Use of Tannin Additions in the Production of Red Wines

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Tannins

• Importance
  – Sensory Attributes
    • Astringent
  – Antioxidant
  – Formation of Polymeric Pigments

• Condensed and Hydrolysable Tannins
  – Grapes contain Condensed in Skin, Seed, Stem
  – Oak Barrels contain Hydrolysable and Condensed (primarily Hydrolysable)

• Oenotannins
  – Extract dried into powder
  – Grapes, Barrels, Exotic Trees, Oak Galls
Grape Tannins

• Condensed Tannins
• Main Tannins found in Wine
• Origin
  – Skins (0.5-1.2 mg/berry)
  – Seeds (3.0-4.0 mg/berry)
  – Stems (/?/racchis)
Oak Tannins

- Ester linkages hydrolyze under acidic aqueous conditions of wine
- Castalagin may directly contribute to astringency of wine
- Synergetic effect with wine tannins
  - Some evidence of direct impact
Oenological Tannins

- Removal of Protein Haze
- Deactivation of Laccase Enzyme
- Sulfide Removal
- Removal of Veggie Aroma
- Sacrificial Tannins
- Color Stabilization
- Astringency Modification
Protein Haze Removal

• Addition of tannin to remove proteins
  – Primarily used for protein stabilizing beer
  – Potential use for white wine production
    • Condensed tannins favored
      – Cross-linking mechanism linear relationship
      – Potential added bitterness or aroma
• Research Scale Immobilized Tannins
  – Reaction with metals and proteins
Laccase

• Tannins are well known enzyme inhibitors
  – Goldstein and Swain 1965
• Tannin Addition Friend or Foe?
• Impurity: monomeric phenolics (substrates for enzyme)
  – Residual bitterness
• Compete with Laccase for O$_2$?
  – Laccase affinity for oxygen is 0.16 -0.32 mg/L
  – Solubility of O$_2$ in water
    • 0°C – 15 mg/L O$_2$
    • 10°C – 11.4 mg/L O$_2$
    • 20°C – 9.1 mg/L O$_2$
    • 30°C- 7.7 mg/L O$_2$
Fruit & Wine Tannins

MR: \( y = 447 - 18x; r = -0.11; p = 0.30; r^2 = 0.01 \)

SY: \( y = 334 - 15x; r = -0.05; p = 0.61; r^2 = 0.003 \)
Sacificial Tannins

- Fruit & Wine Tannins
  - Poor correlation
- Grape Fining Agent
  - Cell walls, polysaccharides
- Tannin Sponge Theory
  - Very large tannins occupy binding sites
  - Must occupy all binding sites for tannins to escape
    - Simplistic Idea
- No thorough examination of early additions
  - Canuti et al. 2012 added grape and gallnut tannins to Sangiovese primarily observed color change
Polymeric Pigments

• Heterogeneous mixture
  – HSO$_3^-$ resistance (partial)
  – pH color shift small
  – Possible reduction in astringency

• Anthocyanins react with multiple classes
  – Aldehydes
  – Keto-Acids (Pyruvate)
  – Tannins
  – Hydrolysable tannins (in test tubes only)

• Some Data Supports Addition of Tannins
  – Primarily Excessive Additions
  – Small Additions provide temporary increase
    • Copigmentation or oxidation prevention?
Astringency

- Impact depends on target wine
  - Original amount of tannins
  - 100 mg/L added to 100 mg/L: 2-Fold Increase
  - 100 mg/L added to 1000 mg/L: 10% increase
- Additions of 200 mg/L – 400 mg/L
  - No improvement
    - Parker et al. 2007 (200 mg/L)
    - Bautista-Ortin et al. 2007 (400 mg/L)
- Change in Aroma Observed not Astringency
  - Parker et al. 2007
  - Diaz-Plaza et al. 2002
Purity: OIV CODEX

- Water extracts that are dried
  - Powder must be 98% water soluble
- International Oenological Codex (2013)
  - COEI-1-TANINS : 2009
- Not the most stringent set of rules
- Estimation of Total Phenolics in powder must be greater than 65% (gallic acid)
- Condensed tannins use (DMACH) 10 mg/g (1%)
- Ellagitannins use nitrous acid 20 mg/g (2%)
- Limits on yellow $\text{A}_{420\text{nm}}$ and red color $\text{A}_{520\text{nm}}$
- Specific Definitions: Grape = 50 mg/g Catechin (5%)
  - 0.5 mg/g procyanindin
Purity: Literature

- Discrepancies in labeling and content
- Lack of relationship between total phenolics and tannins
  - Obreque-Slíer et al. 2009
- 12-48% of Total IRP is PPT (CE)
  - Harbertson et al. 2012
  - Keulder 2005 thesis
- Better purity than OIV requirements
Experimental

- Cabernet Sauvignon Wine from Columbia Valley WA
- Biotan by Laffort (Tanin VR Grape)
  - Grape Tannin: Information Confusing listed in units of non-flavonoid (coumaric acid)
  - Total phenolics > 65%
- Tanin Galacool by Laffort
  - Chestnut gall tannin
  - Hydrolysable tannins
  - Total phenolics > 80%
  - Used for deactivation of Laccase
- US: 150 mg/L Tannic Acid Addition is legal
Tannin Analysis

BIOTAN GRAPE TANIN

Linear PPT: $y = 0.44x - 4.76$

Exponential PPT

TANIN GALACOOL

Figure 1.

Figure 2.

Exponential PPT
Tannins and Total IRP

Predicted 85 and 350 mg/L Addition of Tannin for Biotan
Found 53 and 187 mg/L Addition for Biotan
## Anthocyanins and Polymeric Pigments

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Anthocyanins (mg/L)</th>
<th>SPP ($A_{520nm}$)</th>
<th>LPP ($A_{520nm}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>330±3.5</td>
<td>1.75±0.06</td>
<td>1.99±0.04 ab</td>
</tr>
<tr>
<td>+ Biotan 200 mg/L</td>
<td>319±2.5</td>
<td>1.71±0.03</td>
<td>1.93±0.02 c</td>
</tr>
<tr>
<td>+ Biotan 800 mg/L</td>
<td>321±4.5</td>
<td>1.77±0.06</td>
<td>2.15±0.06 ab</td>
</tr>
<tr>
<td>+ GT 150 mg/L</td>
<td>322±3.5</td>
<td>1.71±0.02</td>
<td>2.03±0.08 abc</td>
</tr>
<tr>
<td>+ GT 600 mg/L</td>
<td>324±9.0</td>
<td>1.66±0.05</td>
<td>2.21±0.02 a</td>
</tr>
</tbody>
</table>
Sensory Evaluation

Fig. 4. Discriminant Analysis of the sensory data of the control wine (CTRL) and wines added with tannins (BIO200, BIO800, GAL150, GAL600).
Conclusions

• Significant Tannin, LPP and Total IRP impacts
• Sensory Evaluation
  – Tannin Addition Wines Characterized
  – Primarily Negative Attributes
    • Brown Color, Bitter Flavor and Earthy Aroma
      – BIOTAN 800 mg/L most Earthy
    • Bitterness Change consistent with greater Total IRP
  – Lower concentration additions had no detrimental impacts but small improvement in phenolics
Comments

• Purity Needs to Change
• Standard should be the same
  – Catechin Equivalents for Condensed Tannins
  – Gallic Acid for Hydrolysable Tannins
  – Use of Tannic Acid is confusing
    • Mixture of different compounds
• Legal Amount Allowable Needs to Change
• Many use tannins as flavorant
  – Tannins come with “friends”
  – Threshold for odorants ng/L, µg/L
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