Introduction

• What is wine quality?
• Wine composition
  • Main phenolics in wine
• Sensory characteristics
  • Impact of phenolic compounds
• Color and tannin management
What is wine quality?

- Balanced wine with no faults
  - Balanced
    - Good acid/pH, RS, body and flavor
  - ↑Quality with ↑complexity
    - Multi-dimensional

What is wine?

- 1% Glycerol
- 0.4% Organic acids
- 0.1% Tannins and phenolics
- 0.5% Other compounds

Tannin

Anthocyanins

Ellagitannin
Wine Aroma

**Grape-derived**
- Monoterpenes (floral, fruity)
- Norisoprenoids (floral, perfumy)
- Methoxypyrazines (bell pepper, asparagus)
- Thiols (fruity aromas)
- Aliphatic phenylpropanoids

**Fermentation & yeast derived**
- Esters and higher alcohols (fruity aromas)
- Volatile phenols (leather, barnyard, medicinal, spicy)
- Sulfur (asparagus, corn, molasses, cabbage, onion, rubber)

**Aging & Oak derived**
- Furans derivatives (toasty and caramel)
- Lactones (coconut, woody, sweet, vanilla)

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**Aroma wheel**

Ann Noble (1995) UC Davis
Grape and Wine Phenolics

Anthocyanin
Flavonols
Tannins (flavan-3-ols)

Hydroxycinnamates

Closer look at tannins

- Tannin building blocks
  - catechin (C), epicatechin (EC), epigallocatechin (EGC), and epicatechin gallate (ECG)
- Differences between skin and seed tannins
  - Mean degree of polymerization (mDP) for skin tannin are ~30; seed tannins are ~10 (Souquet et al. 1996)
  - Proportion of ECG units is different in seeds (~30%) and skins (~5%) (Cheynier et al. 2006)

Hypothetical tannin tetramer (Adams 2006)
A Molecular Mechanism for Phenolic Extraction

All steps are likely a function of temperature and EtOH

In Mouth Perception

- Compositional impact on mouthfeel perception

<table>
<thead>
<tr>
<th>Tannin</th>
<th>Matrix</th>
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<tr>
<td>Concentration</td>
<td>Composition</td>
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<tr>
<td>Amount</td>
<td>Skin/Seed</td>
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<td>Size distribution</td>
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Sensory Properties of Phenols

- Tannins or proanthocyanidins
  - Main contributors to bitterness and astringency
  - Larger tannin more astringent and drying than smaller tannin
  - Ratio of astringency to bitterness increase with mDP


Bitterness and Astringency

- Monomers more bitter than astringent
- Ratio of astringency to bitterness ↑ with ↑ mDP

Sensory Properties of Phenols

- Only above tetramer major contributor to astringency
- Hydroxycinnamic acids – astringent and bitter
- Flavonols – maybe bitter
- Ellagitannins – close to sensory threshold in wine
  - Small astringency contribution


Sensory Properties of Phenols

- Tannins or proanthocyanidins (PA)
  - Main contributors to bitterness and astringency
  - Larger tannin more astringent and drying than smaller tannin
  - Ratio of astringency to bitterness increase with mDP
  - Seed tannin more astringent (coarse, dry) than skin tannin of equivalent size
  - Indicate – ‘coarseness’ and ‘dryness’ of astringency increase with galloylation

Polymeric Phenols and Astringency

- During wine maturation and ageing
  - Anthocyanins and PA polymerise with each other by different mechanisms
  - Influenced by grape composition, presence of wood (hydrolyzable) tannins

Different Polymeric Pigments

- Pyranoanthocyanin
- Direct Condensation
- Aldehyde Bridged (methylmethine)

Polymeric pigments and mouthfeel

- Anthocyanins have no taste or tactile effect
- How do you explain differences between white wine and red wine?
- Wine pigments/polymeric pigments
  - Increases astringency fine grain attributes
  - Increase viscosity/mouth coating perception

Sensory Properties of Pigments

- Anthocyanins have no taste or mouthfeel
- How do you explain difference between white wine and red wine?
- New polymeric phenols/pigments – wine maturation
  - Methylmethine-bridged flavanols more bitter than similar tannins, lower astringency

Sensory Properties of Pigments

- DA of different ‘model wines’ made with and without added anthocyanins
  - Pol. Pigments add to astringency “dry”, “grippy”, “viscosity”, “fine emery”

- Polymeric pigment fraction from wine
  - High molecular weight (HMW) highly pigmented - less astringency – mDP not known
    - Incorporation of anthocyanins into polymers decrease astringency
  - These conclusions are based on “dry tannin” rating
  - Study can’t guarantee equal tannin conc – quantification methods not optimal
  - Known that mDP decrease with wine aging


Astringency and other MouthfeelTerms

Matrix effects

- **Astringency** ↓ with increased EtOH
  - Impact on protein-tannin interactions
  - EtOH ↑ viscosity
- **Bitterness** ↑ with increased EtOH
- **Astringency** ↓ with polysaccharides and proteins
  - Binds with tannin
  - Polysaccharides ↑ viscosity
- **Glycerol**
  - Similar to polysaccharides ↑ viscosity
Matrix effects

• Astringency ↑ with high acidity or high ionic strength (salt Na⁺)
  - Acid astringent in own right
  - Acid and salts reduce viscosity of saliva
• Astringency ≈ with sugar content
  - Can be more difficult to perceive
• Bitterness ↓ with increasing sugar

Correlation Between Wine Composition and Sensory Descriptive Analysis

• Aroma profiles, some correlations to individual or group of compounds
• Acid ~ acidity, sugar ~ sweetness
• Alcohol ~ hotness

Correlation Between Wine Composition and Sensory Descriptive Analysis

- Bitterness and astringency on molecular level not explained
- Contradicting results due to sample prep, sensory analysis methods?
- Links between astringency and phenol conc
- High skin tannin conc have been linked to higher ratings in red wines

Impact of Color and Tannin Management on Wine Composition

- Fruit processing
- Cold soak
- Heat treatment
  - Thermovinification
  - Flash détente
- Yeast
- SO₂
- Macerating Enzymes
Impact of Color and Tannin Management on Wine Composition

- Tannin
- Fermentation temp
- Cap Management
- Extended maceration
- $O_2$
- Oak contact

Extraction during Fermentation

- Anthocyanins from skins
  - Early during fermentation (3-5 days)
- Seed and skin tannin/proanthocyanidins (PA)
  - Increase extraction with temp, % EtOH
  - Polymerization reactions between anth and PA or between PA and PA
Fruit processing

- Crushing
  - Study with Merlot, 0 – 100% crushed fruit, 25% increments (Cerpa-Calderon et al., 2008)
    - 75% fruit ↑ skin and seed PA (79%)

Cold soak/maceration

- Must at 10 – 15°C for several days before fermentation
- Results varies in and between varieties
  - Color ↑↓↓
    - Pinot noir show mostly no or neg effect
  - ↑ Seed tannin (Busse-Valverde et al., 2010, Moreno et al., 2013)
- Potential factors: berry ripeness and starting grape composition (cultivar) as well as fermentation temp


Cold soak – other factors

- Reynolds et al. 2001 ↑ anth with low ferm temp (15, 20°C) not 30°C
- CS no sensory impact on Cab Sauv, Barbera, Syrah, Malbec, Merlot and Pinot noir (Casassa 2015)
- No signf differ between control and cold soak aroma via sensory eval although chem differ in Cab Sauv (Gardner et al., 2011)

Saignée (prefermentation juice runoff)

- After 4 months – Anth ↑ Flavonoid ↑, 9 varieties – 10% runoff (Zamora, 1994)
- After 6 months no differ in Syrah with 10 and 20% runoff (Gawel et al., 2001)
- ↑ Anth ↑ tannin with ~ 16% runoff in Merlot (Harbertson et al., 2009)
Heat Treatment

- Thermovinification (best effect Pinot noir)
  - Increase anth and skin tannin extraction
  - Need skins in contact with juice
  - Loss of varietal character
- New Technology: Flash–Détection (Flash Release)
  - Increase extraction of phenols up to 50% if ferment with skins
  - Tested with Grenache, Mourvedre, Carignan

Fermentation Additions

- Different levels of $\text{SO}_2$ additions
  - Can be a difference in color and anth extraction early on
  - After 6 months no significant effect
Fermentation Additions

- Yeast
  - Previously found no great impact on non-volatile composition (Sacchi, 2005)
  - Differences between strains/species
    - ↓Anth, ↑tannin *Sacch cerevisiae* compared to *Sacch bayanus*
    - *Sacch Bayanus* ↑color
  - Aroma profiles are influence by both grape composition, fermentation conditions and yeast (Styger, 2011)

Macerating Enzymes

- Breaks down skin cell walls
- Increase juice yield (skin:juice ratio)
  - Enzymatic activities
    - Pectolytic – polygalacturonase, pectin methyl esterase, or pectin lyase
    - Cellulase – thought to release tannin
    - Hemicellulase – thought to release tannin
    - Acid protease
Macerating Enzymes

- Varied effect depending on enzyme used
  - Due to enzyme activity or grape composition?
- In general
  - ↑ Color intensity or no effect
  - ↑ or no effect on tannin conc
  - ↑ Extraction rate

Use of Exogenous/Commercial Tannin

- Tannin addition for following purposes or problem correction:
  - Contribute to mouthfeel/taste
  - Protect against oxidation enzymes,
  - Assist to precipitate proteins,
  - Modify aromas including vegetative aromas
  - Increase aging potential
  - Stabilize wine color
- Few scientific publications about effect of commercial tannin addition
Fermentation with oak

- Am or French oak chips (4 or 8 g/L) or Am or French barrels
- Analysis by descriptive analysis
  - Am oak chips: coconut, vanilla, bitterness, astringency compared to barrels
  - Oak origin more visible in chips compared to barrels
  - Quantity of chips used greater impact than oak source
  - All oak treatments vegetative aroma


Fermentation Temperature

- ↑ Temp, ↑ color + phenol extraction + pol pigments
- Lower temp preserve more fruit character
- Opt temp ±30°C (86°F) (Pinot noir, Pinotage)
- Other studies looked at lesser known varietals
  - Ex. Vranac (opt temp 24–27 °C)

Influence of temp on extraction

- Cabernet Sauvignon
- ↑Temp:
  - Increase flavanol extraction + rate
  - Increase malv-3-gluc extraction rate

Cap Management

- Why?
  - Keep cap moist for yeast activity
  - Reduce temp gradient between cap and liquid for yeast activity
  - Increase skin contact for phenol extraction etc.
Influences on extraction: Cap Management Techniques

- Punch-down, pump-over (various irrigators), rotor, delestage, submerged cap, timed gas-pressure release (Ganimede), pneumatage
- Studies compared punch-down, pump-over, rotor and delestage
- Variable effect with cultivar
- Rotor > mechanical punch down > pump over > submerged cape > manual punch down > delestage > Ganimede (order of phenol extraction)

Pump-over frequency/volume

- PO 0.5V, 1V, 2V 2x per day
- Similar extraction
- 1, 2, 4, 8 PO, tot 4 vol
- Similar extraction rates
Even lower levels of pumpovers do not have much effect on phenolic extraction

Malvidin-3-O-glucoside

Tannin

Extended Maceration

• Jim Harbertson ..................
Micro-oxygenation (MOX)

- Dosages:
  - Pre-MLF MOX MLF 10-30 mg/L/month
    - 10-25 days
  - Post-MLF 2-5 mg/L/month
    - 56-252 days
  - O₂ penetration through the barrel estimated at 1.66 and 2.5 ml.L⁻¹.month⁻¹
    - Mostly used in conjunction with wood alternatives
  - ↑ Color density, similar to barrel aging (Gómez-Plaza and Cano-López, 2011)

- ALW

MOX oak alternatives

- Only two studies compare barrel aging directly with MOX
  - Oberholster (2015) found that although chemical difference, panel found MOX + chips similar to Am oak barrel and MOX + staves similar to Fr barrel after 6 months treatment
  - Similarities driven by oak aromas
  - MOX > color, pol pigment


Summary

- Skins are extracted early; seeds later
- Temperature and extended maceration affects seed extraction more than skin extraction
- Pumpover vol/freq small impact
- Cold soak does not seem to have lasting color impact, long periods could increase seed tannin
- MOX and oak alternatives could replace short term barrel aging
  - Will improve polymeric pigment formation and color density

Thank you