Assessments of Ripeness:

Anita Oberholster

On-the-Road in the Foothills:
February 27, 2015

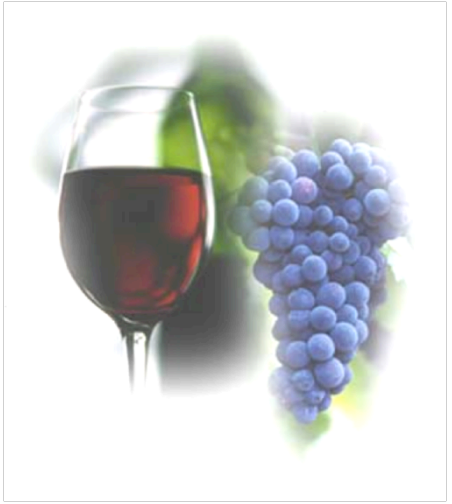
Photo's courtesy of Prof. P. Goussard






Introduction

- Physiological changes during ripening
  - Seeds, skins, pulp
- Compositional changes during ripening
  - Sugars, organic acid, minerals, aroma and phenolic compounds
- Assessment of ripeness in relation to wine style








Berry growth phases

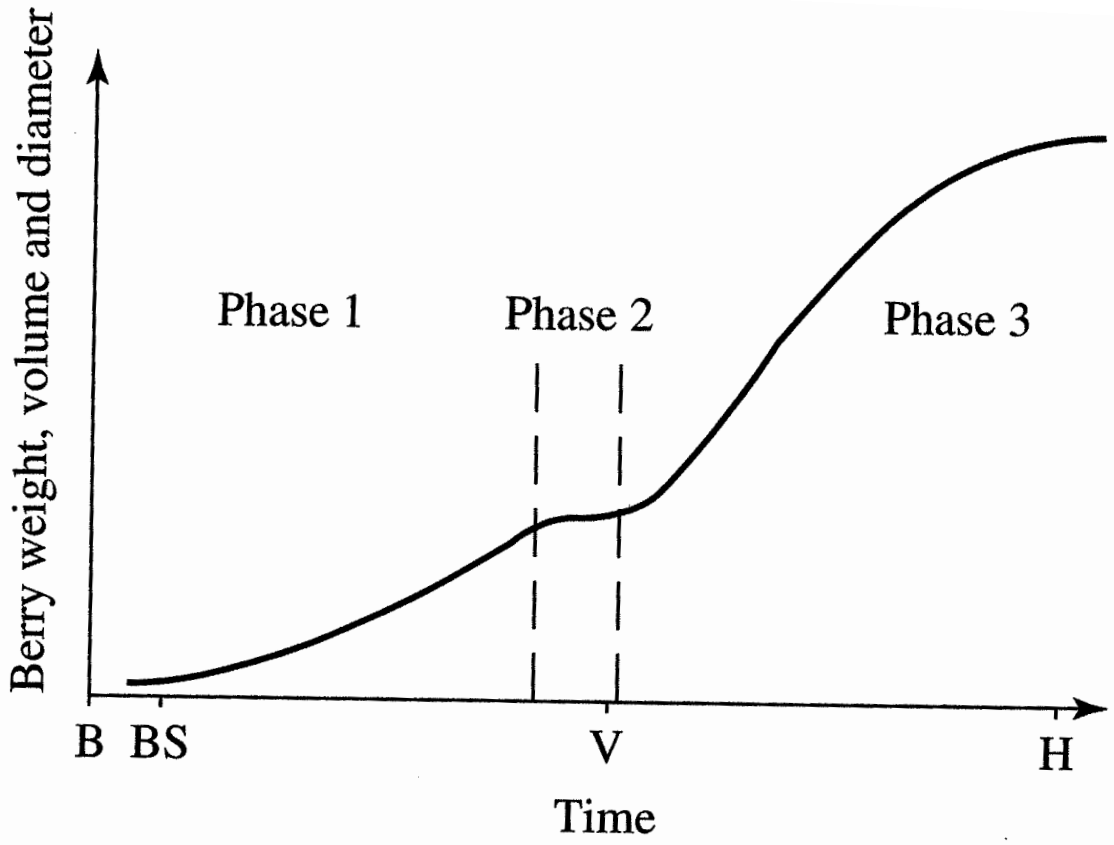
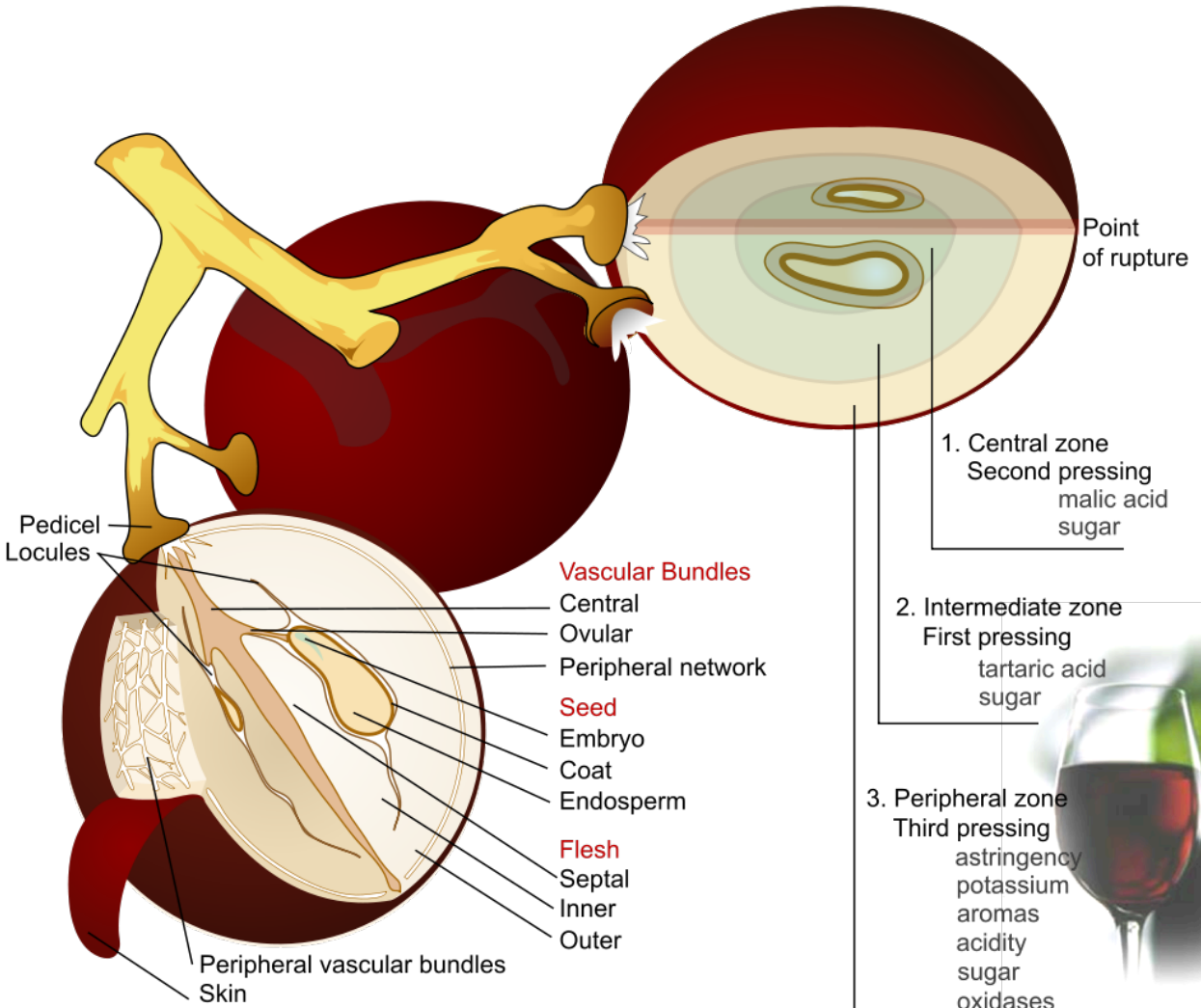


Fig. 10.3. Developmental stages of the grape berry: B, bloom; BS, berry set; V, *véraison;* H, harvest






Berry growth phases

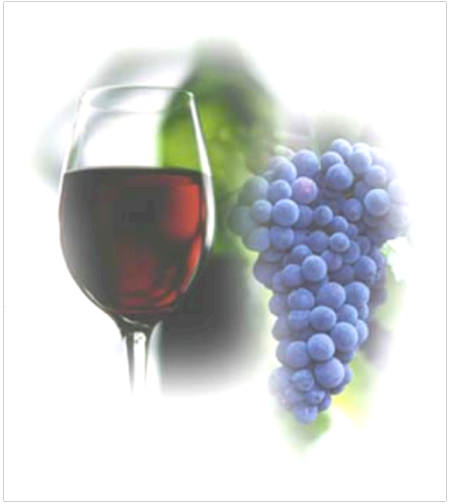







Grape Berry Ripening

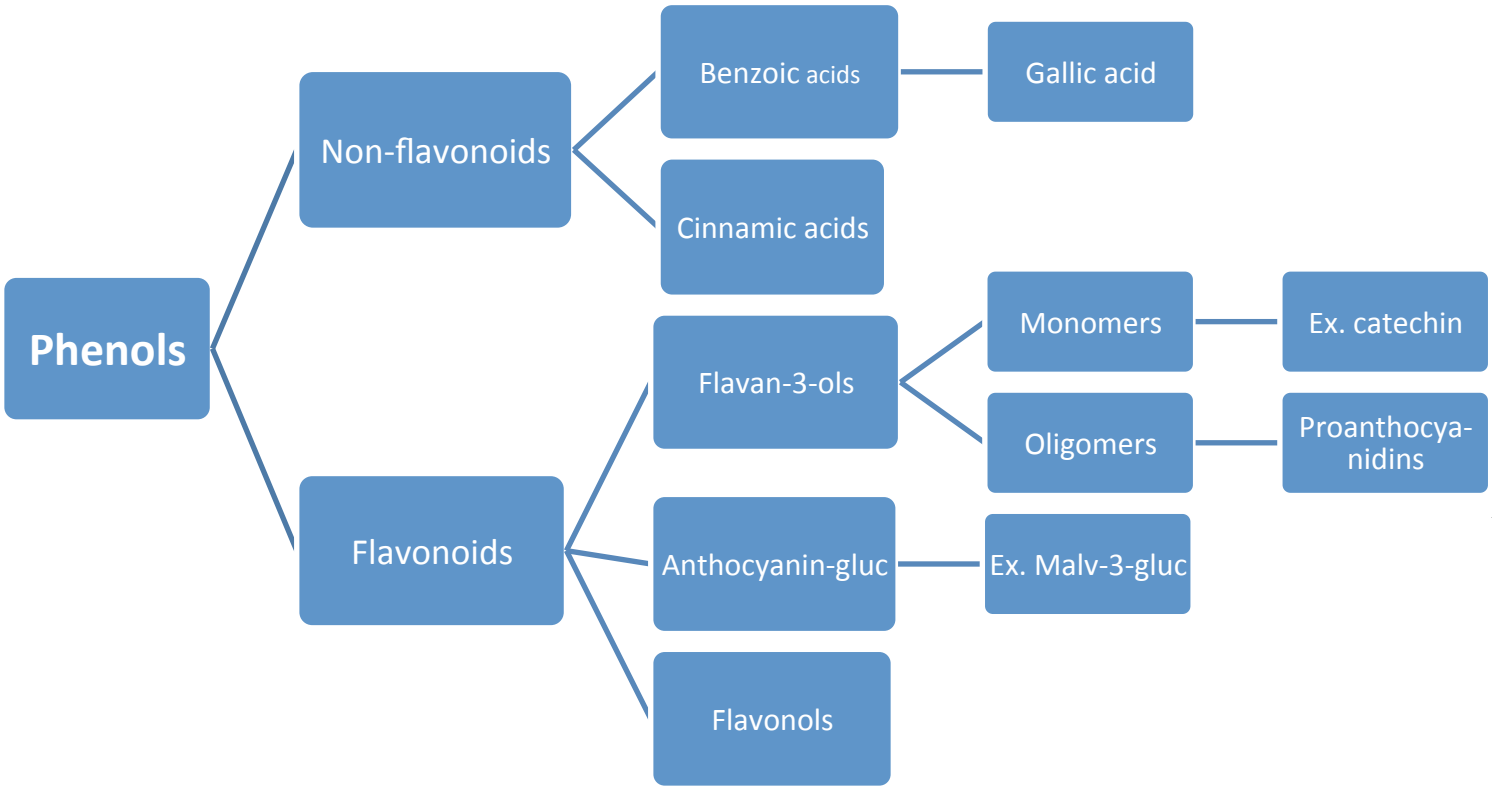
- During maturation both physical and chemical changes
  - 1st growth phase
    - Accumulation of minerals, amino acids, micronutrients and aroma compounds (methoxypyrazines)
    - Accumulation of compounds with max around véraison
      - Tartaric and malic acid
      - Hydroxycinnamic acids
      - Phenols/Tannins





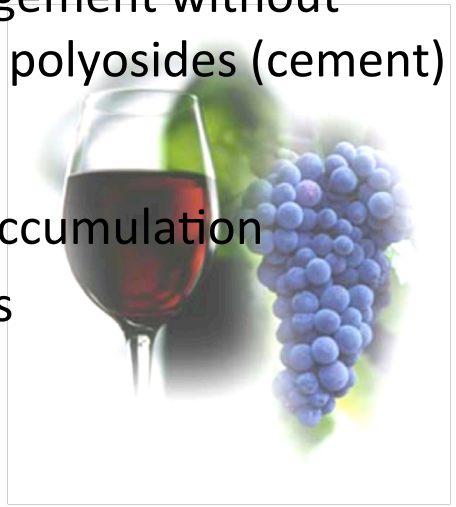



Phenols in grapes *Vitis vinifera*



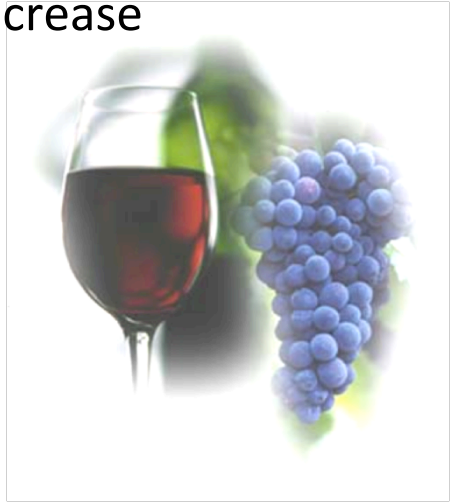
Grape Berry Ripening

- During maturation both physical and chemical changes
- Veraison
  - Marks beginning of ripening
    - Berry softening
      - Cell wall deterioration
      - Cellular multiplications and enlargement without proportional increases in parietal polyosides (cement)
    - Changes in skin color
      - Start of anthocyanin (red color) accumulation
      - Translucent skin in white varieties

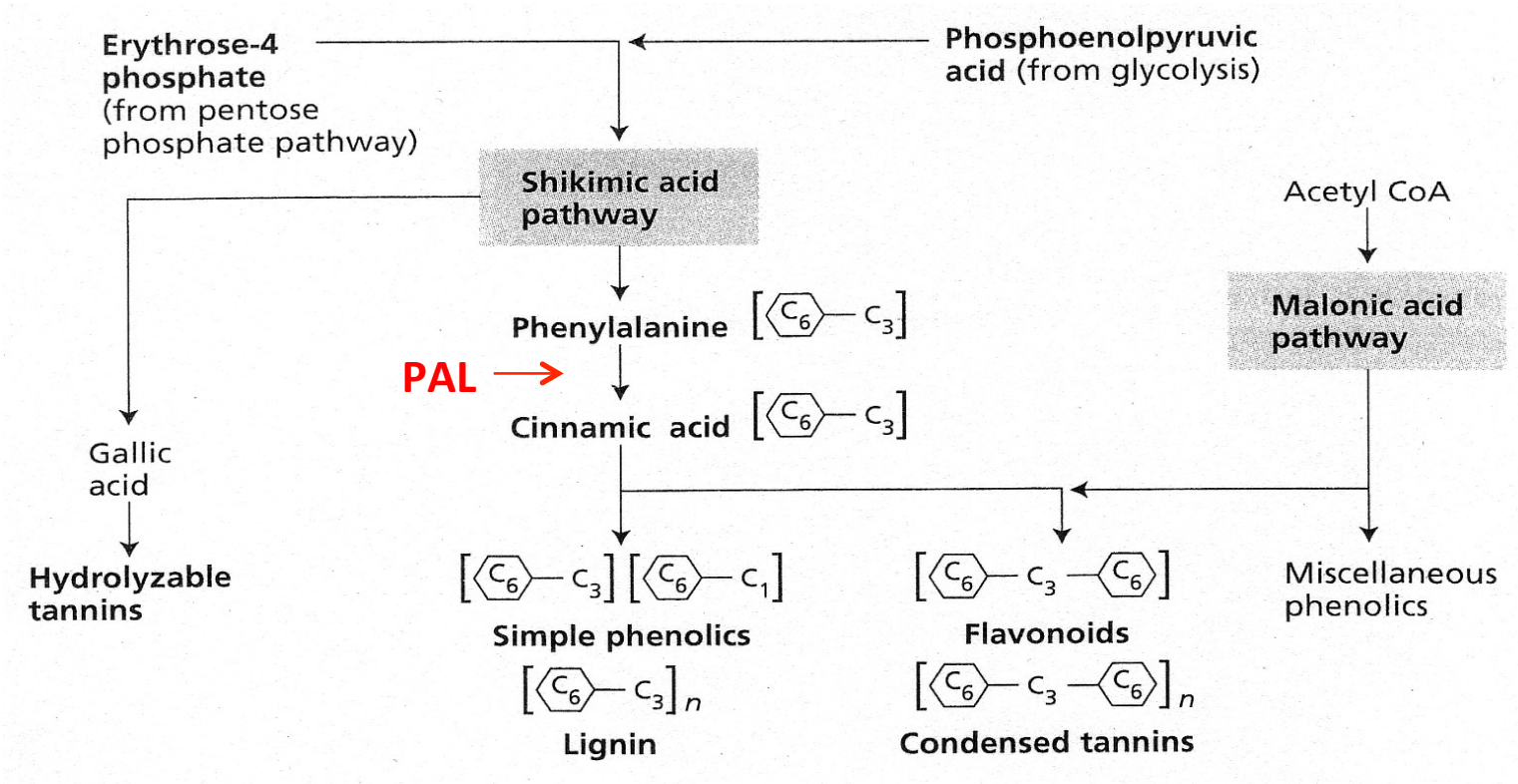


Grape Berry Ripening

- Veraison
  - Marks beginning of ripening
    - Sugar accumulation
      - Rapid increase in glucose and fructose
    - Organic acid decline
      - Rapid decrease in mostly tartaric and malic acid
      - Slower tartaric than malic acid decrease



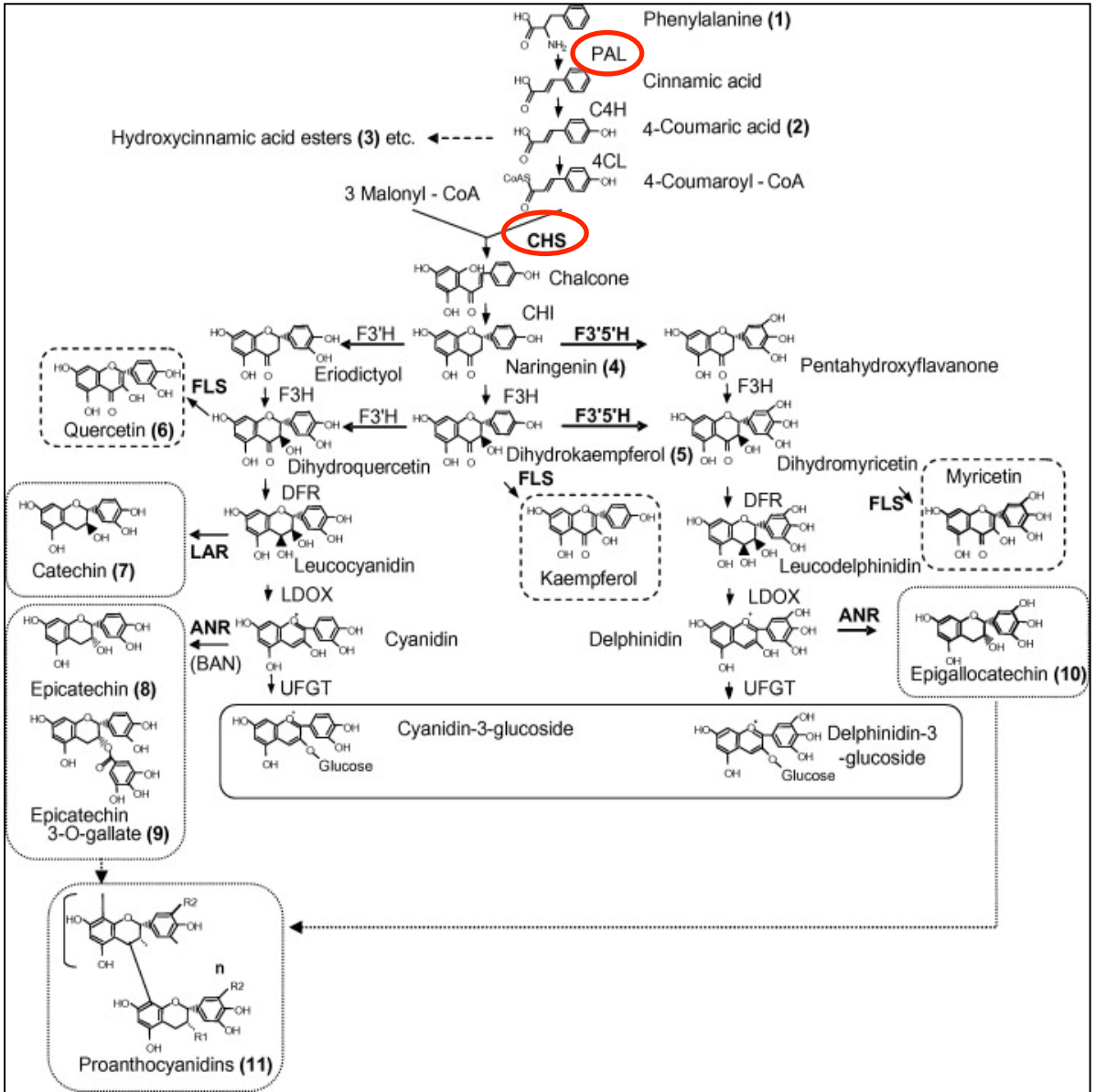
Biosynthesis of plant phenolics








Biosynthesis of plant phenolics



Phenylpropanoid pathway in the grape berry (Koyama *et al.,* 2012)






Biosynthesis of plant phenolics

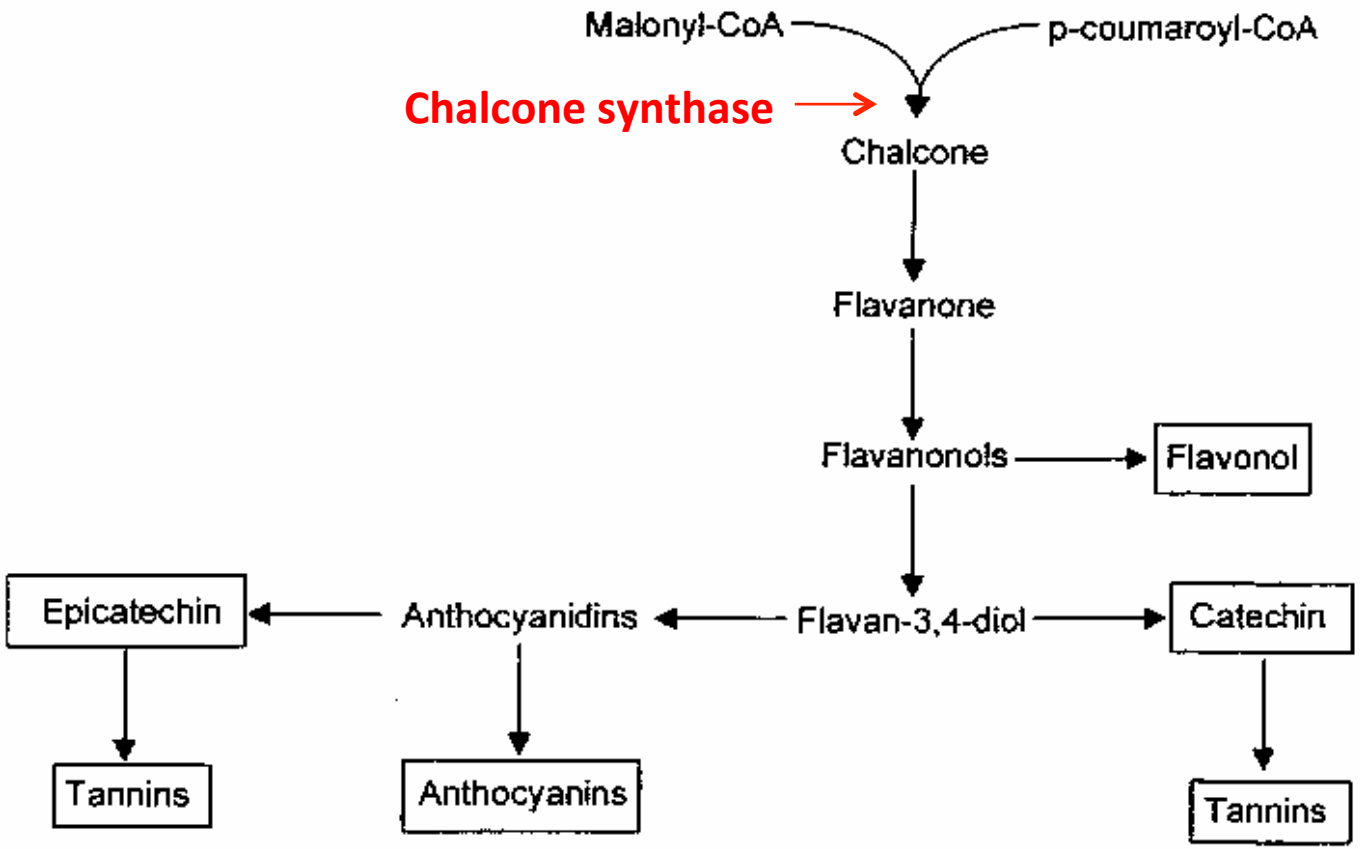
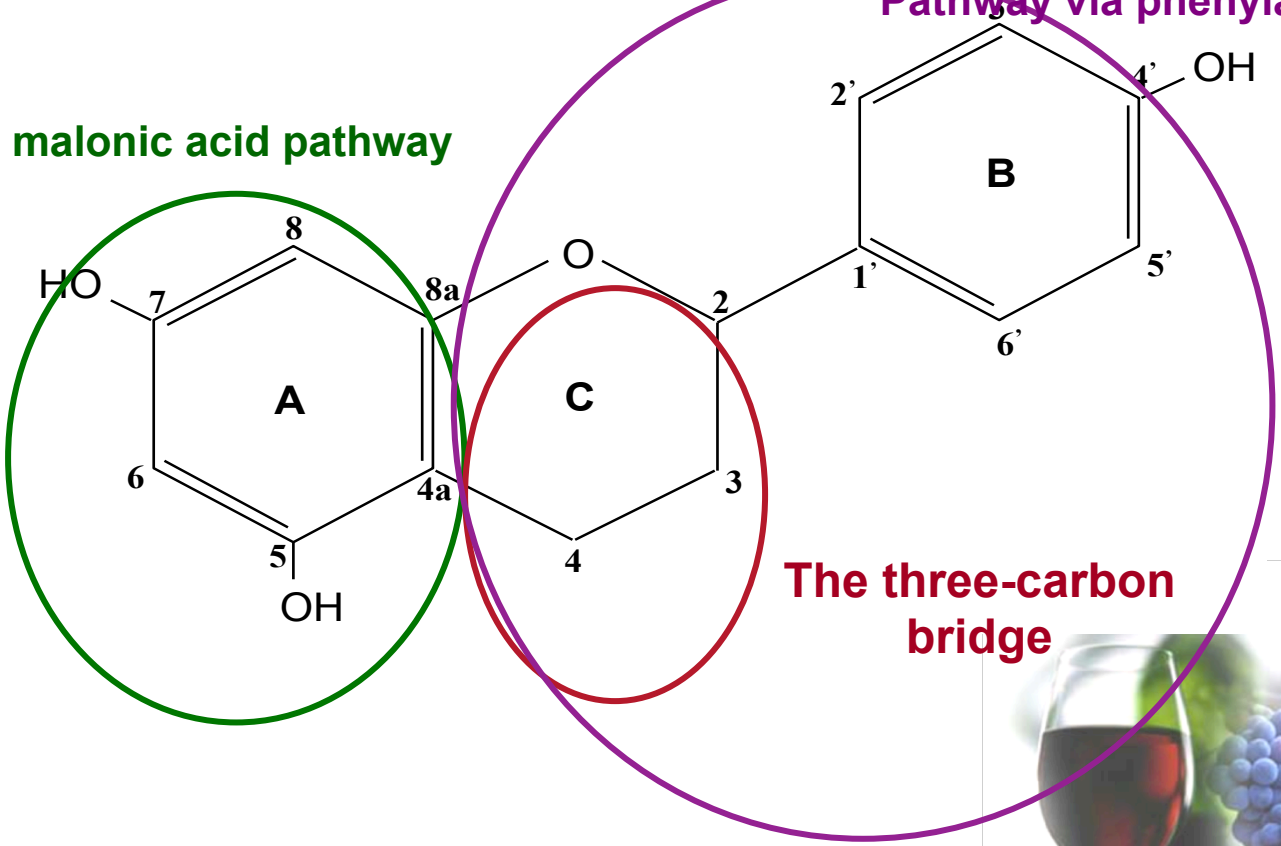


Figure 8 The biochemical pathway to the major flavonoids found in grape berries. Compounds that accumulate in the fruit are outlined by rectangles and the intermediates are present at very low levels.

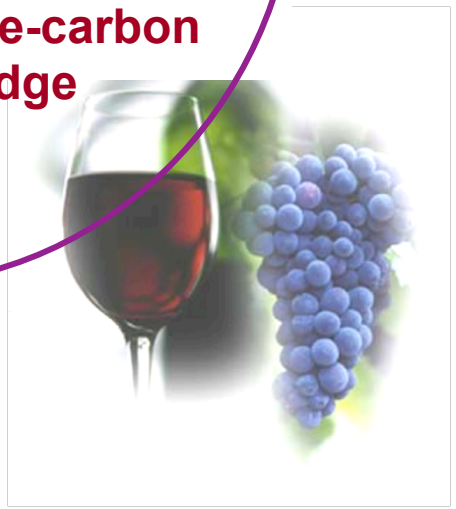
Biosynthesis of plant phenolics

From shikimic acid
Pathway via phenylalanine

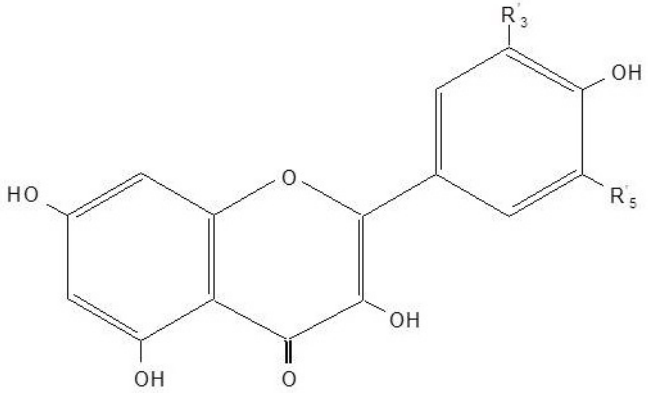
From malonic acid pathway



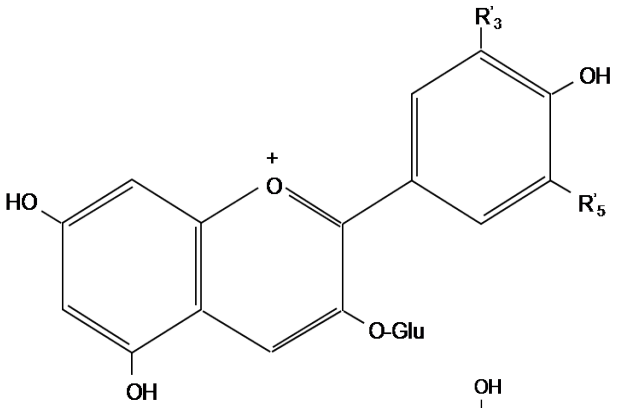
The three-carbon bridge



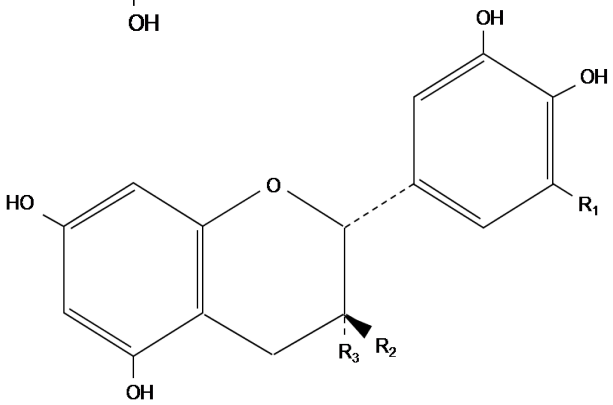
Main Flavonoids



Flavonol
Quercetin-glucuronide
Quercetin-glucoside



Anthocyanin
Malvidin-3-glucoside

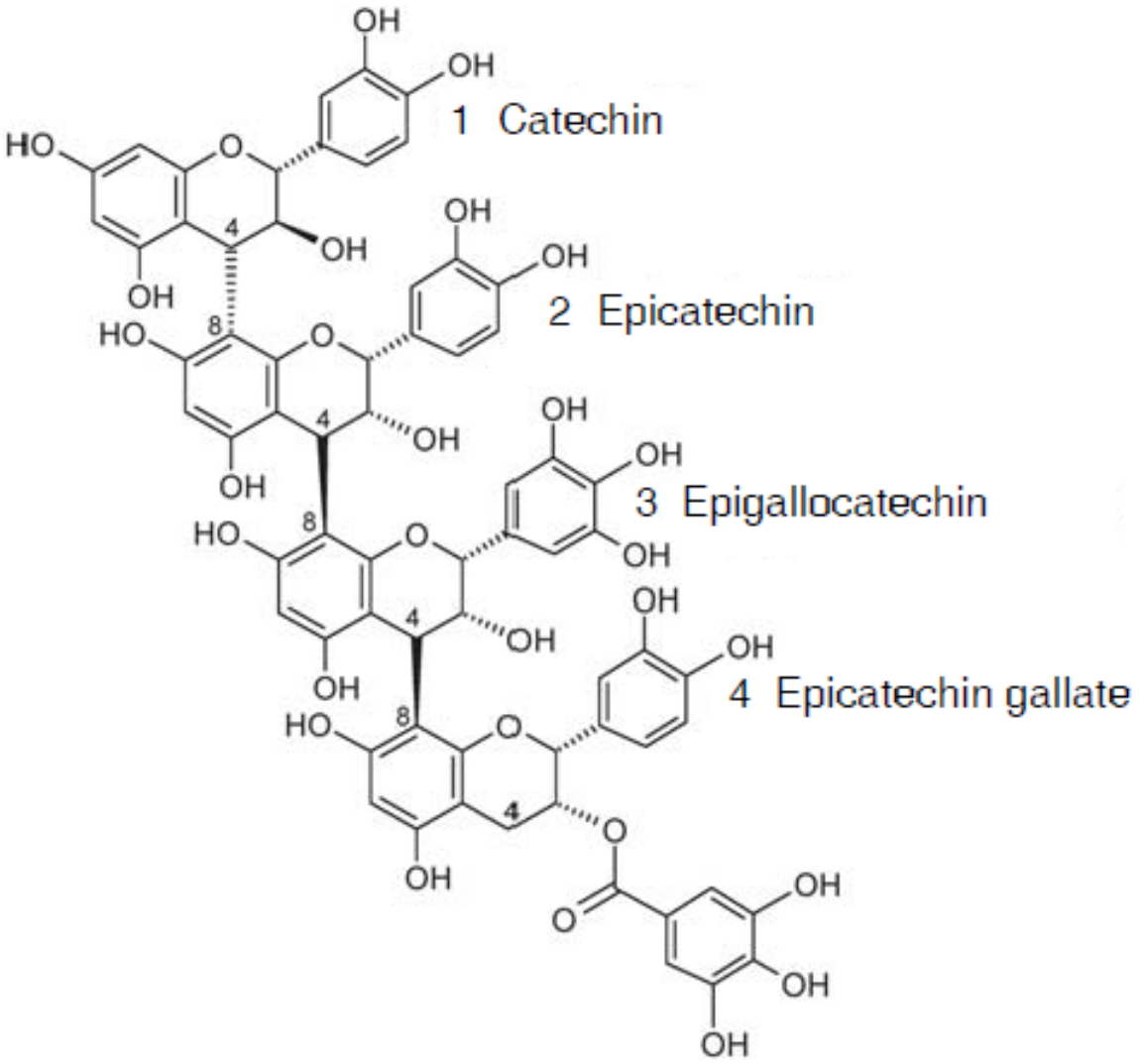


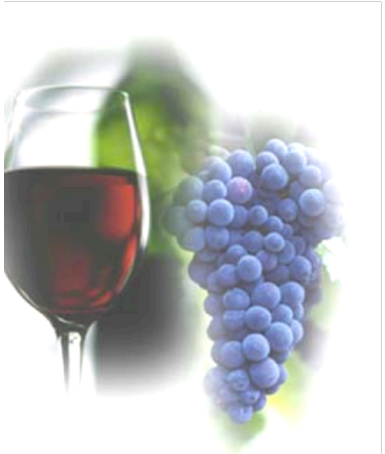
Flavan-3-ol
Catechin
Epicatechin






Proanthocyanidins





Adams (2006), AJEV 57:3

Differences between seed and skin tannins

- Skin tannin
  - mDP ~ 30
  - Little epicatechin-gallate
  - Contains epigallocatechin
- Seed tannin
  - mDP ~ 10
  - Contains more epicat-gallate units
  - No epigallo units

Prieur *et al.* (1994) Phytochem. 36, 781-784.
Souquet *et al.* (1996) Phytochem 43, (2), 509-512.

Grape Berry Ripening

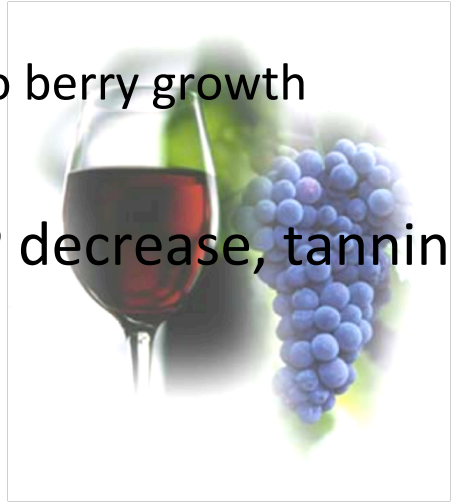
- The study of berry compositional changes during maturation is difficult due to extreme berry variability
- However, in general:
  - Seeds (0 – 6 % of weight)
    - With maturation increase in [phenol] and [tannin]
    - Reach maximum before veraison per berry
    - Post-veraison mDP of tannin decrease
    - Post-veraison seed drying and browning
    - Post-veraison tannin covalently bonded to lignified cell layers





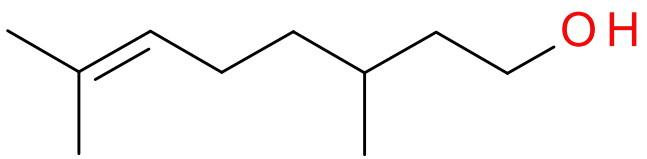

Grape Berry Ripening

- Skins (8-20% of berry weight)
  - Skin phenolics
    - Flavonol synthesize starts at flowering and 1-2 weeks after veraison until ripe
    - Anthocyanins increase from véraison until ripe
    - In overripeness anthocyanins may decrease due to degradation of the grape skin
    - Skin tannin per berry increase until approx. 2 weeks after veraison, then constant
    - Skin tannin conc may decrease due to berry growth
    - Post-veraison mDP increase
  - In general in the whole berry: mDP decrease, tannin (mg/berry) decrease



Grape Berry Ripening

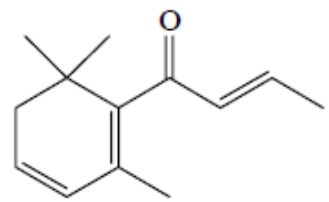
- Skins (8-20% of berry weight)
  - Contains significant amounts of:
    - Aromatic substances
      - » Bound and free monoterpenoids increase from veraison with maturation
      - » Some decrease with over ripening
    - Monoterpenes (fruity, floral)
    - *Muscat, Gewürztraminer*



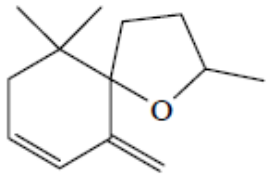
citronellol

Grape Berry Ripening

- Skins (8-20% of berry weight)
  - Contains significant amounts of:
    - Aromatic substances
      - » Carotenoids in skins decrease with maturation with increase with carotenoid-derived volatiles such as norisoprenoids
        - » *β-Damascenone (apple, rose, honey)*
        - » *Vitispirane (green odor of chrysan-themum, flowery-fruity note)*



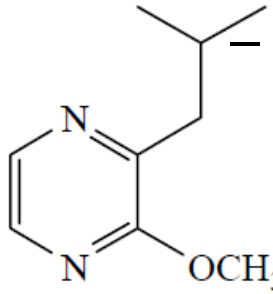
Damascenone



Vitispirane

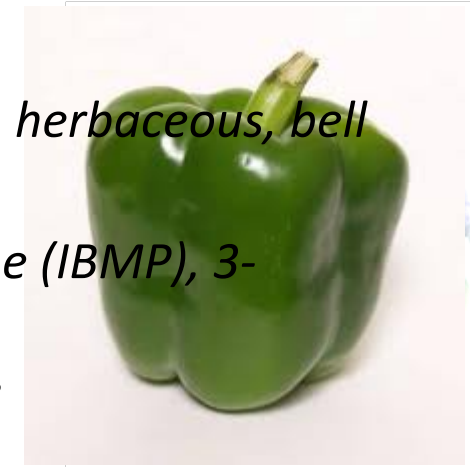
Grape Berry Ripening

- Skins (8-20% of berry weight)
  - Contains significant amounts of:
    - Aromatic substances
      - » Methoxypyrazines – high conc in unripe grapes
      - » Decrease with maturation (light and temp)
      - » Highest conc found in coldest maturation conditions



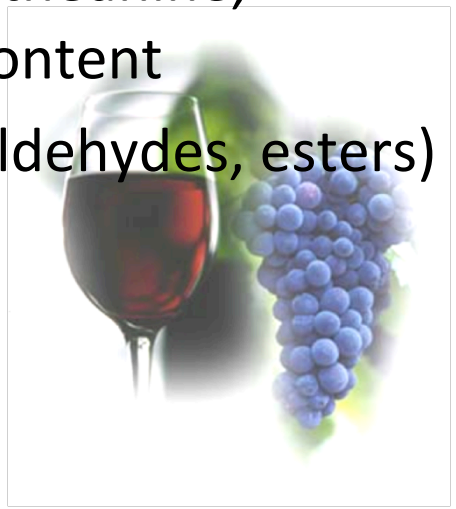
isobutylmethoxypyrazine

- Methoxypyrazines *(vegetative, herbaceous, bell pepper or earthy aroma)*
  - » *2- isobutylmethoxypyrazine (IBMP), 3-butylmethoxy-pyrazine, 3-isopropylmethoxypyraxine*



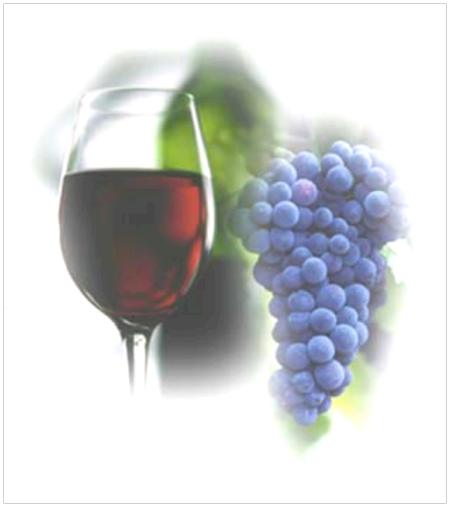
Grape Berry Ripening

- Pulp (75-85% of berry weight)
  - Contains significant amounts of:
    - Cell walls (<1%)
    - Sugars (fructose and sucrose, 0.9 ratio)
    - Acids (tartaric, malic and citric acid)
    - Cations (K, Ca, Mg, Na, Fe)
    - Amino acids (proline, arginine, theanine, glutamic acid) 20-25% tot N2 content
    - Aroma compounds (alcohols, aldehydes, esters)



Grape Berry Ripening

- Pulp:
  - During maturation
    - Decrease in [organic acids]
      - Synthesized until veraison, constant
    - K^+ increase with sugar during maturation
    - N_2 increase from berry set until mid-maturity

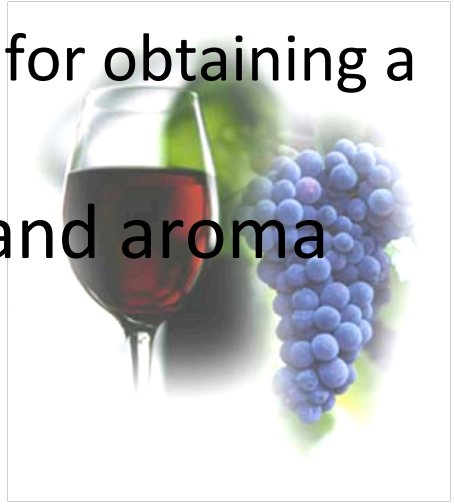







Berry maturation and optimal ripeness

- Definition of maturity varies
- Optimal ripeness can be defined as the optimal berry composition for your wine style
- Technological Maturity: Sugars and acidity
- Phenolic Maturity: Sugar, tartaric acid and phenolic compounds
  - Optimum phenolic composition for obtaining a specific wine style
- Aromatic Maturity: Sugar, TA and aroma profiles - White grapes

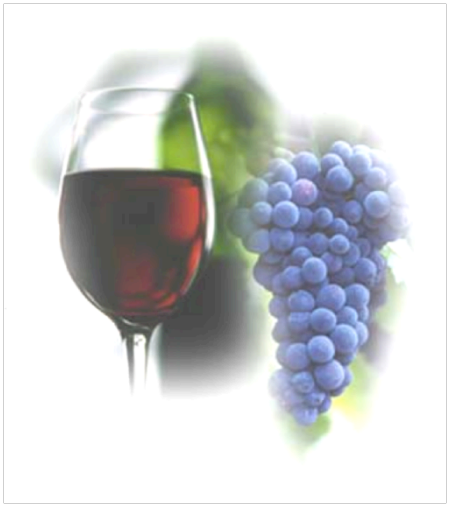







Determination of grape (phenolic) maturity

- Subjective methods
  - Inspection of skins, connection to the pulp
  - Tasting grape skins for specific flavors
  - Investigating the seed color

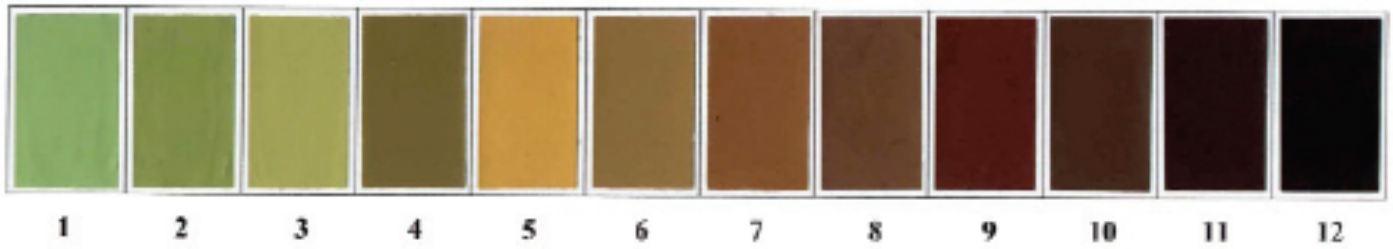







Seed color chart

Figure 2. A colour chart indicating changes in grape seed coat colour during seed development and maturation.



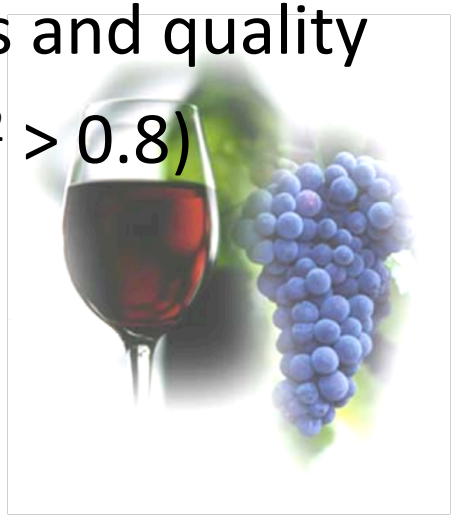
Calculating Grape Seed Colour

Take a random sample of at least 20 seeds from a representative sample of berries.

Ristic and Iland (2005) Austr. J. Grape Wine Res.(11) 43.

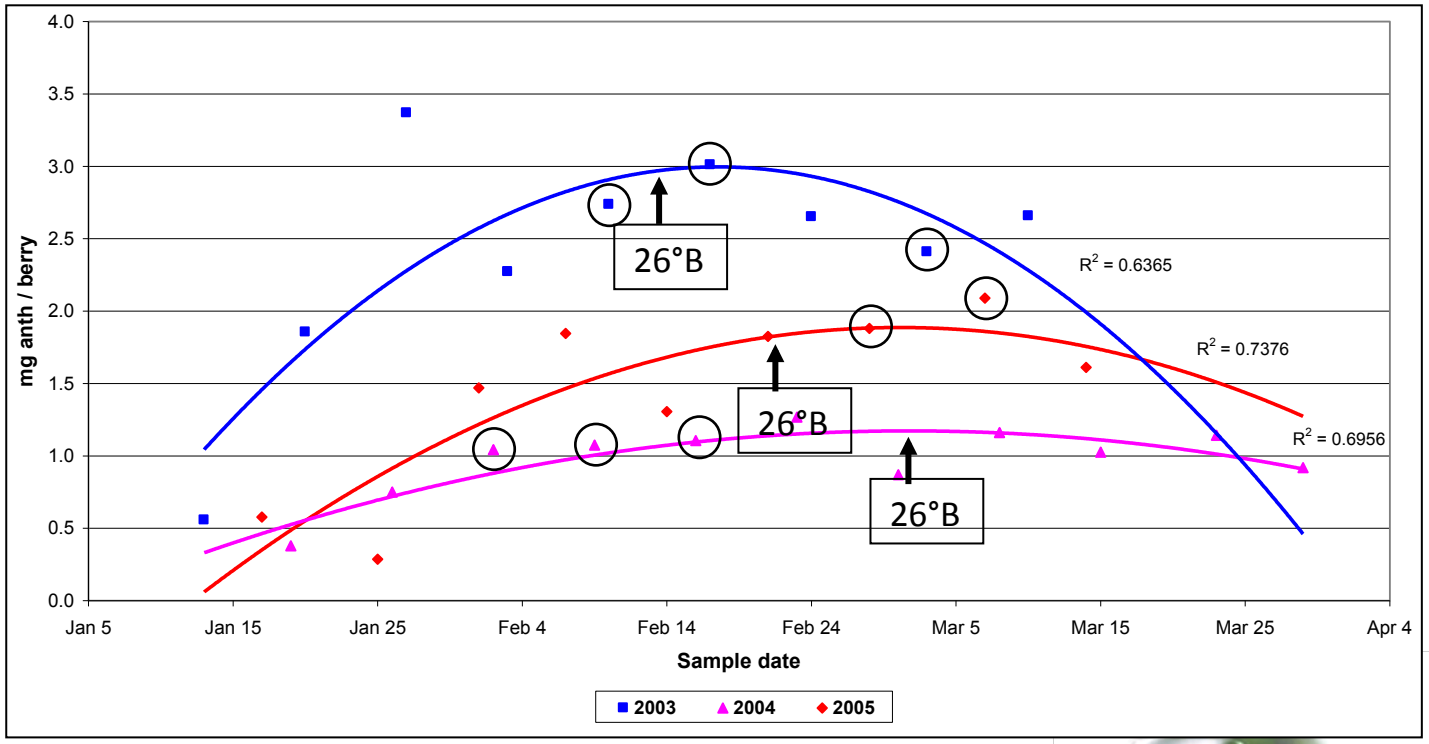
Measurement of phenolic maturity (optimal phenolic composition)

- Extractability assay
  - Color extracted at grape pH and pH 1 (breaks down cell structure). Sudden decrease indicate over ripeness *(Ribéreau-Gayon et al., 2000)*
- Color intensity (520 nm) *(Iland et al., 2000)*
  - Correlation with anthocyanins and quality
  - Winescan good correlation ($r^2 > 0.8$)



Ribéreau-Gayon et al., (2000)
Iland et al,. (2000)

Determine opt ripeness in Cab Sauv grapes~wine quality



- Strong relationship between °Brix, color and grape and wine quality
- Seasonal differences result in larger variance then vineyards in different climatic zones

Oberholster, Botes, Lambrechts (2010), J. Int. Sci. Vigne Vin. Special issue Macrowine, 33-40.

Importance of 280:520 nm or tannin/anth ratio?

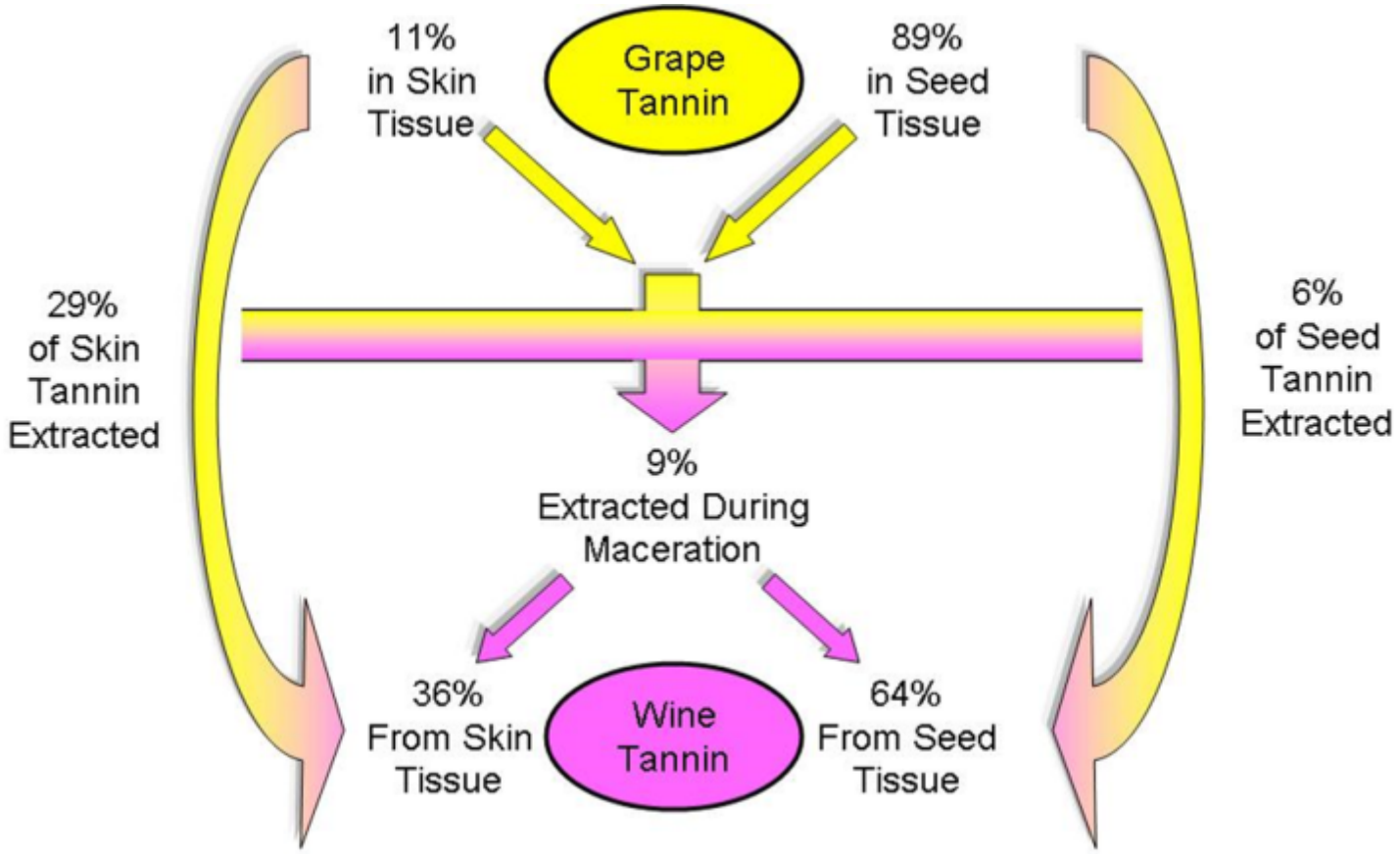
- Ratio tannin/anth mostly between 1 and 3 for best wines
- Large variance over years and between farms
- Kassara and Kennedy found best rated wine had tannin:anth ratio of ±2
  - Higher rated wines – larger contribution from skin tannins
  - Wine color generally increased with tannin conc

Oberholster, Botes, Lambrechts (2010), J. Int. Sci. Vigne Vin. Special issue Macrowine, 33-40.
Kassara and Kennedy (2011) J. Agric. Food Chem. 59: 8409-8412.






Phenol extraction



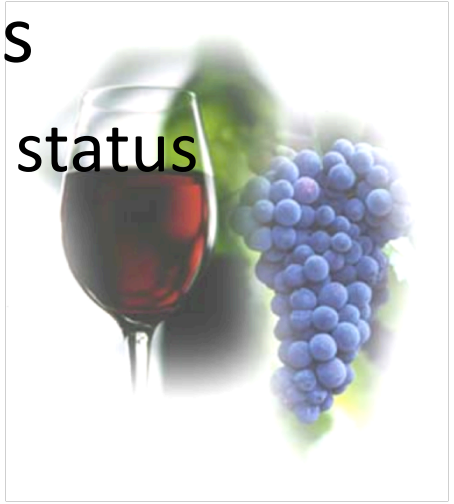
Kennedy, Robinson and Walker, PWV, May/June, 2007



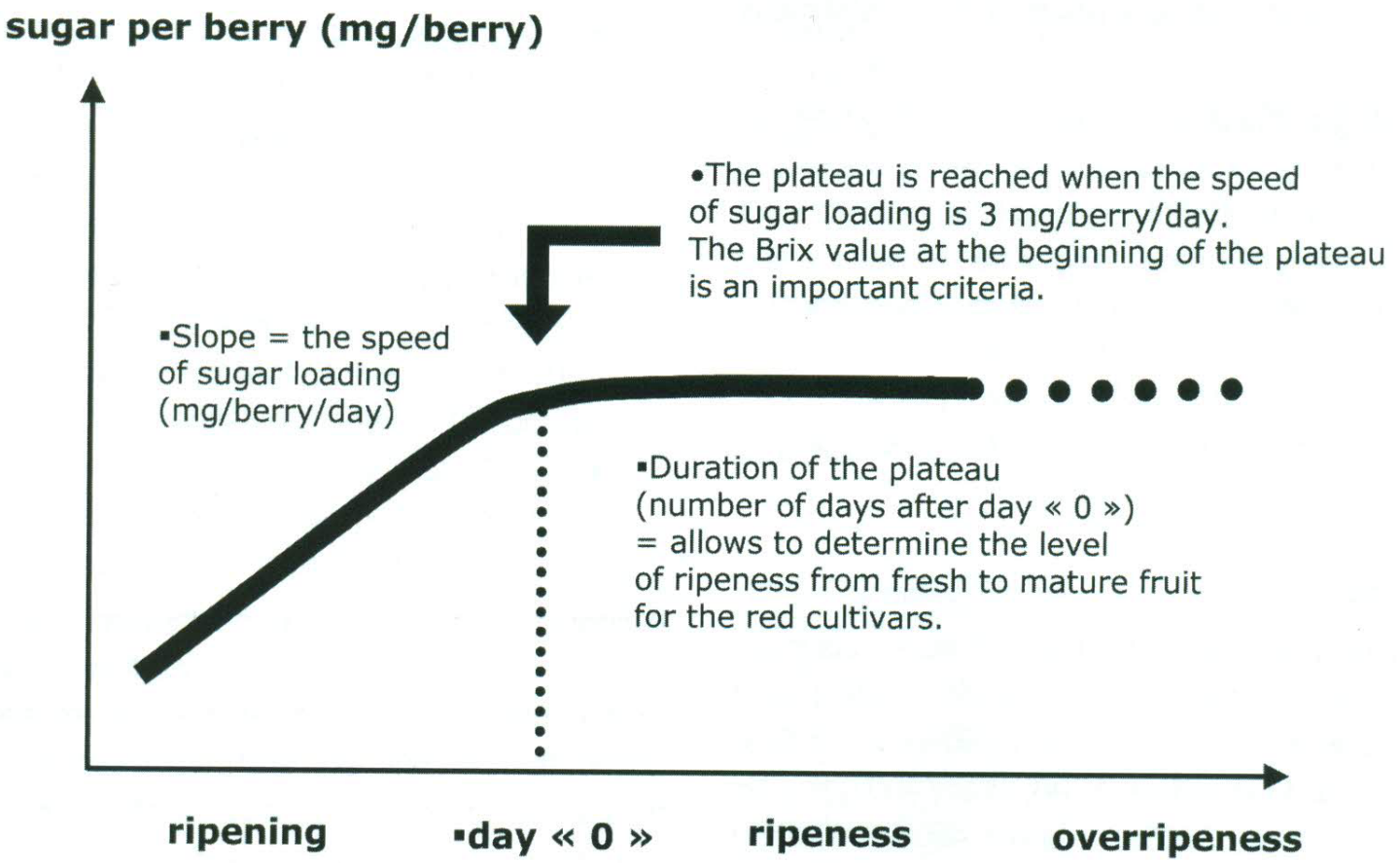



Effect of the climate and environment on berry ripening/content

- Seasonal differences results in large grape composition difference
  - sugar ±10%
  - acid content ± 30-40%
  - up to two-fold variability in tannin + anth content
- In vineyard more skin tannins
  - Reduced vigor and vine water status

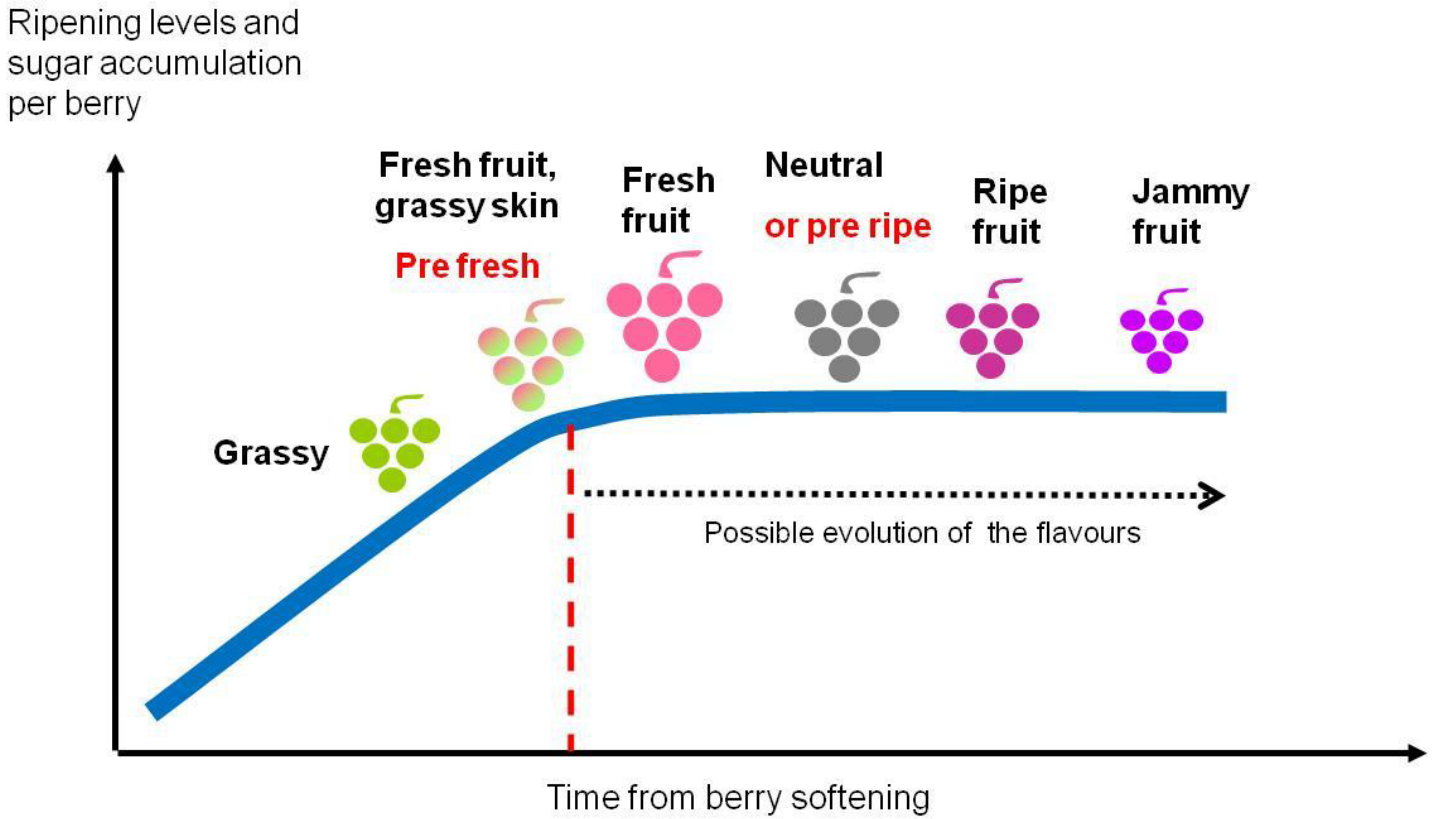


Determining optimal ripeness using sugar loading concept



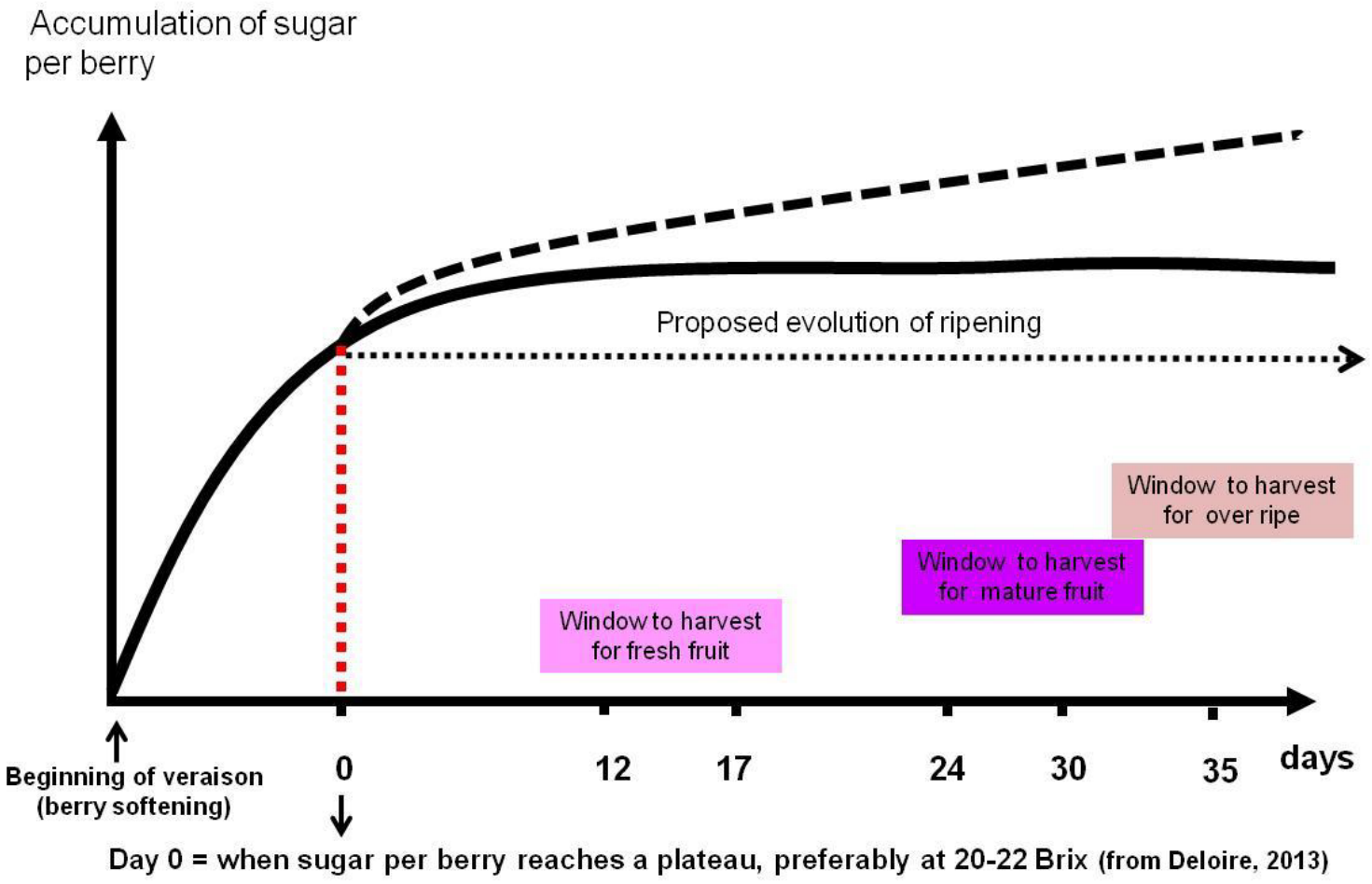
Deloire, 2011

Berry Aromatic Sequence



Deloire, 2014 ASVO proceedings

Berry Aromatic Sequence



Day 0 = when sugar per berry reaches a plateau, preferably at 20-22 Brix (from Deloire, 2013)

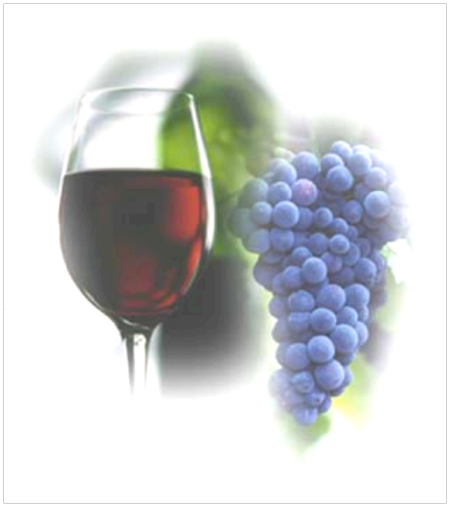
Deloire, 2014 ASVO proceedings






Berry maturation and optimal ripeness

- Wine style limited by terroir
  - Sugar/acid balance in pulp
  - Seeds not brown?
  - Skin phenol and aroma concentration and composition optimal for wine style attainable



Conclusion

- No easy answers
- There will be an optimal time to harvest for your specific terroir and wine style
  - However, this may change seasonally
- Best to build knowledge base of grape composition and related wine quality
- Use history to help with future decisions
- The best grapes make the best wines