Impact of Grape Ripening and Ethanol Content on Sensory Attributes of Merlot, Cabernet Sauvingon and Syrah wines

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Introduction

• Picking Decision: Most Important Choice Winemaker Makes

• Grape ripening alters fundamental aspects of grapes and eventual wine

• Picking Decisions are largely based on desired wine style
  • Impacts include
    • Weather: Rain, Frost
    • Logistics: Vineyard and Winery (crew availability; tank space)
    • Tax Related Issues based on Potential Alcohol
Complex Relationships: Grape and Wine Flavor

• What you taste in fruit is not what you taste in wine?
  • Some flavor compounds are bound as precursors
  • Some flavor compounds are not

• Aroma compounds are changing during ripening

• Some influenced by vineyard practices
  • Sun exposure: Pyrazines, Norisoprenoids (TDN)

• How does wine composition influence this relationship?
  • Ethanol solvates hydrophobic compounds that we smell and taste
  • Chaptalization (addition of Sucrose) is common in cool regions
Experiments Designed to Explore Ripening

- Washington Ideal place to study ripening.
- Long Dry Season with very little rain during harvest months (11 mm)
- Ripening is a universal problem
- The effects of ripening on wine composition is profound
  - Sourness, Body, Color, Astringency, Bitterness, Aroma (nose & mouth)
- Experiments designed to explore ripening effects while controlling for ethanol at each maturity
- Soluble Solids used as main metric for ripeness
- Multiple cultivars explored in presentation and different aspects of ripening effects on wine composition explored.
Hang Time Experiment: Merlot

**Harvest 1: Unripe**
- 20.7 ± 0.5 Brix
- Chaptalize to 24 Brix
- 5 September 2013
- Brix

**Harvest 2: Ripe**
- 24.0 ± 0.2 Brix
- Chaptalize to 28 Brix
- 26 September 2013
- Brix

**Harvest 3: Overripe**
- 20 Brix
- 27.4 ± 0.4 Brix to 24 Brix
- 2 November 2013
WINEMAKING

• 300 kg/Replicate
• 300 L Stainless Steel Tanks
  • Treatment Replicates: n=3
• Yeast (EC-1118)
• 48 hrs. ML (VP41)
• 10 Days Contact Time
  • (26 ± 2°C)
## Fruit Data

<table>
<thead>
<tr>
<th>Harvest</th>
<th>Brix</th>
<th>pH</th>
<th>TA (g/L)</th>
<th>Berry Weight</th>
<th>Color (mg/g FW)</th>
<th>Skin Tannins (mg/g FW)</th>
<th>Seed Tannins (mg/g FW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UNRIPE</td>
<td>20.7</td>
<td>3.57</td>
<td>7.83 c</td>
<td>0.98 a</td>
<td>0.65 a</td>
<td>0.60 a</td>
<td>3.68 b</td>
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<tr>
<td>Ripe</td>
<td>23.9</td>
<td>3.73</td>
<td>5.56 a</td>
<td>1.18 b</td>
<td>0.73 a</td>
<td>0.60 a</td>
<td>3.06 a</td>
</tr>
<tr>
<td>OVERRIPE</td>
<td>27.4</td>
<td>3.73</td>
<td>6.60 b</td>
<td>0.99 a</td>
<td>0.99 b</td>
<td>0.99 b</td>
<td>3.66 b</td>
</tr>
</tbody>
</table>

Overripe fruit is mainly characterized by concentration effects from dehydration.

Intuitive Impacts: More color and skin tannins
Counter Intuitive Impacts: TA increase, Seed Tannin Increase

Drop in yield about 20-25% when ripening to 28 Brix
<table>
<thead>
<tr>
<th>Harvest</th>
<th>EtOH  % (v/v)</th>
<th>pH</th>
<th>TA (g/L)</th>
<th>RS (g/L)</th>
<th>Dynamic Viscosity (cP)</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UNRIPE</td>
<td>13.86</td>
<td>3.63</td>
<td>5.01 b</td>
<td>3.11 a</td>
<td>1.35 c</td>
<td>0.9857 a</td>
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<tr>
<td>RIPE</td>
<td>14.03</td>
<td>3.73 b</td>
<td>4.52 a</td>
<td>2.56 a</td>
<td>1.29 a</td>
<td>0.9860 a</td>
</tr>
<tr>
<td>OVERRIPE</td>
<td>13.95</td>
<td>3.73 b</td>
<td>5.15 b</td>
<td>4.11 a</td>
<td>1.32 b</td>
<td>0.9872 b</td>
</tr>
</tbody>
</table>

**Ethanol**

<table>
<thead>
<tr>
<th>Ethanol</th>
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<tbody>
<tr>
<td>Low</td>
<td>11.59 a</td>
<td>3.60 a</td>
<td>4.86 a</td>
<td>1.94 a</td>
<td>1.22 a</td>
<td>0.9884 c</td>
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<tr>
<td>Med</td>
<td>14.04 b</td>
<td>3.72 b</td>
<td>4.88</td>
<td>1.89 a</td>
<td>1.33 b</td>
<td>0.9860 b</td>
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<tr>
<td>High</td>
<td>16.22 c</td>
<td>3.77 c</td>
<td>4.93</td>
<td>5.94 b</td>
<td>1.43 c</td>
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</tbody>
</table>

OVERRIPE: Greater Viscosity and Lower Density

More EtOH: Yeast struggle (Higher RS); Greater Viscosity, Lower Density
<table>
<thead>
<tr>
<th>Harvest</th>
<th>Anthocyanins (mg/L)</th>
<th>SPP ($A_{520nm}$)</th>
<th>LPP ($A_{520nm}$)</th>
<th>Tannins (mg/L)</th>
<th>Total Iron Reactive Phenolics (mg/L)</th>
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<tbody>
<tr>
<td>UNRIPE</td>
<td>249 a</td>
<td>0.90 b</td>
<td>0.54 c</td>
<td>564 b</td>
<td>1571 a</td>
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<tr>
<td>RIPE</td>
<td>469 b</td>
<td>1.11 c</td>
<td>0.31 a</td>
<td>440 a</td>
<td>1521 a</td>
</tr>
<tr>
<td>OVERRIPE</td>
<td>524 c</td>
<td>0.82 a</td>
<td>0.40 b</td>
<td>792 c</td>
<td>2338 b</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Ethanol</th>
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<tbody>
<tr>
<td>Low</td>
<td>430</td>
<td>0.87 a</td>
<td>0.32 a</td>
<td>537 a</td>
<td>1655 a</td>
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<tr>
<td>Med</td>
<td>410</td>
<td>0.91 a</td>
<td>0.41 b</td>
<td>591 b</td>
<td>1766 b</td>
</tr>
<tr>
<td>High</td>
<td>403</td>
<td>1.06 b</td>
<td>0.52 c</td>
<td>669 c</td>
<td>2008 c</td>
</tr>
</tbody>
</table>

High Ethanol Impacted: Tannins, Total IRP
Sensory Panel Work

• Descriptive Analysis
• Sourness, Bitterness, Astringency, Sweet, Body
• Aromas by aroma and flavor
  • Vegetal, bell pepper, smokey, white pepper, floral, spice, red fruit, plum, dried fruit, oak
Sensory Evaluation PCA

Dim 1 x Dim 2

SEPARATION BY ETHANOL
HIGH, MEDIUM, LOW
Explain that one to me again
Henry’s Law

• Tendency of molecule to partition between liquid and vapor phases
  • Henry’s law is used in relatively dilute systems (Ethanol vs. aroma compounds)
    • 46-49 M H₂O or 2-2.8 M Ethanol vs. mM, µM, nM Aroma Compounds
  • Vapor-liquid equilibrium data are represented in terms of K values
  • K value is vapor liquid distribution ratio

• Can be really complex of course:
  • Influenced by Chemical Equilibrium
  • Temperature (of course)
  • Ionic Strength (more salt tends decrease solubility of gases)
  • Solvent mixtures (EtOH + Water)!!!
  • Non-ideal solutions (sucrose)
Ethanol Dominated Sensorial Evaluation

• Wines with similar ethanol were more similar to each other than the wines made from fruit picked at 20, 24 and ~28 Brix

• Low Ethanol: sourness, vegetal, bell pepper and earthy flavors.

• Medium Ethanol: vegetal, earthy and floral aromas.

• High Ethanol: Astringent, Bitter, Hot, Body, Sweet, Alcohol; Aromas & Flavors: Red Fruit, Plum, Oak, Smokey, White Pepper
Winemaking Procedure

- Syrah and Cabernet Sauvignon
- Wines replicated sugar content of other maturity treatments
  - Controlled for maturity vs. ethanol effects
Experimental Design

• Pick fruit at different soluble solids: 20 Brix, 24 Brix, 28 Brix

• Represent different winemaking eras and extraction effect
  • ~ 12 %, 14%, & 16% (v/v) Ethanol

• Ethanol is controlled for at each harvest by dilution or sugar addition
  • Must is bled off prior to dilution (bleed off/water back)

• Cultivars and Collaboration
  • SMWE donated fruit and labor for picking. Thanks!
  • Syrah (Paterson)
  • Cabernet Sauvignon (Cold Creek)
  • Merlot (Paterson)
Winemaking Procedure

- Wines fermented in triplicate
  - 200 L scale, 54 total wines
  - TJ/Boulton Fermentors
- Inoculated with EC 1118 (10^6 cells/mL)
- Simultaneous ML fermentation (~48 hours post using VP41)
- Nutrient Addition
  - FermaidK (0.25 g/L), DAP (200ppm), GoFerm (0.3g/L)
- No acidity adjustments
  - Water for saignée/water back had 5 g/L tartaric acid
- Chaptalization with 80 Brix sugar solution
- 10 day maceration
## 2016 Syrah

<table>
<thead>
<tr>
<th>Alcohol Treatment</th>
<th>ALCOHOL (% v/v)</th>
<th>pH</th>
<th>TA (g/L)</th>
<th>Anthocyanins (mg/L)</th>
<th>Tannins (mg/L)</th>
</tr>
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<tbody>
<tr>
<td>Harvest</td>
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<tr>
<td>22.1 BRIX</td>
<td>13.75</td>
<td>3.53</td>
<td>6.20 a</td>
<td>424 c</td>
<td>187 b</td>
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<tr>
<td>24.6 BRIX</td>
<td>13.42</td>
<td>3.57</td>
<td>6.20 a</td>
<td>574 b</td>
<td>146 b</td>
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<tr>
<td>25.6 BRIX</td>
<td>13.09</td>
<td>3.54</td>
<td>5.90 b</td>
<td>651 a</td>
<td>347 a</td>
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<td>p-value</td>
<td>0.839 ns</td>
<td>0.874 ns</td>
<td>&lt;0.05</td>
<td>&lt;0.001</td>
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<td>Alcohol Treatment</td>
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</tr>
<tr>
<td>20 Brix</td>
<td>10.66 c</td>
<td>3.40 b</td>
<td>6.27 a</td>
<td>530</td>
<td>168 a</td>
</tr>
<tr>
<td>24 Brix</td>
<td>13.51 b</td>
<td>3.61 a</td>
<td>5.87 b</td>
<td>551</td>
<td>229 a</td>
</tr>
<tr>
<td>28 Brix</td>
<td>16.09 a</td>
<td>3.64 a</td>
<td>6.15 a</td>
<td>568</td>
<td>280 a</td>
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<td>p-value</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.01</td>
<td>0.738 ns</td>
<td>0.075 ns</td>
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Syrah Sensory PCA

DIMENSION 1 X-AXIS DRIVEN BY ETHANOL & DIMENSION 2 Y-AXIS DRIVEN SULFUR & SOURNESS
Syrah Sensory: Alcohol Dominated Sensory

- Bitter Taste Increased with more ethanol
- Viscosity Mouthfeel mainly effected by ethanol
- Astringency Perception Increased with Ethanol (impacted by ripeness)
- Jammy Fruits aroma was influenced by alcohol
  - More jammy aroma with more ethanol
- Solvent aroma increased with ethanol
## 2016 Cabernet Sauvignon

<table>
<thead>
<tr>
<th>ALCOHOL (% v/v)</th>
<th>pH</th>
<th>TA (g/L)</th>
<th>Anthocyanins (mg/L)</th>
<th>Tannins (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>HARVEST</strong></td>
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<tr>
<td>20.9 BRIX</td>
<td>13.17</td>
<td>3.28 b</td>
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<td>390 c</td>
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<tr>
<td>23.3 BRIX</td>
<td>13.76</td>
<td>3.45 a</td>
<td>6.80 b</td>
<td>463 b</td>
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<tr>
<td>26.4 BRIX</td>
<td>13.60</td>
<td>3.51 a</td>
<td>7.17 b</td>
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<tr>
<td><strong>p-value</strong></td>
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<tr>
<td><strong>Alcohol Treatment</strong></td>
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</tr>
<tr>
<td>20 Brix</td>
<td>11.06 c</td>
<td>3.34</td>
<td>7.18</td>
<td>554</td>
</tr>
<tr>
<td>24 Brix</td>
<td>13.32 b</td>
<td>3.44</td>
<td>7.04</td>
<td>523</td>
</tr>
<tr>
<td>28 Brix</td>
<td>16.16 a</td>
<td>3.46</td>
<td>7.39</td>
<td>533</td>
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<tr>
<td><strong>p-value</strong></td>
<td>&lt;0.001</td>
<td>0.115 ns</td>
<td>0.307 ns</td>
<td>0.924 ns</td>
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Cabernet Sauvignon Sensory

DIMENSION 1 X-AXIS DRIVEN BY ETHANOL & DIMENSION 2 Y-AXIS DRIVEN BY HARVEST DATE
Cabernet Sensory: Ethanol Dominates but significantly impacted by Ripeness

- Dimension 1 (x-axis)
- Bitter Taste Increased with more ethanol
- Viscosity Mouthfeel mainly effected by ethanol
- Astringency Perception effected by Ethanol (not much impact)

- Dimension 2 (y-axis)
- Harvest 1 wines in Upper quadrant dominated by green character
- Harvest 2 wines in Middle of PCA
- Harvest 3 wines in Negative quadrant (Jammy Berries)
Conclusions

• Ethanol dominates sensory profile of wine but specific to the cultivar
  • Syrah became more jammy, viscous & bitter with more ethanol
  • Cabernet Sauvignon more complex
    • Veggie aroma declined as a result of ripening not ethanol
    • Ethanol made wines more jammy, viscous and bitter
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