TANNIN EXTRACTION, ADDITION, AND RETENTION
WHAT ARE TANNINS?

Plant polyphenolics capable of cross-linking collagen fibers in animal hides

...a purely functional categorization.

Capable of precipitating proteins
TANNINS PRECIPITATE PROTEINS

- Bind with proteins in saliva
  - loss of lubrication
  - activation of epithelial mechanoreceptors

- Close correlation with perceived palate roughness
TANNINS IN RED WINE

- Perceived mouthfeel
  - astringency
  - texture
  - structure
- Long-term color stability
  - co-pigmentation
- Tannin amount, size correlates to bottle price
GRAPE TANNINS

Pulp: hydroxycinnamic acids, no tannin

Skins: longer condensed tannin polymers

Seeds: shorter condensed tannins

Stem: tannins
GRAPE TANNINS

- Condensed tannins
  - Ogliomers or polymers (short or long chains) of flavan-3-ols (smaller phenols)

- Originate in skins and seeds
  - seeds = higher content, low extractability
  - skin tannin larger component in wine

- Concentration varies by:
  - cultivar
  - site
  - viticultural practices
FLAVAN-3-OLS

(+)-Catechin

(-)-Epicatechin

Gallocatechin gallate
Many forms….

**Variables:**
- Initiator
- Elongator
- Size
  - Degree of polymerization
- Branching
  - Linkage type and location

**Analysis:** break chains, look at pieces

Large tannins are perceived as astringent

Small tannins are perceived as bitter

CONDENSED TANNINS
During ripening:

- Tannin length (mDP) increases
- Extractability decreases
Anthocyanins and skin tannins are rapidly extracted

Extraction of seed tannin is slower

Color stabilization is limited by availability of tannin
Mean values for >1000 CA, OR, WA, and AU red wines

50-fold range in wine tannin concentration

*V. vinifera*: 30-1895 mg/L
Ave: 544 mg/L
Hybrids: 30-100 mg/L

Tannin concentration range in grapes is 3-4 fold

Harbertson et al. AJEV 2008
WHERE’S THE TANNIN?

Hypothesis:
Binding to cell wall material, especially pectins and polysaccharides

Hanlin et.al. *AJGWR*, 2009
ADDING IT UP

Amount of tannin extracted from grape

Amount of exogenous tannin added

Amount of tannin bound to pomace

Amount of tannin retained in wine
TANNIN ADDITIONS

- What’s in a tannin?
  - Grape-derived condensed tannins
  - Plant (non-grape) derived condensed & hydrolyzable tannins
  - A mix of any of the above
## TYPES OF TANNINS

<table>
<thead>
<tr>
<th></th>
<th>Condensed</th>
<th>Hydrolyzable</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grape derived</td>
<td>tannin:protein = 20:1</td>
<td>Wood derived</td>
</tr>
<tr>
<td>tannin:protein = 20:1</td>
<td></td>
<td>tannin:protein = 40:1</td>
</tr>
<tr>
<td>Temperature independent</td>
<td></td>
<td>Temperature ↑ binding</td>
</tr>
<tr>
<td>Ethanol independent</td>
<td></td>
<td>Ethanol ↓ binding</td>
</tr>
<tr>
<td>Potential for color stabilization activity</td>
<td></td>
<td>No known potential for color stabilization</td>
</tr>
</tbody>
</table>

Harbertson et.al. Vit 2010
WHAT’S IN A TANNIN?

- Tannins < 50%
- What’s the rest?
  - non-tannin phenols
  - activity?
  - solubility and drying agents
  - non-phenolic plant material (= flavor?)

To effect sensory changes, additions much higher than manufacturer recommended may be necessary

<table>
<thead>
<tr>
<th>Product</th>
<th>Tannin content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biotan</td>
<td>43%</td>
</tr>
<tr>
<td>Tannin VR Supra</td>
<td>20%</td>
</tr>
<tr>
<td>Gallacool</td>
<td>23%</td>
</tr>
<tr>
<td>Oenologique</td>
<td>19%</td>
</tr>
<tr>
<td>Tanin Plus</td>
<td>21%</td>
</tr>
<tr>
<td>Quertanin</td>
<td>34%</td>
</tr>
<tr>
<td>Tan’Cor</td>
<td>35%</td>
</tr>
<tr>
<td>Tan’Cor Grand Cru</td>
<td>28%</td>
</tr>
</tbody>
</table>

Modified from Harbertson et.al. Food Chem 2012
<table>
<thead>
<tr>
<th>Product Name</th>
<th>Tannin Source</th>
<th>Recommended Dosage</th>
<th>Protein PPT Linearity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biotan</td>
<td>Grape</td>
<td>100-400 mg/L</td>
<td>Linear</td>
</tr>
<tr>
<td>Tannin VR Supra</td>
<td>Grape + Oak</td>
<td>300-500 mg/L</td>
<td>Linear</td>
</tr>
<tr>
<td>Tanin Galacool</td>
<td>Gall Nut Oak Tree</td>
<td>50-300 mg/L</td>
<td>Non-linear</td>
</tr>
<tr>
<td>Tanin Plus</td>
<td>American Oak</td>
<td>50-300 mg/L</td>
<td>Non-linear</td>
</tr>
<tr>
<td>Quertanin</td>
<td>Limousin Oak</td>
<td>100-200 mg/L</td>
<td>Linear</td>
</tr>
<tr>
<td>Tan’Cor</td>
<td>Grape and Oak</td>
<td>100-300 mg/L</td>
<td>Linear</td>
</tr>
<tr>
<td>Tan’Cor Grand Cru</td>
<td>Grape and Oak</td>
<td>100-300 mg/L</td>
<td>Linear</td>
</tr>
<tr>
<td>Oenotan</td>
<td>Oak</td>
<td>20-100 mg/L</td>
<td>Non-linear</td>
</tr>
<tr>
<td>Taninraisin</td>
<td>Grape</td>
<td>50-200 mg/L</td>
<td>Linear</td>
</tr>
<tr>
<td>Taningal</td>
<td>Gall Nut Oak Tree</td>
<td>10-120 mg/L</td>
<td>Non-linear</td>
</tr>
<tr>
<td>Vintinil AJ11</td>
<td>Querbacho</td>
<td>50-300 mg/L</td>
<td>Linear</td>
</tr>
<tr>
<td>Vintinil VR</td>
<td>Querbacho</td>
<td>50-400 mg/L</td>
<td>Non-linear</td>
</tr>
<tr>
<td>Vintinil AS</td>
<td>Querbacho, Oak, Tara</td>
<td>50-100 mg/L</td>
<td>Non-linear</td>
</tr>
</tbody>
</table>

Harbertson et.al. Vit 2010
## ADDITION TIMES

<table>
<thead>
<tr>
<th>Type</th>
<th>Fermentation</th>
<th>Cellaring</th>
<th>Finishing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Addition</td>
<td>Grapes at crusher or during first pumpover</td>
<td>During racking; 3-6 weeks prior to bottling</td>
<td>3-6 weeks prior to bottling</td>
</tr>
<tr>
<td>Goals</td>
<td>Color stabilization Mouthfeel/structure Antioxidant</td>
<td>Color stabilization Mouthfeel/structure</td>
<td>Mouthfeel/structure Flavored agent</td>
</tr>
</tbody>
</table>

- Condensed tannins best for color stabilization at fermentation
- Hydrolyzable may promote fuller mid-palate and softer mouthfeel (lower, slower protein interaction)
THE BINDING ISSUE...

Tannins added when grape solids are present are lost through binding.

Tannin additions in hybrids should be much higher than advertised.

Hypothesis: most effective retention with post-dejuicing additions.

Color stability additions may need to be extremely large.
WHAT ABOUT ENZYMES?

Add enzyme or exogenous tannin

High Binding
Tannin remains bound to insoluble cell wall materials

Low Binding
Tannin leaves the insoluble cell wall and enters wine

Illustration by Lindsey Springer
2011 HYBRID RED SURVEY

Hybrid Aroma
Low Tannin
Color Stability
High Acidity
Storage

78 WINEMAKERS

MN
WI
MI
PA
NY
A core–shell column approach to a comprehensive high-performance liquid chromatography phenolic analysis of *Vitis vinifera* L. and interspecific hybrid grape juices, wines, and other matrices following either solid phase extraction or direct injection

David C. Manns, Anna Katharine Mansfield*

Department of Food Science, Cornell University, New York State Agricultural Experiment Station, Geneva, NY 14456, USA

**Abstract**

Four high-throughput reverse-phase chromatographic protocols utilizing two different core–shell column chemistries have been developed to analyze the phenolic profiles of complex matrices, specifically targeting juices and wines produced from interspecific hybrid grape cultivars. Following pre-fractionation...
HPLC ANALYSIS OF PHENOLIC FRACTIONS

**Anthocyanin Fraction**
- Anthocyanins
- Monoglycosides, diglycosides
- Coumarylated, acylated...
- Grape reaction product (GRP)

**Non-anthocyanin Fraction**
- Flavanols
- Flavonols
- Hydroxybenzoic acids
- Hydroxycinnamates

**Polymeric Fraction**
- Condensed tannins
- Polymeric color
BioTan (Laffort) addition @ 400ppm ≈ 200ppm tannin addition (estimated 47% condensed tannins)
### HYBRID WINE TANNINS

<table>
<thead>
<tr>
<th>Variety</th>
<th>Exogenous Tannin Added</th>
<th>Increase from Control Wine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Marechal Foch</td>
<td>200 ppm</td>
<td>39 ppm (9.8%)</td>
</tr>
<tr>
<td>Corot noir</td>
<td>200 ppm</td>
<td>24 ppm (6.0%)</td>
</tr>
</tbody>
</table>

- Winemaking processes initially increased amount and average size of tannin extracted into must
- No difference in final wines
- Average tannin molecule was small (mDP<3), contributing to bitterness rather than astringency
- Exogenous tannin added to must is not fully recovered in wine
Later additions = greater impact
- Higher tannin concentrations
- Higher mDP

Sensory impacts uncertain
- mDP suggests bitterness...threshold?
- Artifact effects?

Explore higher concentration additions
TO BE DETERMINED:

- Binding potential by varietal
- Effect of pectolytic enzymes on binding potential
- Variable binding potential for condensed vs. hydrolyzable tannin products
- Balancing tannin retention with early additions required for color stabilization, or to diminish unpleasant sensory characteristics
Enological tannins may be lost due to binding activity, much more so in hybrids.

Post-dejuicing additions should be the most enduring (in theory!)

Condensed tannins react more strongly with proteins and have known color stability activity.

Bench trials for cellaring or finishing tannins are essential.
CONFUSED?

- You’re not alone.
- There’s a WHOLE lot we don’t know about tannin chemistry…
- …like how to measure individual tannin polymers… or mechanisms… or compounds responsible for sensory characteristics…
ACKNOWLEDGEMENTS
 WANT TO LEARN MORE?


27 February – 1 March

events.cals.cornell.edu/bevny2014

grapesandwine.cals.cornell.edu/appellation-cornell

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