Wine Structure – Phenolics from Grape and Oak

- Phenolics – structures and terms
- Grape phenolics
- Harvest color and tannins measurements
- Changes during fermentation
- Pressing off – permanganate index
- Color, spectroscopic characterization
Phenolics

phenol

\[
\text{O} \quad \text{H}
\]

[benzene ring with a hydroxyl group]
Phenolics

- The content of phenolics in mature grape berries will ultimately influence the flavor and quality of the resulting wine product.
- Many factors, environmental and cultural, will influence the content and quality of phenolics within the grape berry itself.
- Full bodied red wines generally contain higher levels of polyphenolics and tannins, and are deep red in color due to the presence of anthocyanins.
Phenolics

- Phenolics provide color, bitterness and astringency, and longevity (they are anti-oxidants) to wine.
- Phenolics are an additional parameter -- beyond sugar and acid -- used to judge grape and wine quality.
- Methods of analysis can provide information where previously intuition was the only guide.
The Phenolic content of Red grapes & wine

- **Epidermis (Skin)**
  - Anthocyanin
  - Tannin
  - Flavonols
  - Stilbenes

- **Mesocarp (Pulp)**
  - Cinnamates
  - Flavonols
  - Stilbenes

- **Seed (Outer Integument)**
  - Catechins
  - Tannin
  - Gallic Acid

Oxidation
Enzymatic
Non-enzymatic
Copigmentation
Polymeric Pigment (non-tannin)
Tannins
“Pigmented Polymers”
Functional Classes of Phenolics

• Grape Pigments
  – Anthocyanins

• Wine Pigments
  – Small Polymeric Pigments (SPP)
  – Large Polymeric Pigments* (LPP)

• Phenolics
  – Tannins (Phenolic polymers ppt. Protein)
  – Non-Tannin Phenolics (Total Iron Reactive Phenolics minus Tannins)

*Pigmented Tannins
Non-Tannin Phenolics

Small phenolics
- Antioxidants
- Brown polymers

Cinnamates (Pulp)

Flavonols (Skin)

Catechins (Seed)

Bitter!
Anthocyanins

<table>
<thead>
<tr>
<th>Compound</th>
<th>R₁</th>
<th>R₂</th>
<th>R₃</th>
<th>R₄</th>
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<tbody>
<tr>
<td>Delphinidin-3-O-glucoside</td>
<td>OH</td>
<td>OH</td>
<td>OH</td>
<td>O-glucose</td>
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<tr>
<td>Cyanidin-3-O-glucoside</td>
<td>OH</td>
<td>OH</td>
<td>H</td>
<td>O-glucose</td>
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<tr>
<td>Petunidin-3-O-glucoside</td>
<td>OCH₃</td>
<td>OH</td>
<td>OH</td>
<td>O-glucose</td>
</tr>
<tr>
<td>Peonidin-3-O-glucoside</td>
<td>OCH₃</td>
<td>OH</td>
<td>H</td>
<td>O-glucose</td>
</tr>
<tr>
<td>Malvidin-3-O-glucoside</td>
<td>OCH₃</td>
<td>OH</td>
<td>OCH₃</td>
<td>O-glucose</td>
</tr>
<tr>
<td>Malvidin-3-O-acetylglucoside</td>
<td>OCH₃</td>
<td>OH</td>
<td>OCH₃</td>
<td>O-acetylglucose</td>
</tr>
<tr>
<td>Malvidin-3-O-p-coumarylglucoside</td>
<td>OCH₃</td>
<td>OH</td>
<td>OCH₃</td>
<td>O-p-coumarylglucose</td>
</tr>
</tbody>
</table>
Procyanidins

catechins

leucoanthocyanidins

flavonoids
Mechanism for the Formation of Acetaldehyde

\[
\text{OH} \quad \text{OH} \quad \leftrightarrow \quad \text{O} \quad \text{O}
\]

\[
\text{R} \quad \text{C} \quad \text{C} \quad \text{H}_3 \text{C} \quad \text{H} \quad + \quad \text{O}_2 \quad \text{H}_2\text{O}_2 \quad \rightarrow \quad \text{R} \quad \text{C} \quad \text{C} \quad \text{H}_3 \text{C} \quad \text{H} \quad + \quad \text{H}_2\text{O}_2
\]

\[
\text{OH} \quad \rightarrow \quad \text{O}
\]

\[
\text{H}_3\text{C} \quad \text{C} \quad \text{H} \quad + \quad \text{H}_2\text{O}_2 \quad \rightarrow \quad \text{H}_3\text{C} \quad \text{C} \quad \text{H} \quad + \quad \text{H}_2\text{O}
\]
Procyanidin

catechin R1=H, R2=OH
epicatechin R1=OH, R2=H

+ CH₃CHO
Portosins – an example of a small polymeric pigment (SPP)
Tannin
Polymeric Pigments (LPP)

Tannin-Anthocyanin

Anthocyanin-Tannin
We Also Know That Oak from Barrels or Adjuncts Contributes Some Phenolics to A Wine
Oak – Barrels & Adjuncts

- 40 – 50% Cellulose
- 20 – 25% Hemicellulose
- 25 – 35% Lignin
- 5 – 10% Tannin
- about 0.5% of other minor constituents
Cellulose

Very stable glucose based polymer
does not decompose significantly in wine barrel coopering and toasting
While Cellulose from Oak is an important component with regard to the uptake and loss of water and alcohol, it does not contribute phenolic compounds.
Hemicellulose

Smaller polymeric structure based on other (mostly 5-carbon) sugars

Degrades during seasoning & toasting to produce a number of compounds of sensory importance

(for example furfural and hydroxymethylfurfural,
Hemicellulose (about 20 - 25%)

The backbone of hemicellulose consists of simple sugars - about 200 - principally xylose. On toasting these release simple sugars and these in turn caramelise to give sweet associated aromas. "Markers" include:

- Acetic acid release
- 5-hydroxymethyl furfural
- Furfural

This unit is present on about 7 in every 10 sugar units, and present on about 1 in 10 sugar units.
Lignin

Degradation begins during the initial seasoning of the wood, and continues to a significant extent during processing.

These processes produce a number of compounds that are generally considered positive in terms of flavor/aroma enhancement.

- vanillin
- eugenol
- 4-methyl guaiacol
Vanillia is the most desirable of all flavourings to emerge from Oak during maturation.

Vanillia from “Guaiacyl” lignin (G)
Syringaldehyde from “Syringyl” lignin (S)

Lignin (about 25 - 35%)

Oak contains many lignins, Some more useful to us than others And some that is wine soluble

G:S ratio in untreated oak lignin = 1:1
G:S ratio in toasted oak lignin = 1:2 – 1:4 depending mainly upon the toasting process
Hydrolyzable Oak Tannins

Easily hydrolyzed enzymatically or by acid or base conditions

Forms free gallic acid or hexahydroxydiphenic acid (lactonizes to ellagic acid)

gallotannins or ellagitannins
Tannins (0.5 – 10%) 

Vescalagin / Castalagin (56% of total in fresh oak)

changes on seasoning and toasting

hexahydroxy diphenic acid

Gallic acid

D-glucose

hexahydroxy diphenic acid

Ellagic acid
Minor Components

Derived from raw wood

terpenes

oak lactones
<table>
<thead>
<tr>
<th>Tannin breakdown</th>
<th>Steam volatile phenols ('smoke')</th>
</tr>
</thead>
<tbody>
<tr>
<td>gallic acid</td>
<td>phenol</td>
</tr>
<tr>
<td>ellagic acid</td>
<td>guaiacol</td>
</tr>
<tr>
<td>castalagin*</td>
<td>o-cresol</td>
</tr>
<tr>
<td>vescalagin*</td>
<td>m &amp; p cresol</td>
</tr>
<tr>
<td><strong>Hemicellulose caramelization</strong></td>
<td>4-ethyl phenol</td>
</tr>
<tr>
<td>5-hydroxymethyl furfural</td>
<td>4-methyl guaiacol</td>
</tr>
<tr>
<td>furfural</td>
<td>4-ethyl guaiacol</td>
</tr>
<tr>
<td>5-methyl furfural</td>
<td><strong>Oak lactones</strong></td>
</tr>
<tr>
<td><strong>Wine phenolics</strong></td>
<td>trans lactone</td>
</tr>
<tr>
<td>protocatechuic acid</td>
<td>cis lactone</td>
</tr>
<tr>
<td>catechin</td>
<td><strong>Other</strong></td>
</tr>
<tr>
<td>epicatehin</td>
<td>scopoletin</td>
</tr>
<tr>
<td>chlorogenic acid</td>
<td><strong>Volatile esters</strong></td>
</tr>
<tr>
<td>myricetin</td>
<td>acetaldehyde</td>
</tr>
<tr>
<td>quercetin</td>
<td>diethyl acetal</td>
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<tr>
<td><strong>Lignin degradation</strong></td>
<td>ethyl acetate</td>
</tr>
<tr>
<td>vanillic acid</td>
<td>ethyl butyrate</td>
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<tr>
<td>syringic acid</td>
<td>ethyl hexanoate</td>
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<tr>
<td>vanillin</td>
<td>hexyl acetate</td>
</tr>
<tr>
<td>syringealdehyde</td>
<td>ethyl octanoate</td>
</tr>
<tr>
<td>coniferaldehyde</td>
<td>ethyl decanoate</td>
</tr>
<tr>
<td>sinapaldehyde</td>
<td>phenylethyl acetate</td>
</tr>
</tbody>
</table>

Minor Components
The Influence of Oak Wood on Barrel Maturation

- **Cellulose**
  - no direct effect
  - wood sugars ("body")

- **Hemicellulose**
  - caramelisation products
  - color

- **Lignin**
  - increase in blended complexity
  - production of vanilla
  - promotion of oxidation products

- **Oak Tannins**
  - production of astringency
  - removal of off-notes (e.g. rubbery)