Management of Phenols and Microoxygenation

Enology-Grape Chemistry Group
Virginia Tech

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Presentation Goals

- Nature of grape and wine phenols
- Chemistry of tannin-anthocyanin polymer formation
- Our research on microoxygenation

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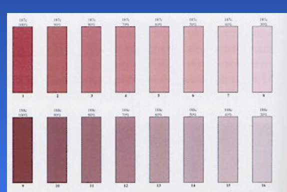
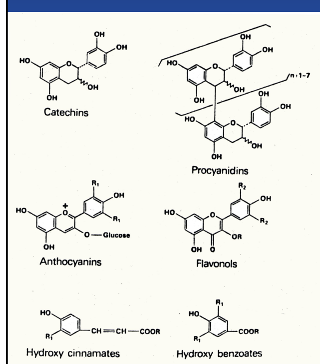
Grape and Wine Color

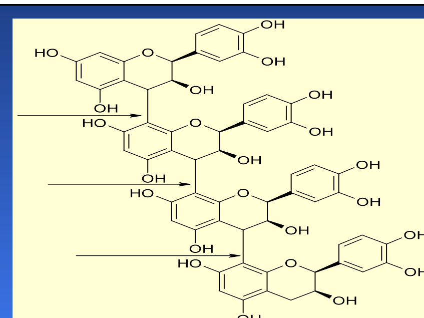




- Structure
- Sources:
  Skin, seeds, pulp, stems, oak, addition products
- Association with other compounds, macromolecules
- Size or degree of polymerization (DP
- Sensory features:
  Astringent / Bitter / Col

Tannin Perception

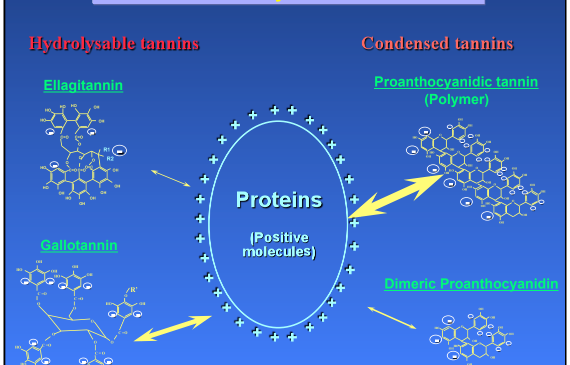
Glycerol
Acidity
Manoproteins
Sugar – Tannin – Source/Structure
Ethanol
Anthocyanins
Pectin



Redistributing the DP of the monomers, and polymers

Breakage and reformation at (4→8) and (4→6) bonds

Reactivity of tannins



Source: Scott Labs

Nature of Astringency

- Stereo-specific nature
- Size
- Number of OH
- Skin tannin DP ≈ 40
  finer grain of coarseness, not as lingeri
- Seed and stem tannin DP ≈ 15

Red Wine Color

pH

Cofactors — Oxidation

Anthocyanin

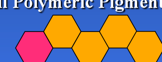
Age — Structure

Tannin/ Pigment Polymers

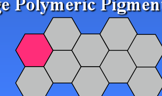
Grape and Wine Pigment

Monomeric Anthocyanins (MP) — Red

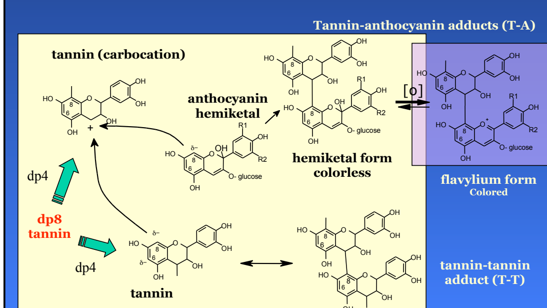
Small Polymeric Pigments (SPP) — Red / Brown



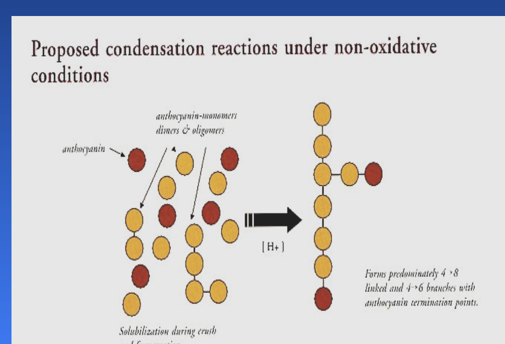
Large Polymeric Pigments (LPP) — Red / Brown



Proposed mechanisms leading to T-A and T-T adducts under non-oxidative conditions

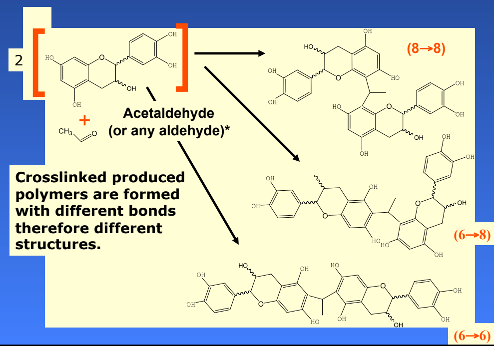


Source: McCord, 2005



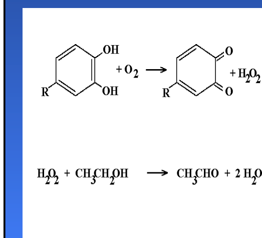
Source: McCord, 1990

Crosslinking with aldehydes

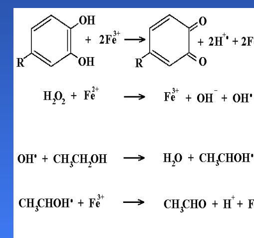


Acetaldehyde Production in Wine

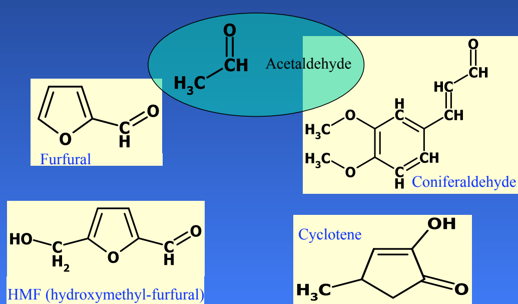
Oxygen exposure (microx)

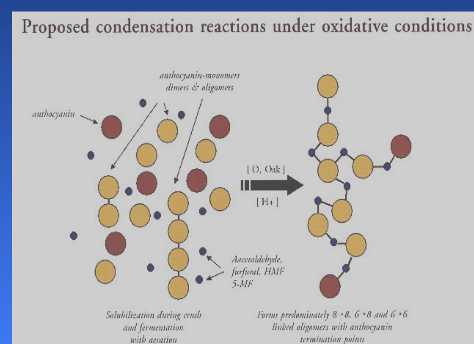


Heavy metal attack



Aldehyde Compounds Extracted from Oak Capable Of Crosslinking Tannins and Anthocyanins





Source: McCord, 1990

Phenol Relationships

- Polymeric pigment formation impacts color, color stability, and mouthfeel
- Tannin and anthocyanin concentration effects concentration of polymers like LPP
- Low concentration of tannin – cannot form polymers
- Whichever is limiting will determine amount of polymeric pigment
- Stability of color is best when the ratio of anthocyanin : tannin is 1 : 4
- What are viticultural and winemaking impacts?

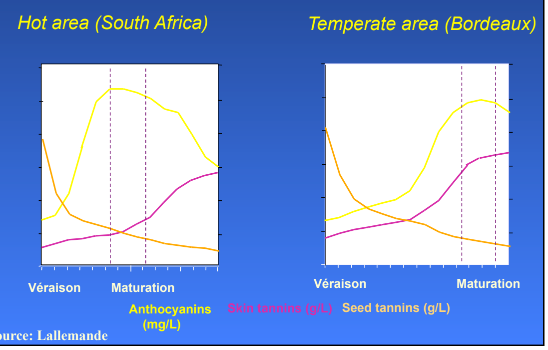
Spectral Color

- Anthocyanin concentration
- Polymeric anthocyanins
  - SPP (small polymeric pigments)
  - LPP (large polymeric pigments)
- Cofactor concentration
  Copigmentation can provide 4 to 10X more color
  - Non-Flavonoids
  - Flavonols
  - Arginine
  - Enological tannins? – NO

Spectral Color

- Variation in cofactor concentration more important than anthocyanin
- Lots of seasonal variation
- Large cultivar differences

Phenolic maturity



Source: Lallemande

Grape and Wine Color

- Change in grape anthocyanin concentration = Change in wine color
- Change in grape anthocyanin ≠ Change in wine color
- No change in grape anthocyanin = Change in wine color

Pinot noir

- Skin tannin concentration X 6
- Seed tannin concentration X 2
- Yet 30 X difference in wine tannin concentration

Source: Adams, 2008

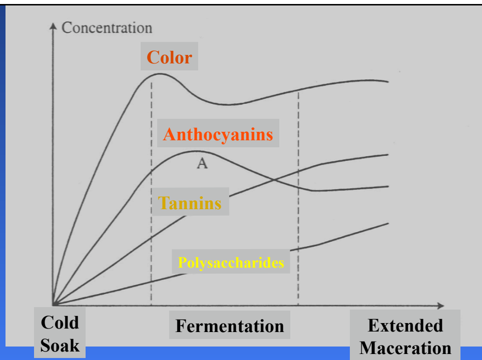
Extraction Mainly a Function of:

- Phenolic maturity – stems, cap stems, skins, seeds, pulp
- Temperature
- Contact
- Alcohol content

Winemaking Techniques Influencing Phenols

Main Effects

- Concentration of phenolic elements
- Size of tannin (DP)
- Degree of galloylation
- Degree of trihydroxylation



Source: Glories (1993)

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Cold Soak Variables

- Varieties
- Seasons
- Duration
- Temperature

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Cold Soak Effects

- Increased anthocyanin extraction
- Increased tannin extraction
- Change in A / T ratio
- Increase in spectral color?
- Increase in DP
- Increase in wine tannin

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Saignée

- How much?
- ↑ Tannins
- ↑ DP

Effect of Micro-Oxygenation on Wine Phenols and Sensory Profiles

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Microoxygenation Potencial

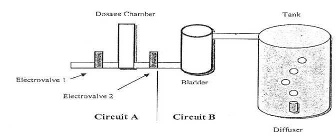
- Improve wine mouthfeel
- Increase in volume or palate weight
- Color stability
- Ameliorate “green” herbaceous aromas
- Ameliorate SLO character

Microoxgenation Variables

- Quantitative and Qualitative nature of phenols
  - degree of polymerization
- Timing
- Concentration of oxygen
- Wine temperature
- Sulfur dioxide concentration
- The wine

Types of Microoxygenation

- ***Micro-bullage***

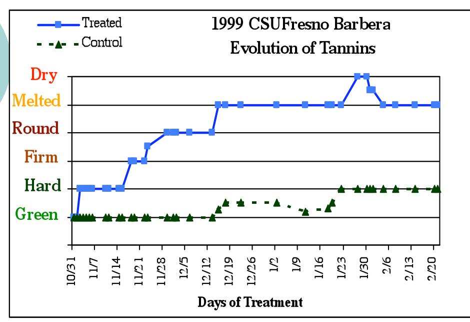


- ***Dense polymer membrane***

Sensory Evaluation

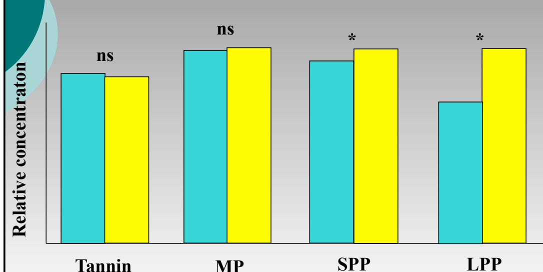
- 16 trained subjects
- Intensity scale 1-9
- Aroma Descriptors
  - fruit, veggy, spicy, oak, herbal, oxidation
- Taste Descriptors
  - fruit, veggy, green-tannin, tannin-grit, plushness, off-aroma

Tannin Development



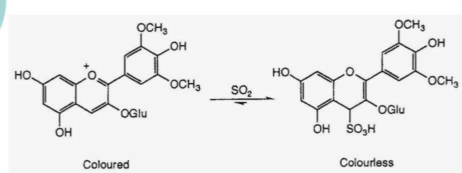
Source: Zoecklein et al., 2003

Microoxygenation

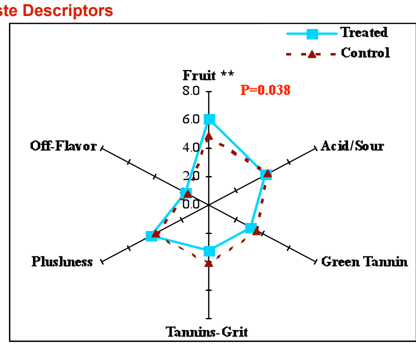


Source: Zoecklein et al., 2003

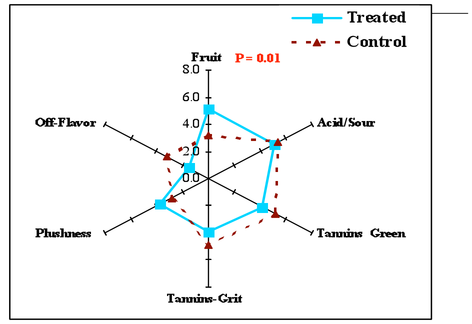
Equilibrium Between Colored Malvidin-3-glucoside and its Colorless Bisulfite Addition Product



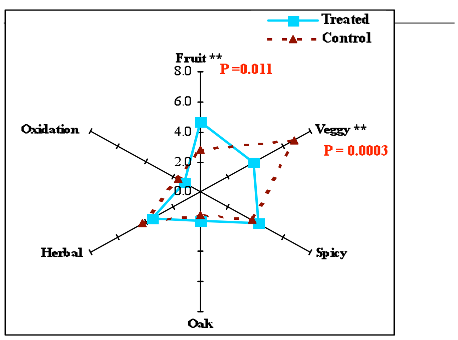
QDA Wine Station #2 (Lodi, Cabernet Sauvignon)
Taste Descriptors



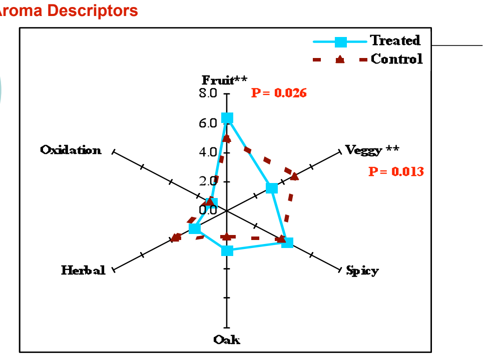
QDA Wine Station #3 (Napa Valley, Merlot)
Taste Descriptors



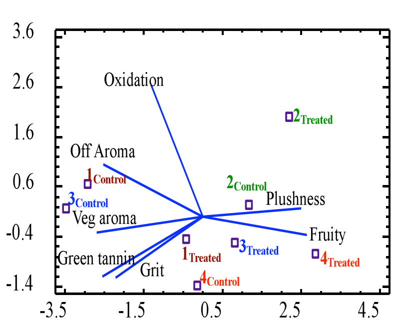
QDA Wine Station #3 (Napa Valley, Merlot)
Aroma Descriptors



QDA Wine Station #4 (Napa Valley, Cabernet)
Aroma Descriptors



PCA graph*



*From 8 wines evaluated in study

Correlation Coefficients

P Value	R Value (Correlation Coeficient)						
	Fruit	Vegetative	Oxidation	Off aroma	Green Tannin	Tannin Grit	Plushness
Fruit		-0.938	-0.448	-0.958	-0.836	-0.590	0.784
Vegetative	0.0006***		0.354	0.862	0.910	0.796	-0.782
Oxidation	0.2661	0.3903		0.600	0.127	0.233	-0.389
Off aroma	0.0002***	0.0059*	0.1184		0.711	0.471	-0.770
Green Tannin	0.0097**	0.0017**	0.7642	0.0482*		0.841	-0.824
Tannin-Grit	0.1237	0.018*	0.5783	0.2394	0.0088*		-0.721
Plushness	0.0212*	0.0218*	0.3410	0.0253*	0.0119*	0.0436*	

Phenolic Results

- 8 different wines.
- The average results showed the following trends:
  - Increases in visible color
  - Increases in color intensity
  - Increases in polymeric color
  - Increases in browning
  - Increases in age related factors

Microoxgenation Issues

- **Timing and Concentration of Oxygen Concentration of pigment polymers**
- **Structural phase**
- **Harmonization phase**
- **Sulfur dioxide concentration**

Much more info on phenols and microoxgenation at www.vtwines.info