Research Advances in Tannin Management

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General Outline

• Sample of Completed Work
• Does seed browning influence seed tannin extraction during winemaking?
• Vineyard vs. Winery: Which one controls phenolic composition of wine?
Major Fruit Ripening Phenomenon

- Softening
  - First indication of ripening
- Color Change
  - Coincides softening in red varieties
  - Loss of chlorophyll
- Sugar Accumulation
- Acidity Decline
  - Metabolism and dilution
- **Astringency decline**
- Increase in Aroma Compounds
- Decline in Disease Resistance
  - Ripening: A prelude to rotting
Seed and Skin Tannins

- Heterogeneous Mixture
  - Primarily Astringency & some Bitter
  - Large Astringent; Small Bitter
  - Sub-Unit Effect

- Skin
  - Ave. DP= 32 Std. Dev.=?
  - Epigallocatechin Ext. Units
  - 0.3 mg-1.2 mg/berry CE

- Seed
  - Ave. DP= 10 Std. Dev.=?
  - Epigallocatechin Gallate Term.
  - 3.0-5.0 mg/berry CE

- Wine
  - Ave. DP= 4 Std. Dev.=?
  - Mixture; dependent on winemaking
  - 50-2000 mg/L CE
Skin and Seed Tannin: Ripening

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

**Seed Tannins**
- Harsh Astringency Owing to EC Gallate
- Longer Ripening Mellows Astringency

Browning of Seed Coincides with Decline of Tannins & Catechins
- Visual Seed Maturity?
- Low Tannin extractability?
Little Green Men Seeds

• How does Seed Maturity Influence Extraction during Winemaking?
• Do green seeds make wine more tannic?
• Experimental Design Tricky
• Factors thought to influence Seed Tannin Extraction
  • Fruit Maturity
  • Ethanol Concentration
  • Extended Maceration
• 2-years of Fruit & Wine Data Collected
• 1-year of Sensory
Experimental Design

- **Merlot** (clone 3) from Paterson (2011 & 2012)
- Two Harvests
  - 20 & 25 Brix
- 2011: Sept 22 (wait 33 days) October 25
- 2012: Sept 13 (wait 34 days) October 17
Experimental Design II

Sucrose concentrate (81 Brix)

Dechlorinated water with 4.5 g/L TA

Early harvest
(20.35 ± 0.16 Brix)
Harvest date
9/22 (2011)
9/13 (2012)

Late harvest
(24.91 ± 0.46 Brix)
Harvest date
10/25 (2011)
10/17 (2012)

Chaptalized to 25 Brix

Saignée & water-back to 20 Brix

Control

Ethanol % v/v

Extended maceration

3 tanks replicates

Ethanol adjustment

Low

Control

(a)

Ethanol

11.72

Extended maceration

(b)

Control

14.42

3 tanks replicates

High
Berry Chemistry

![Bar charts showing Brix, skin tannins, and seed tannins for early and late harvest dates.](chart.png)
2011 Season

<table>
<thead>
<tr>
<th>Early harvest</th>
<th>Late harvest</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.14 ± 0.2 b</td>
<td>2.97 ± 0.1 c</td>
</tr>
<tr>
<td>4.20 ± 0.07 c</td>
<td>5.45 ± 0.20 a</td>
</tr>
</tbody>
</table>

2012 Season

<table>
<thead>
<tr>
<th>Early harvest</th>
<th>Late harvest</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.69 ± 0.3 a</td>
<td>3.15 ± 0.1 b</td>
</tr>
<tr>
<td>3.78 ± 0.03 d</td>
<td>4.76 ± 0.08 b</td>
</tr>
</tbody>
</table>

Concentration: mg/g FW
Seed-color value
(Ristic and Iland 2005)
<table>
<thead>
<tr>
<th>ANOVA FACTOR</th>
<th>TREATMENT</th>
<th>ANTHOCYANINS (mg/L)</th>
<th>TANNINS (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Season (S)</td>
<td>2011</td>
<td>386</td>
<td>390</td>
</tr>
<tr>
<td></td>
<td>2012</td>
<td>365</td>
<td>539</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.881</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>Maturity (M)</td>
<td>Early</td>
<td>259 b</td>
<td>473</td>
</tr>
<tr>
<td></td>
<td>Late</td>
<td>492 a</td>
<td>456</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&lt;0.0001</td>
<td>0.855</td>
</tr>
<tr>
<td>Maceration (W)</td>
<td>Control</td>
<td>416 a</td>
<td>373</td>
</tr>
<tr>
<td></td>
<td>EM</td>
<td>335 b</td>
<td>558</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&lt;0.0001</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>EtOH Adjust (EtOH)</td>
<td>Low 11.7%</td>
<td>370</td>
<td>438</td>
</tr>
<tr>
<td></td>
<td>High 14.4%</td>
<td>381</td>
<td>491</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.176</td>
<td>0.141</td>
</tr>
<tr>
<td>W x M</td>
<td></td>
<td>0.649</td>
<td>0.258</td>
</tr>
<tr>
<td>W x S</td>
<td></td>
<td>0.021</td>
<td>0.298</td>
</tr>
<tr>
<td>W x EtOH</td>
<td></td>
<td>0.874</td>
<td>0.899</td>
</tr>
<tr>
<td>W x M x S</td>
<td></td>
<td>&lt;0.0001</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>W x M x S x EtOH</td>
<td></td>
<td>0.005</td>
<td>0.065</td>
</tr>
</tbody>
</table>
Tannin Recovery

533 ±15 mg/L (a)

554 ±29 mg/L (a)
Impact of Extended Maceration

477 ±42 mg/L (b)  

610 ±59 mg/L (a)
Impact of EtOH

523 ± 46 mg/L (a)

564 ± 17 mg/L (a)
Polymeric Pigment Formation
Sensory

- Conducted Pro-Bono by Dr. Hopfer & Dr. Heymann UC Davis
- Descriptive Analysis
  - Trained panel (n = 11)
- Aroma, Taste, Mouthfeel Attributes selected by Consensus
  - Taste & Mouthfeel: Sweet, Sour, Salty, Bitter, Hot, Astringency, Viscous
  - Aroma: Alcoholic, Chemical, Fresh Veg, Cooked Veg, Earthy, Barnyard, Black Pepper, Red Berry, Fruit, Dark Fruit, Dried Fruit, Chocolate, Caramel
- Color: Wine Color Poster (Les couleurs du vin) reference
- Panelists evaluated color by tilting the glass nearly horizontally and moving it over poster until the color matched the reference.
- Color: Lightness, Red and Yellow
- Principal component analysis with confidence ellipses constructed using Hotelling’s test for $p < 0.05$
PCA Dimensions 1 & 2
Maturity
Extended Maceration
Ethanol Adjustment (Dim 1 vs Dim 3)
Simplified Sensory

**ASTRINGENCY**

- NB Early Control: CD
- CHAP Early Control: B
- NB Early EM: BC
- CHAP Early EM: A
- NB Late Control: D
- S/WB Late Control: D
- NB Late EM: AB
- S/WB Late EM: BCD
Summary I

- Tannin extraction from seeds was unaffected by 30 days of fruit maturation
- Extraction of tannin by extended maceration was independent of maturity
- Late harvest shifted wine aroma and mouthfeel towards more viscous, sweet and fruit-derived aromas
- Astringency of wines wasn’t dramatically impacted by picking decision
- Impact of Ethanol
  - EtOH adjustment on early harvest fruit lowered fresh veg
  - Saignee/water back on late harvest increased perception of vegetal and earthy notes
  - Ethanol had positive impact on overall sensory profile but no impact on phenolic extraction
Take Home Message I

• Maybe little green seeds are less important than we thought
• Perhaps use seed color as secondary information that is less important than: Color, Flavor
• Impact of ethanol on vegetal aromas unexpected but interesting and worthy of follow-up
• Results suggest ethanol concentration may be responsible for diminishing vegetal characters in some cases when we attributed decline to change in fruit composition
Cultural Practices & Environmental Impacts: Anthocyanins and Tannins

- Washington State: Primarily Semi-Arid Growing Conditions
  - Main Cultivars Grown: CS, MR, SY
  - Vineyard Studied: Cold Creek Vineyard in Southeastern WA
  - GDD °C ~1800
  - Precipitation: ~120 mm Annually & ~ 40 mm Seasonally
- Deficit Irrigation is widely practiced in Washington
- Withholding water during key developmental periods reduces berry size, vine yield and increases phenolics in grapes and wine
  - Early and Full Season Deficits Increase [Skin Tannin] [Anthocyanins]
  - Seed Tannins only impacted due to berry size change
  - Deficit Irrigation should be key to central dogma of wine quality
    - Low Yield = High Quality
Winery Phenolic Management Techniques

• Extended Maceration
  • Longer Contact Time (20 – 60 days typically)
  • Seed Tannin Extraction
  • Carried out to increase astringency and improve mouthfeel
• Pre-Fermentation Juice Removal
  • Saignée
  • Done to emulate a smaller berry size
  • 5-18% is easy
  • 25-32% is very difficult
    • Must eventually becomes like a rock
3-Year Irrigation Experiment: Yields small colorful berries

<table>
<thead>
<tr>
<th>Treatments</th>
<th>Fruit set-véraison</th>
<th>Véraison-harvest</th>
<th>Berry wt. (g)</th>
<th>Yield (kg/vine)</th>
<th>Pigments mg/g FW</th>
<th>Skin Tannins mg/g FW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Full Irrigation: 100% ET&lt;sub&gt;c&lt;/sub&gt;</td>
<td>100%</td>
<td>100%</td>
<td>1.06 a</td>
<td>6.4 a</td>
<td>0.95 b</td>
<td>0.86 a</td>
</tr>
<tr>
<td>Industry Std: 70% ET&lt;sub&gt;c&lt;/sub&gt;</td>
<td>70%</td>
<td>70%</td>
<td>1.08 a</td>
<td>5.6 a</td>
<td>0.99 b</td>
<td>0.67 b</td>
</tr>
<tr>
<td>Late Irrigation: 25/100% ET&lt;sub&gt;c&lt;/sub&gt;</td>
<td>25%</td>
<td>100%</td>
<td>0.95 b</td>
<td>5.7 a</td>
<td>1.04 b</td>
<td>0.79 a</td>
</tr>
<tr>
<td>Full deficit: 25% ET&lt;sub&gt;c&lt;/sub&gt;</td>
<td>25%</td>
<td>25%</td>
<td>0.84 c</td>
<td>3.0 b</td>
<td>1.31 a</td>
<td>0.66 b</td>
</tr>
</tbody>
</table>

Evapotranspiration (ET) is the sum of evaporation and plant transpiration from the Earth's land and ocean surface to the atmosphere. Evaporation accounts for the movement of water to the air from sources such as the soil, canopy interception, and waterbodies.
So who would win a fight between…

• T-Rex and Great White Shark?
• Lion and Tiger?
• Snake and Mongoose?
• Great White Shark and Orca?
• Answer: Clearly it depends.
• Land vs. Water; Future vs. Past

• We pit vineyard vs. winery in these experiments
• Which one controls phenolic content of wine?
• Deficit Irrigation in the Vineyard vs….Extended Maceration & Saignée
• Not really.
• But it makes it more exciting.
Exp. Design Year 1: Does RDI or Extended Maceration impact Tannin Structure?

Vineyard Treatment

Control
10 Days

Extended Maceration
30 Days

All Ferments fermented with EC-1118 and within 48 hrs. inoculation with VP41 ML strain
All Ferments (n=2), 300 L Ghidi Stainless Steel Variable Capacity Tanks
Tannin Structure Evaluation Method

• Method Issues
  • Mean degree of Polymerization
  • Average with no Std. Dev.

• Extracts Fractionated
  • Prep-Scale Diol Column
  • 1-fraction per min collected

• Analysis
  • Phloroglucinolysis
  • Tannin Polymer Information
    • Terminal Unit
    • Extension Unit
    • Size
YEAR : Tannin Structure

Tannin distribution by concentration: RDI

![Graphs showing tannin distribution by concentration for different ETc values (100%, 70%, 25/100%, 25%) with mean degree of polymerization (mDP) ranging from 2 to 18. Each graph includes monomers and shows the concentration (mg/L CB) of (-)-epigallocatechin, (+)-catechin, (-)-epicatechin, and (-)-epicatechin-gallate. A statistical note indicates n.s. and p = 0.971.]
Effect of EM and RDI

Tannin distribution by concentration: maceration

$p < 0.0109$
Effect of EM and RDI

Quantitative Descriptive Analysis 2011

(B) 25% ETc
25/100% ETc
70% ETc
100% ETc
Exp. Design Year 2: Can Saignée compensate for berry size differences?

Vineyard Treatment

Control
- 10-Day Maceration
- EC-1118 + VP41 ML
- Simultaneous Ferments

Extended Maceration
- 30-Day Maceration

Saignée
- 10-Day Maceration
- 16% Volume Removed
Anthocyanins (mg/L)  

Impact of saignée on pigments evident but diminishes over 120 days

Impact of saignée on tannins more pronounced on larger berries
Summary II

• RDI Treatments did not impact extraction beyond initial concentration differences
• Saignée could not compensate for differences from RDI for anthocyanins.
• Saignée increased anthocyanins initially but differences were gone by day 120  
  • Differences were observed in formation of polymeric pigments
• Saignée was most effective on largest berries (~1 g/berry; 100% Etc & 70% Etc)  
  • Difficult to concentrate wines from very small berries!
• EM reduced anthocyanins, wine color saturation but increased seed tannin extraction
Take Home Messages II

• Winemaking Techniques vs. Vineyard Techniques: A Draw!
  • Extended Maceration has impact on tannin structure and perception of astringency whereas RDI did not
  • Saignée could not compensate for RDI Treatments for color
  • Extended Maceration & saignée impacted tannins, wine color and had more evident impact than vineyard treatments
  • Increase in tannins from saignée was similar to EM and might be a simpler solution than tying up tank space

• Vineyard Treatments Reduce Yield too much
  • 25% ETc reduced yield by 66% but differential gain in phenolics and color did not outweigh crop reduction
  • 25/100 % ETc was best choice for maintaining yield and some phenolic improvements
Acknowledgements

• Washington Wine Commission
• Chateau Ste. Michelle Wine Estates
  • Russell Smithyman and Bill Riley
• My coauthors


Astringency & Bitterness

<table>
<thead>
<tr>
<th>Harvest/ Skin Contact /EtOH</th>
<th>Astringent</th>
<th>Bitter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Early Control</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Natural Brix</td>
<td>3.42 cd</td>
<td>2.08 c</td>
</tr>
<tr>
<td>Chaptalized</td>
<td>3.87 b</td>
<td>2.14 bc</td>
</tr>
<tr>
<td>Early Extended Maceration</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Natural Brix</td>
<td>3.80 bc</td>
<td>2.25 bc</td>
</tr>
<tr>
<td>Chaptalized</td>
<td>4.33 a</td>
<td>2.55 ab</td>
</tr>
<tr>
<td>Late Control</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Natural Brix</td>
<td>3.27 d</td>
<td>2.29 bc</td>
</tr>
<tr>
<td>Saignee/Water Back</td>
<td>3.24 d</td>
<td>1.93 c</td>
</tr>
<tr>
<td>Late Extended Maceration</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Natural Brix</td>
<td>3.92 ab</td>
<td>3.01 a</td>
</tr>
<tr>
<td>Saignee/Water Back</td>
<td>3.74 bcd</td>
<td>2.22 bc</td>
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</table>