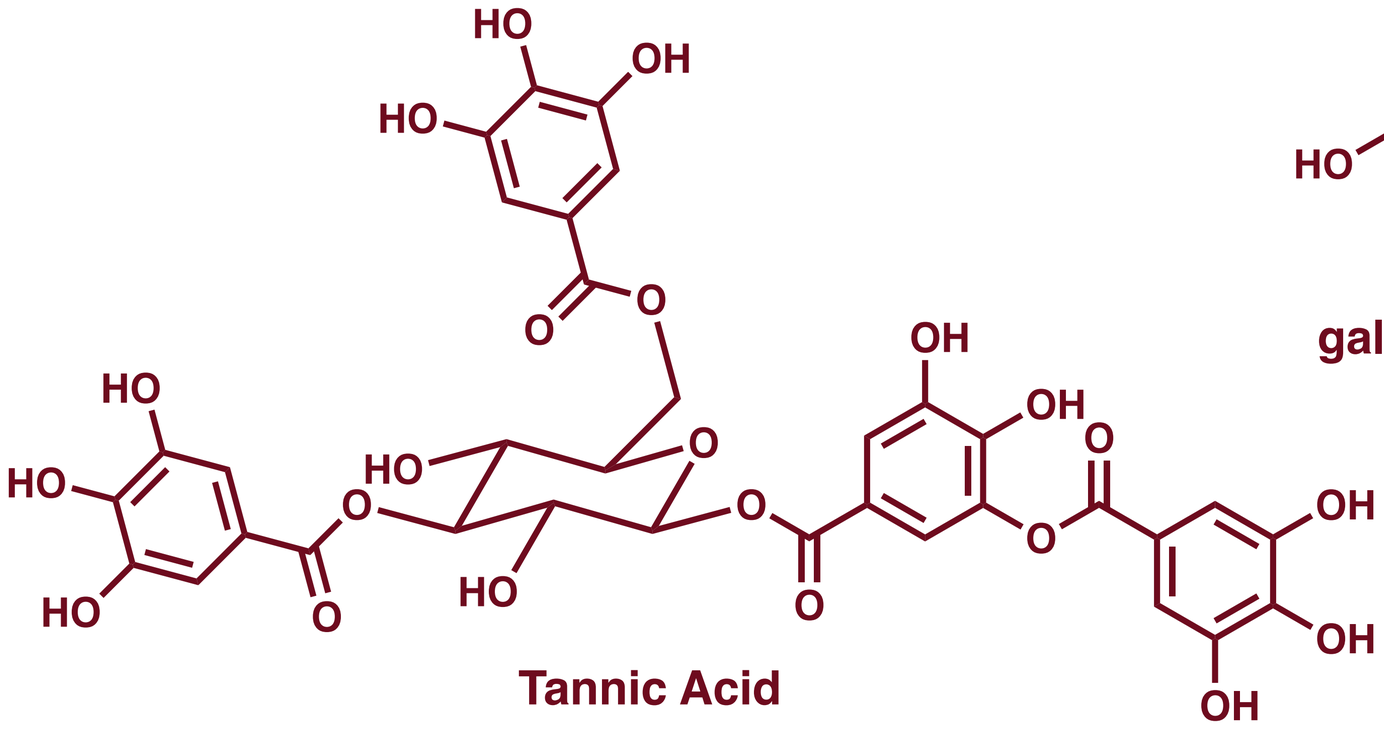
- Hydrolyzable tannins have a carbohydrate core bound to compounds like gallic acid or ellagic acid



gallic acid



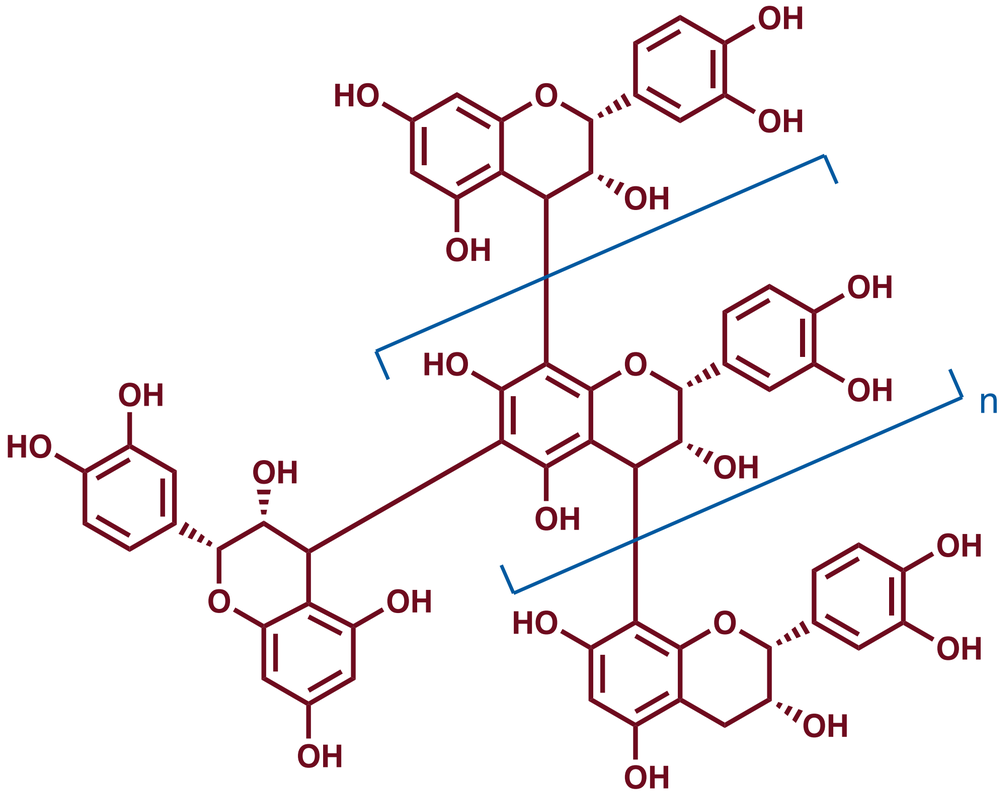
ellagic acid

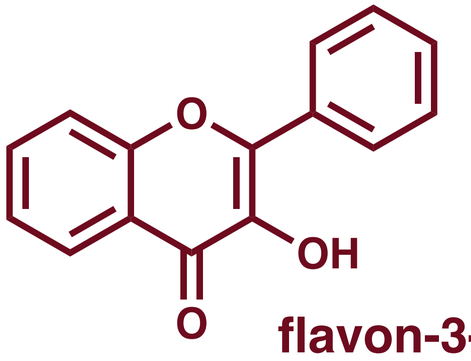


Tannic Acid

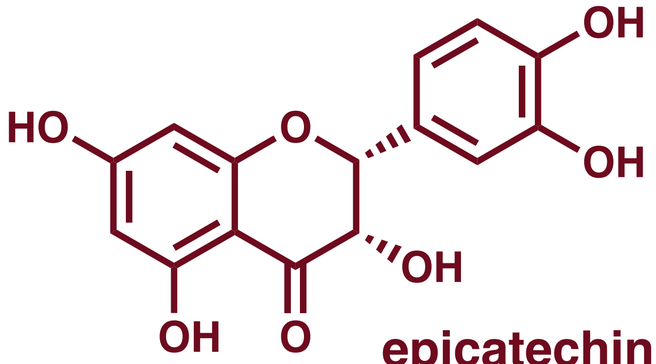
Condensed

- Condensed tannins are oligomers of flavonols largely responsible for colors, astringency, aging potential.

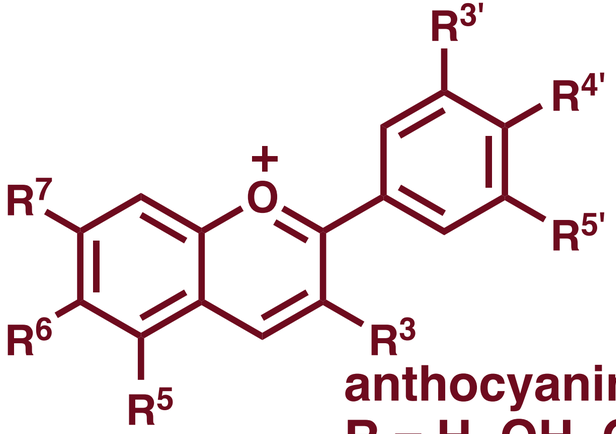




flavon-3-ol



epicatechin



anthocyanins
R = H, OH, OCH_3

Wine Color



White Wines

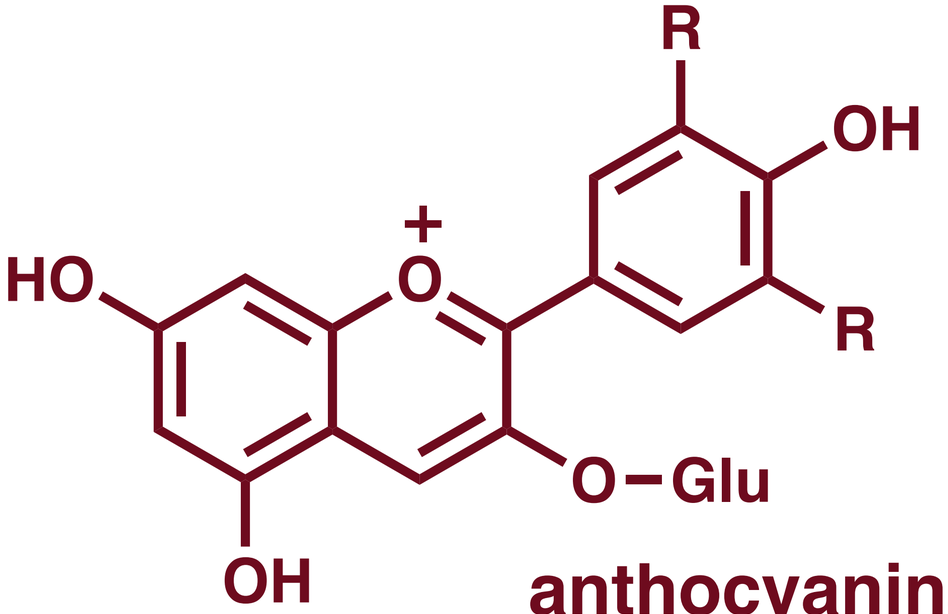
- Green
- Straw
- Gold
- Yellow
- Amber
- Brown

Red Wines

- Purple
- Ruby Red
- Deep Red
- Brick
- Mahogany
- Brown

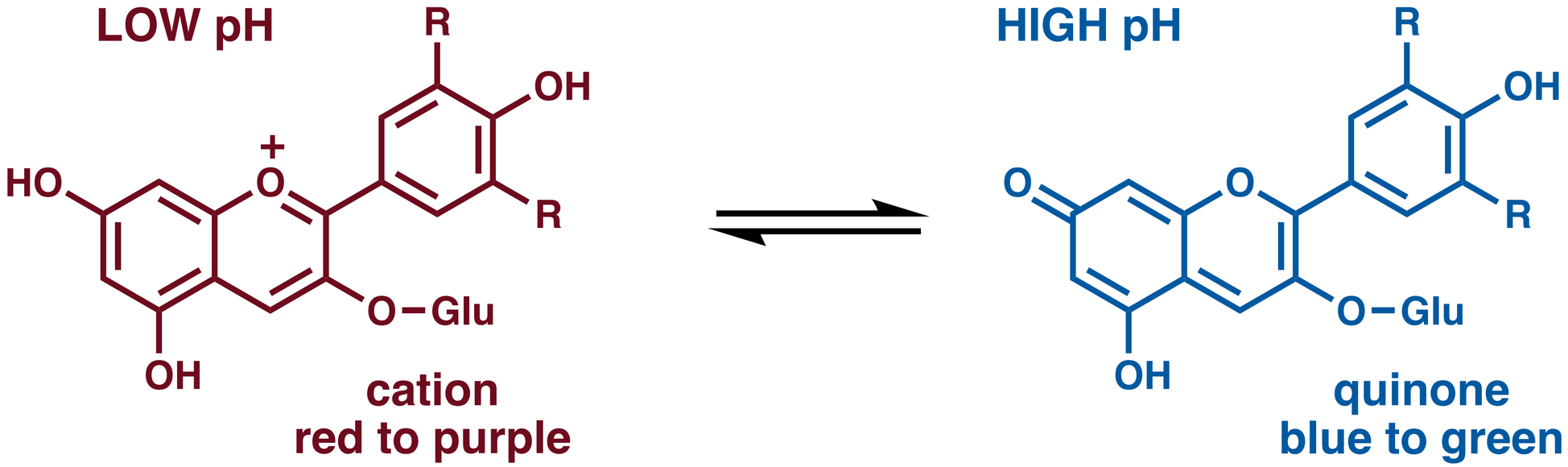
Color in Wine

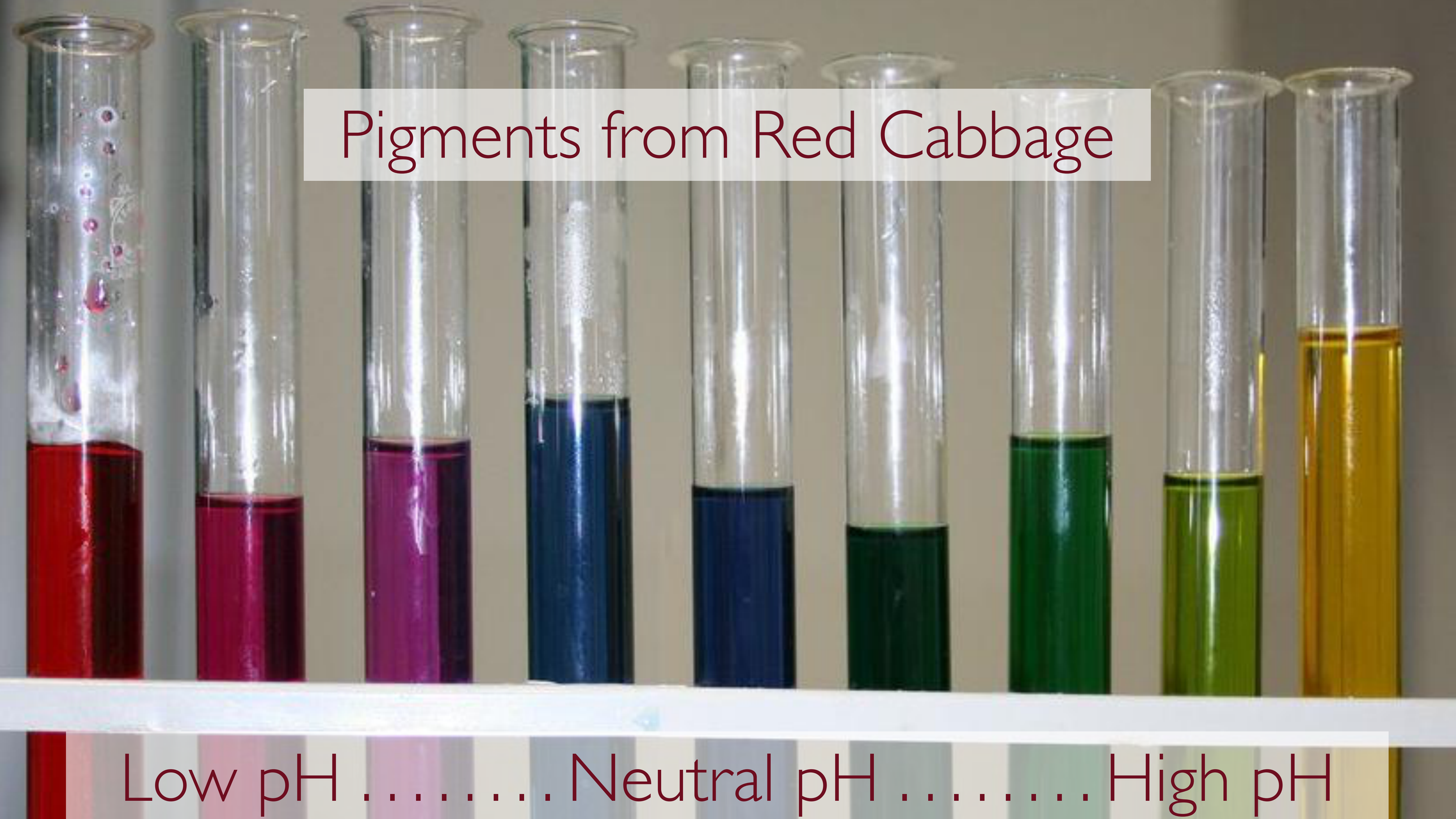
- Phenolic Compounds - anthocyanins
- Found mostly in the skins
- Anthocyanins are water soluble pigments - purple, red, blue colors (depends on pH)
- odorless and nearly flavorless
- antioxidants
- react with tannins
  pyruvic acid and acetaldehyde



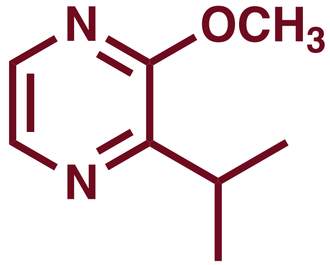
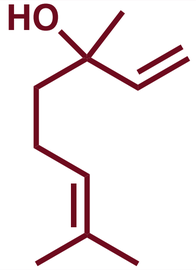
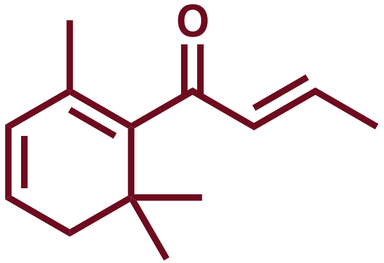
anthocyanins

CHEMISTRY DEMONSTRATION



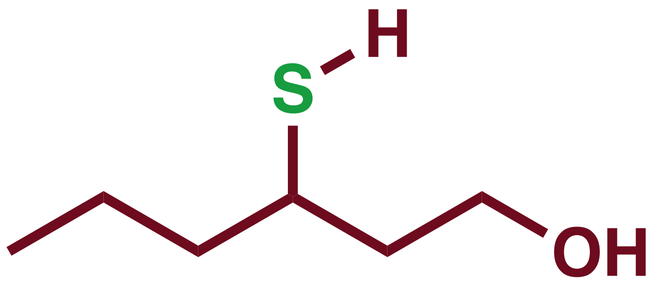

Pigments from Red Cabbage
Low pH ..... Neutral pH ..... High pH

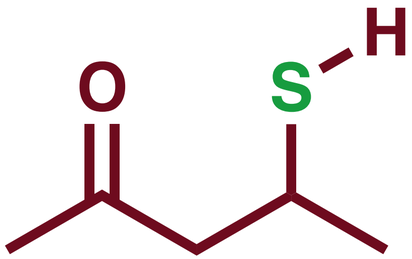
Flavors and Aromas in Wine

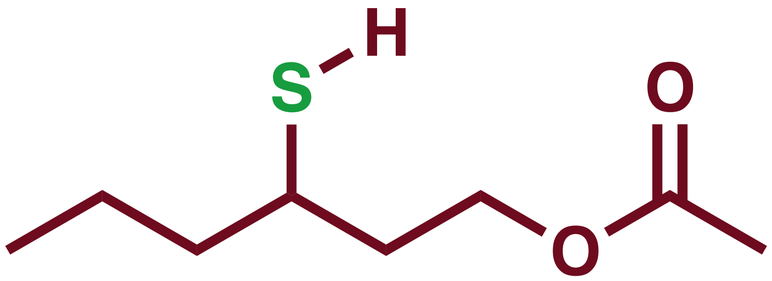
methoxypyrazines		herbaceous, grassy, bell pepper, asparagus	cabernet sauvignon sauvignon blanc
monoterpenes (geraniol, nerol, linalool)		floral aromatics	gewürztraminer muscat riesling
norisoprenoids (vanillin, demascenone, zingerone)		spices, raspberry, vanilla, rose oil	chardonnay syrah pinot noir
mercaptans	 	rotten eggs, rotten cabbage, cat urine, tropical fruits, rubber	most wines can have these

4e winery Mapleton, North Dakota

Is it a flaw?





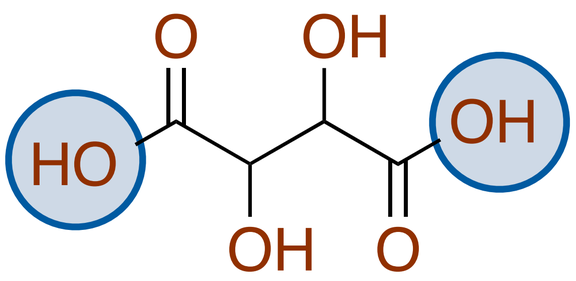


Acidity

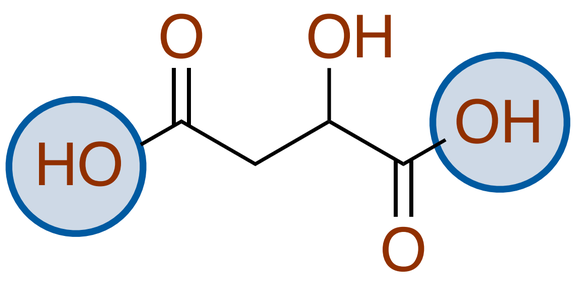
Item	pH
Lemon Juice	1.8-2.3
Distilled Vinegar (5%)	2.4-3.0
Coca Cola	2.8-3.2
Wine	**3.0-3.5**
Tomato juice	4.1-4.6
Coffee	5.5
Milk	6.8
Water	7.0

Acids in Grapes

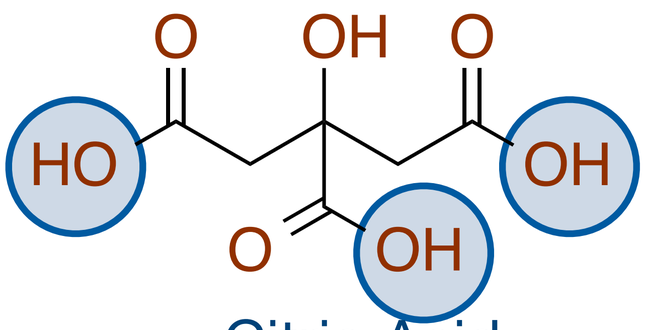
- Primary acids are tartaric acid and malic acid. Some citric acid.



Tartaric Acid



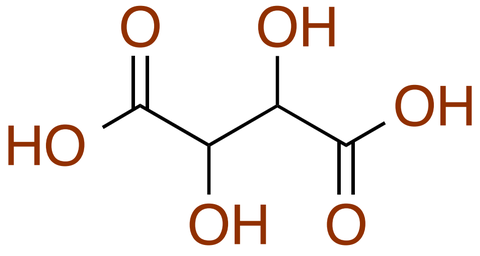
Malic Acid



Citric Acid

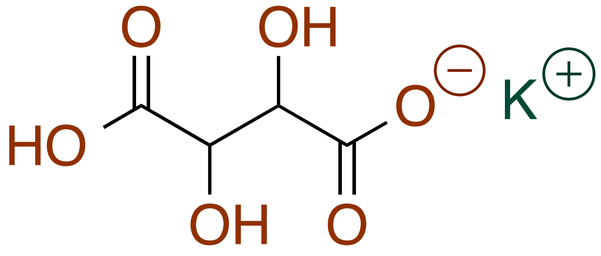
Potassium bitartrate

- "Wine Diamonds" are potassium bitartrate



Tartaric Acid

potassium salts
buffers



potassium bitartrate

Why do we need to worry about acid?

- Acid provides brightness and texture to wine
- Wine low in acid tastes flat and dull
- Affects the color (anthocyanins)
- Provides microbial stability (affects SO_2)
- Wine acids can cause aesthetic problems for wines (precipitates)
- Cold climate hybrid grapes are generally high in acids

Why Sulfites?

- Sulfite is added to provide SO_2 - antibacterial, kills native yeasts and prevents oxidation
- Naturally produced in wine ~ 6 ppm
- Most commercial wine contains 10-40 ppm
- US levels allowed - up to 350 ppm
- Can react with anthocyanins reducing color

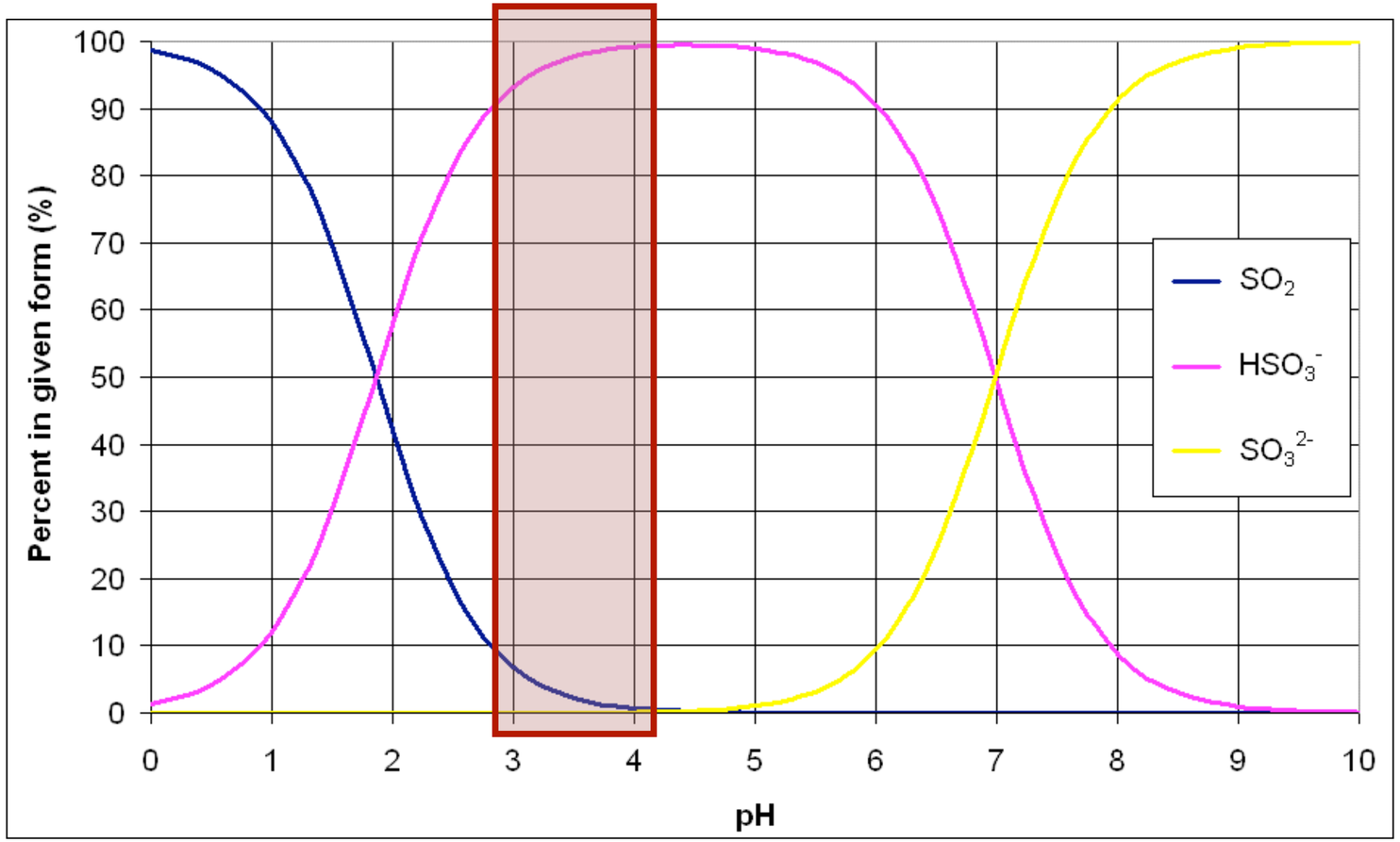
pH and SO_2

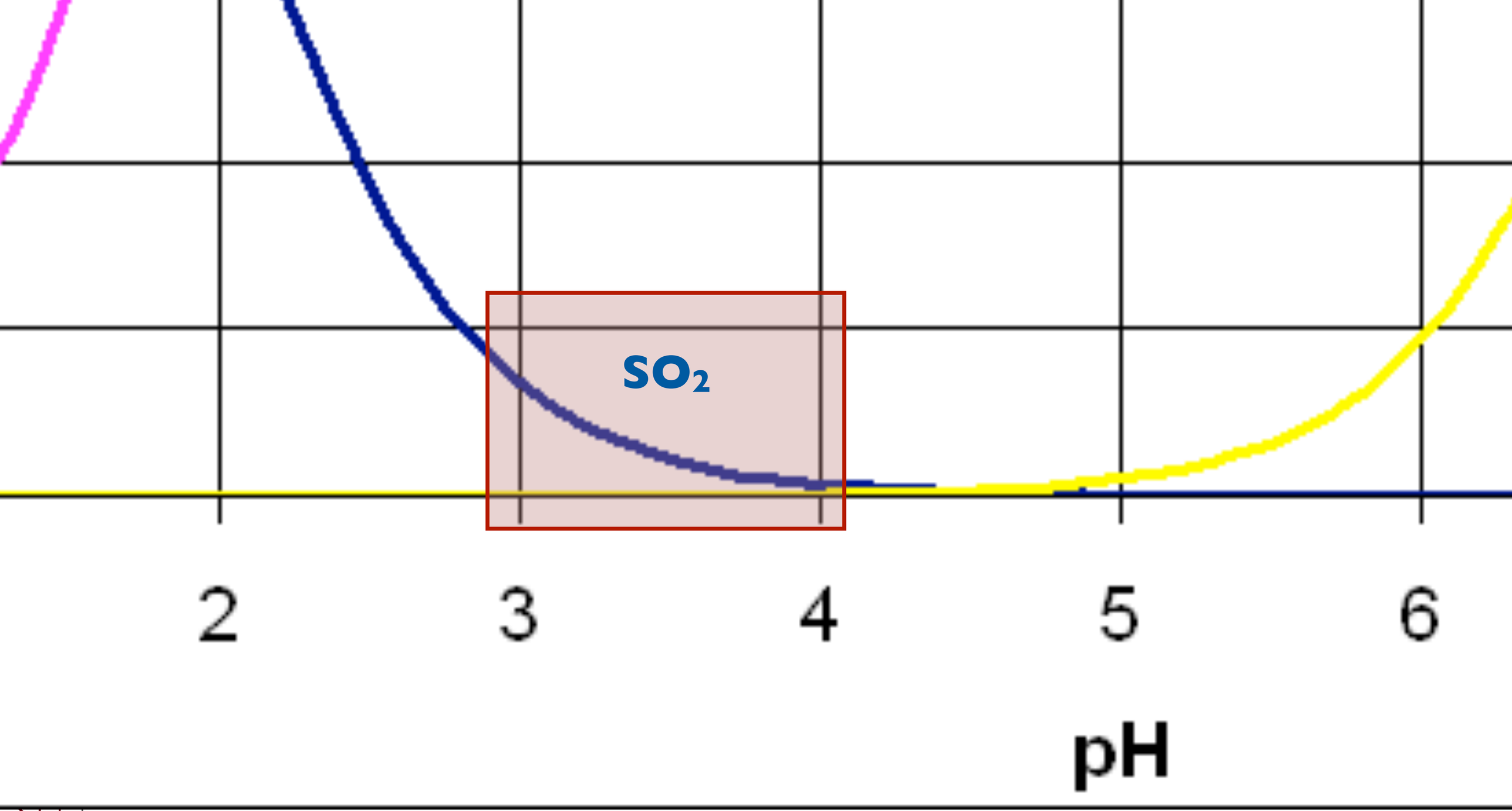
$$SO_2 + H_2O \rightleftharpoons H^+ + HSO_3^- \rightleftharpoons 2H^+ + SO_3^=$$

sulfur dioxide

bisulfite

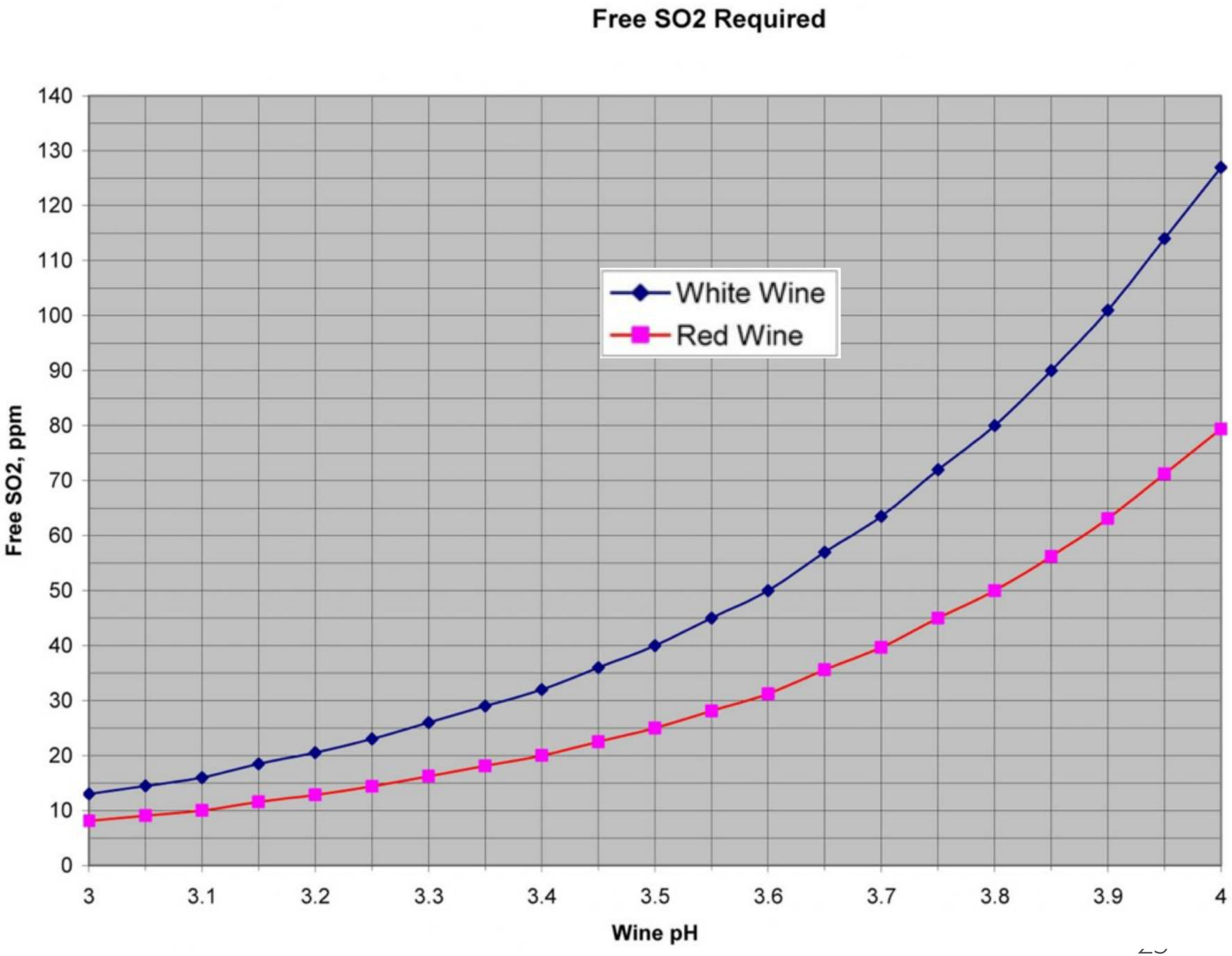
sulfite




SO2
2
3
4
5
6
pH

pH and SO_2

- minimal protective molecular SO_2 = 0.5 ppm (reds), 0.8 ppm (whites)



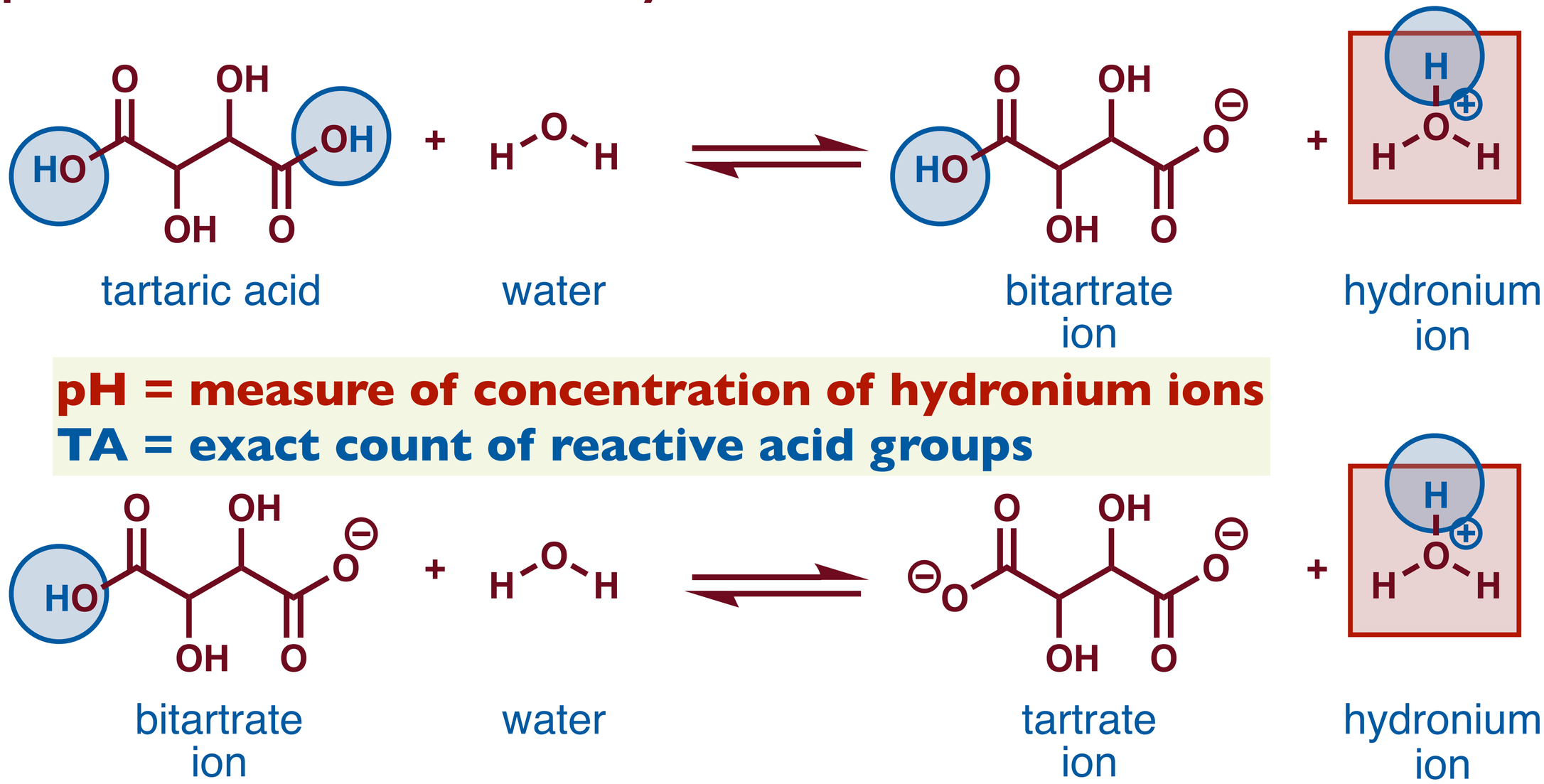
Acid Measurements

- **pH** - a measure of acid strength (free hydronium ions in solution)
  - Acid strength depends on multiple factors including the specific acid type and buffers in solution to bind protons.
  - pH is a logarithmic scale. A one unit change in pH is equal to a ten-fold change in acid strength.

Acid Measurements

- **TA** - Titratable acidity is the measure of how many actual reactive protons are present .
  - This is direct measurement of the number of acidic protons and is linear.
  - We can calculate and predict the change in TA when acids are adjusted.
  - Expressed as grams/liter (or percent) of a reference acid.

pH vs Titratable Acidity



pH = measure of concentration of hydronium ions

TA = exact count of reactive acid groups

Strategies for Managing High Acid Grapes

- Do nothing - balance acidity with sweetness
- Blend with a low acid wine
- Reduce acidity of must or wine
  - Amelioration (dilution with water)
  - Acid reducing yeasts
  - ML fermentation
  - Cold Stabilization
  - Chemical means (potassium or calcium carbonates/ bicarbonates)

Balance acidity with sweetness

- Titratable Acidity and Sweetness Guidelines

Sweetness	TA of must	TA of wine
Dry (<1% RS)	0.8 - 0.9%	0.6%
Semi Dry (1-4% RS)	0.9 - 1.1%	0.7 - 0.9%
Sweet (>4% RS)	1.0 - 1.3%	1.0 - 1.1%

- Our grapes can have TA's higher than this

Blending with a low acid wine

- Acidity can be balanced by blending a high acid wine with a low acid wine
  - Grapes - most likely will need to import lower acid grapes from out of state
  - Blend grape wines with fruit wines
  - Using Pearson's square, you can calculate the volumes you need to blend to reach a target TA
    - pH may be unpredictable

Reduce acidity by amelioration

- Dilute must with water to reduce acidity
  - Dilute based on TA (not pH) to reach a target TA
  - Could dilute flavors and colors - best with full-bodied intensly flavored grapes. e.g. Labrusca varieties.
  - May have to add sugar back to reach desired brix

Acid reducing yeasts

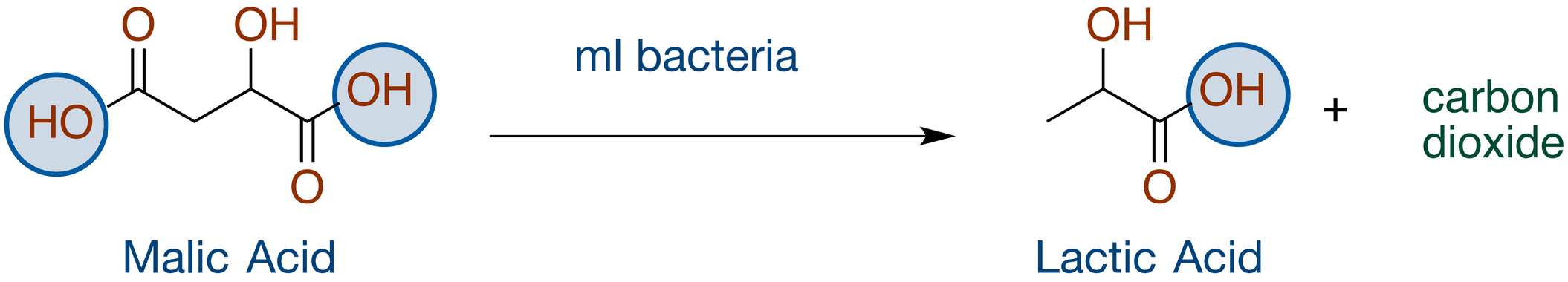
- Some yeasts metabolize malic acid
  - These generally do not form lactic acid - thus it can have a significant reduction in acidity

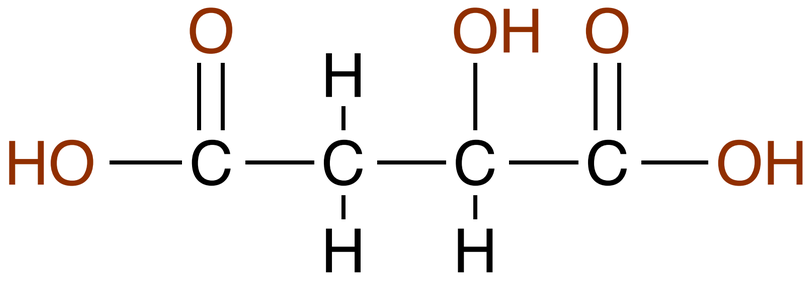
Yeast	Malate reduction
Lalvin C	31 - 34%
Lalvin 71b-1122	20 - 30%
Anchor Exotics	19 - 30%
Uvaferm VRB	20%
Maurivin B	up to 56%

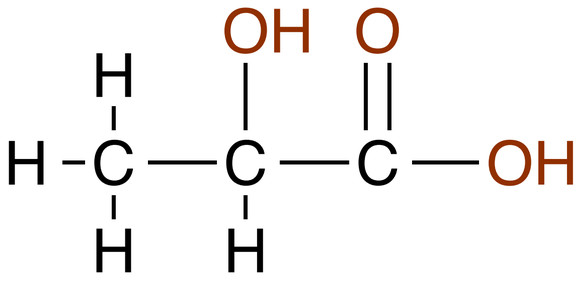
- **Katie Cook** http://northerngrapesproject.org/wp-content/uploads/2014/10/Biological-deacidification.pdf

Malolactic Fermentation

- Bacteria convert malic acid into lactic acid

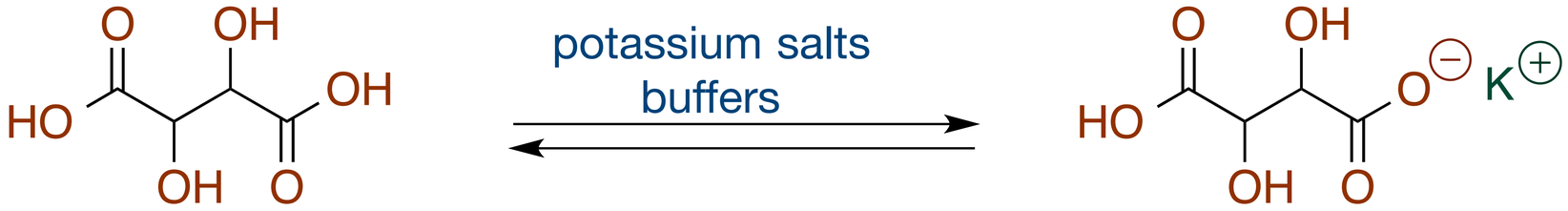






Cold Stabilization

- Chill the wine down to 25 - 30°F for about two weeks.



Tartaric Acid

potassium bitartrate

Chemical Deacidification

- Inorganic bases used to neutralize a portion of the wine acids
  - Potassium Carbonate - K_2CO_3
  - Potassium Bicarbonate - $KHCO_3$
  - Calcium Carbonate - $CaCO_3$
- BEST used on must prior to fermentation
- It introduces K and/or Ca ions into the wine - should be followed up with cold stabilization
  - Calcium tartrates precipitate much slower than potassium tartrates. Thus it is best to age at least 6-8 months before bottling.
- If adjusting after fermentation - not recommended to reduce TA more than 0.2%

Chemical Deacidification

- Test a small sample prior to adjusting the bulk. Check pH to make sure it is not thrown way off
- **$CaCO_3$**
  - 0.67 g/L = 1 g/L Titratable Acidity reduction
- **$KHCO_3$**
  - 0.9 g/L = 1 g/L Titratable Acidity reduction
- **K_2CO_3**
  - 0.6 g/L = 1 g/L Titratable Acidity reduction
- Chemical neutralization affects Tartaric acid first
  - wine may be out of balance in the end if large adjustments are made
  - combine with malic reduction techniques to minimize how much chemical deacidifcation is necessary

Acid Management Guidelines for high acid wines

- Optimal acid ranges for vinifera pre-fermentation
  - Red wine: pH 3.4–3.7, TA 6.0–7.0 g/L, 22–25 °Brix
  - White wine: pH 3.2–3.5, TA 6.0–9.0 g/L, 17–24 °Brix
- *Our hybrid grapes may not necessarily align with these guidelines*
- Keep desired wine style in mind
- USUALLY BEST TO ADJUST pH BEFORE FERMENTATION

Acid Management Guidelines for high acid wines

- **pH < 3.0**
  - Use carbonates to bring pH >3.2 Calcium carbonate - for large adjustments. Potassium carbonate - for smaller adjustments
- **pH 3.0-3.2**
  - *maybe use carbonates to raise the pH*
  - Use acid reducing yeast
  - ML fermentation (reds or chardonnay style whites)
  - Cold stabilization
- **pH >3.2**
  - ML Fermentation
  - Cold stabilization if necessary

After fermentation adjustments

- After fermentation and mL
  - Blending is the best option
  - If you need to adjust acid, best to use potassium bicarbonate followed by cold stabilization
    - *Calcium salts not recommended post fermentation - can give a chalky taste*

Case Study - High Acid Marquette

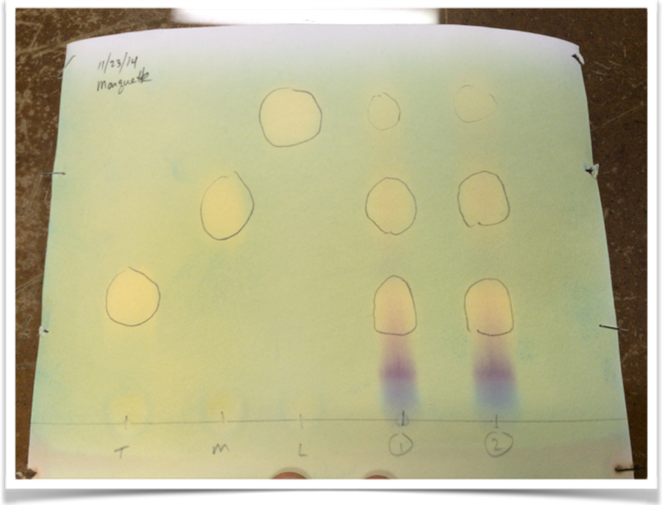
- 285 pounds of Marquette harvested in 2013, crushed and frozen
  - at crush: pH 2.74 TA 13.4 g/L (1.34%) BRIX 24.4
- Thawed Nov 2014
  - pH 2.87 TA 8.3 g/L (0.83%)
  - 1 gal must removed and treated with 175 g $CaCO_3$ for 30 min then added back to the bulk
- The next day
  - pH 3.44 TA 7.5 g/L BRIX 25

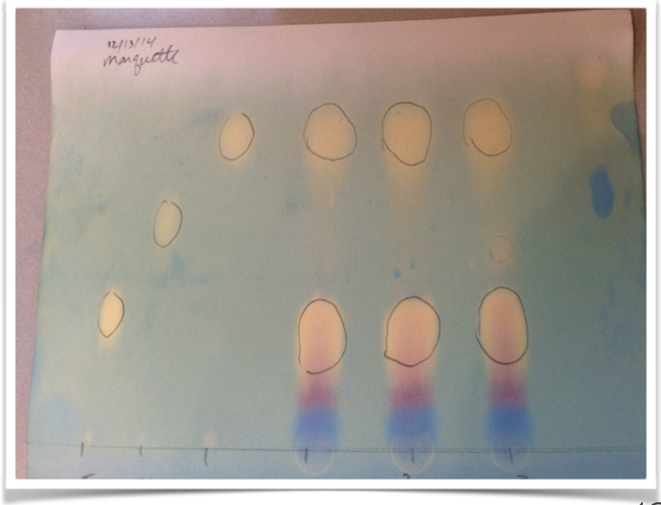
Case Study - High Acid Marquette

- Fermented with Lalvin 71b-1122 for 7 days on the skin then pressed to produce about 20 gal wine.

- MBR 31 ML bacteria added on day 2 of fermentation and secondary fermentation proceeded for 5 weeks

- Ending pH 3.55





What is Wine?

- "Wine is a living liquid containing no preservatives. Its life cycle comprises youth, maturity, old age and death. When not treated with reasonable respect it will sicken and die."

  ~ *Julia Child*

What is Wine?

- "Wine is an evolving complex concoction of chemicals containing, sugars, acids, alcohol, terpenes, polyphenols, esters, tannins, natural preservatives and much more. Its life cycle may be guided by a knowledgeable winemaker and chemistry, but ultimately the fruit quality determines its fate."

  ~ *Greg Cook*