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SMOKE TAINT & WINE MATURATION TOOLS

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On-the-Road in the Foothills
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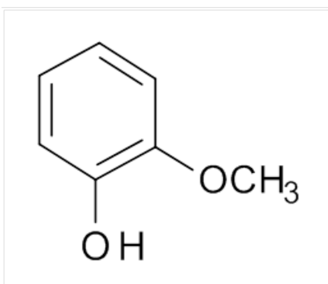
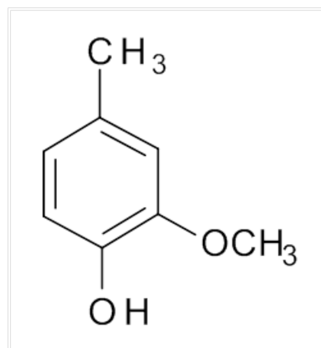
Smoke Taint

Assessment of Smoke Taint

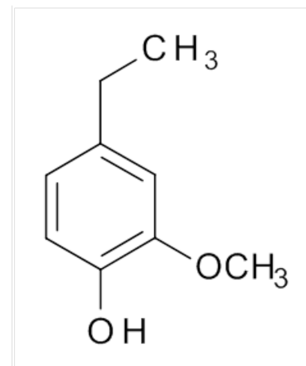
- Sensory evaluation
- Quantification of quaiacol by GC-MS



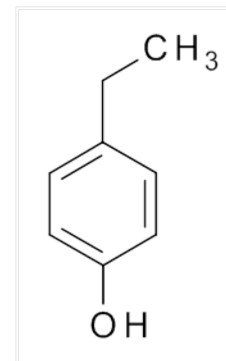
Guaiacol



4-methylguaiacol



4-ethylguaiacol



4-ethylphenol

- Phenolic glycosides by LC-MS/MS

Assessment of Smoke Taint

- **Sensory evaluation**
  - **“Smoke”, “cold ash”, “dirty”, “earthy”, “burnt”, with lingering retro-nasal “ash” character**



Assessment of Smoke Taint

- GC-MS analysis
  - Release glycosidically bound volatiles
    - β-glycosidase
- Guaiacol and 4-Ethylguaiacol
  - Useful markers of smoke taint
  - Although on their own not good enough

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Assessment of Smoke Taint

- Best marker – free and bound phenol
- New LC-MS/MS method to quantify phenol glycosides directly

Timing of smoke exposure

- Merlot vines over 3 seasons
  - Exposed to smoke at key growth stages
    - 10 cm shoots, flowering, pea-size berries, beginning of bunch closure, veraison, grapes with intermediate sugar, berries not quite ripe, harvest

Kennison et al., 2011, 2008. AJGWR

Timing of Smoke Exposure

Grapevine growth stage	Potential for smoke uptake
Shoots 10 cm long	Low
Flowering	Low
Pea-size berries	Variable (low to medium)
Beginning of bunch closure	Variable (low to medium)
Onset of veraison to three days post-veraison	Variable (low to medium)
From seven days post-veraison to harvest	High

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Kennison et al., 2011. AJGWR

Treatments of Smoke-taint Wines

- **Fining agents (egg albumin, casein, activated carbon, gelatine, isinglass, bentonite, yeast cell walls, silica sol, PVPP)**
  - **Lack specificity**
  - **Activated carbon most effective**
    - **Significant ↓ in smoke character and compounds**
    - **Small losses phenolics, no color loss**
  -

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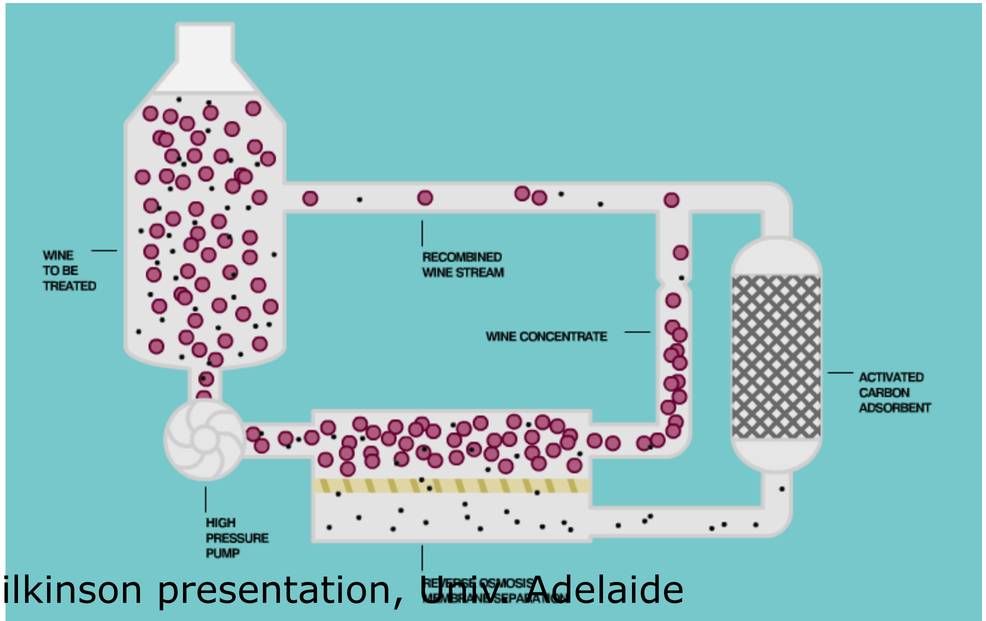
Fidge et al., 2012. AJGWR

Treatments of Smoke-taint Wines

- **Reverse osmosis (RO) and solid phase extraction (SPE)**
  - **Signf ↓ smoke-derived compounds**
- **Taint slowly returned**



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Fudge et al., 2011. AJGWR; picture Wilkinson presentation, Univ. Adelaide

Impact of Winemaking Practices on Smoke Taint (ST)

- Reducing skin contact - ↓ ST
- Selection of yeast strains - ↓ apparent ST
- Oak chips and tannin ↑ complexity ↓ perception ST
    - Avoid barrel/oak profiles with smoky character

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Ristic et al., 2011. AJGWR

Summary

- No fix for smoke taint
- Unpredictable due to precursors
  - Evolves during wine aging
- Actions that can minimize impact
  - Less skin contact – change wine style
  - Fruity yeast
  - Wood contact to add complexity
  - Reduce smoke-taint compounds
    - Fining, RO and SPE

Micro-oxygenation and oak products

MATURATION TOOLS

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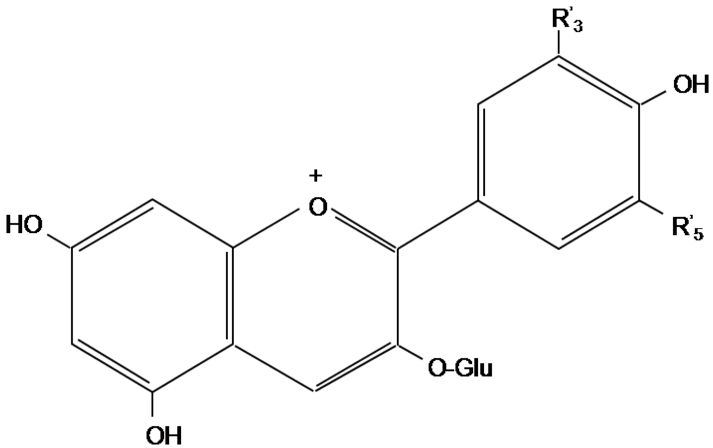
Introduction

- Two studies
  - Influence of different maturation tools (barrels, MOX, wood alternatives) on wine composition and quality
  - Impact of different MOX levels
    - Optimal MOX level vs wine composition
    - Tools to follow MOX progress/impact
- Background
    - Phenols in wine
    - Influence of wood and oxygen
    - Micro-oxygenation

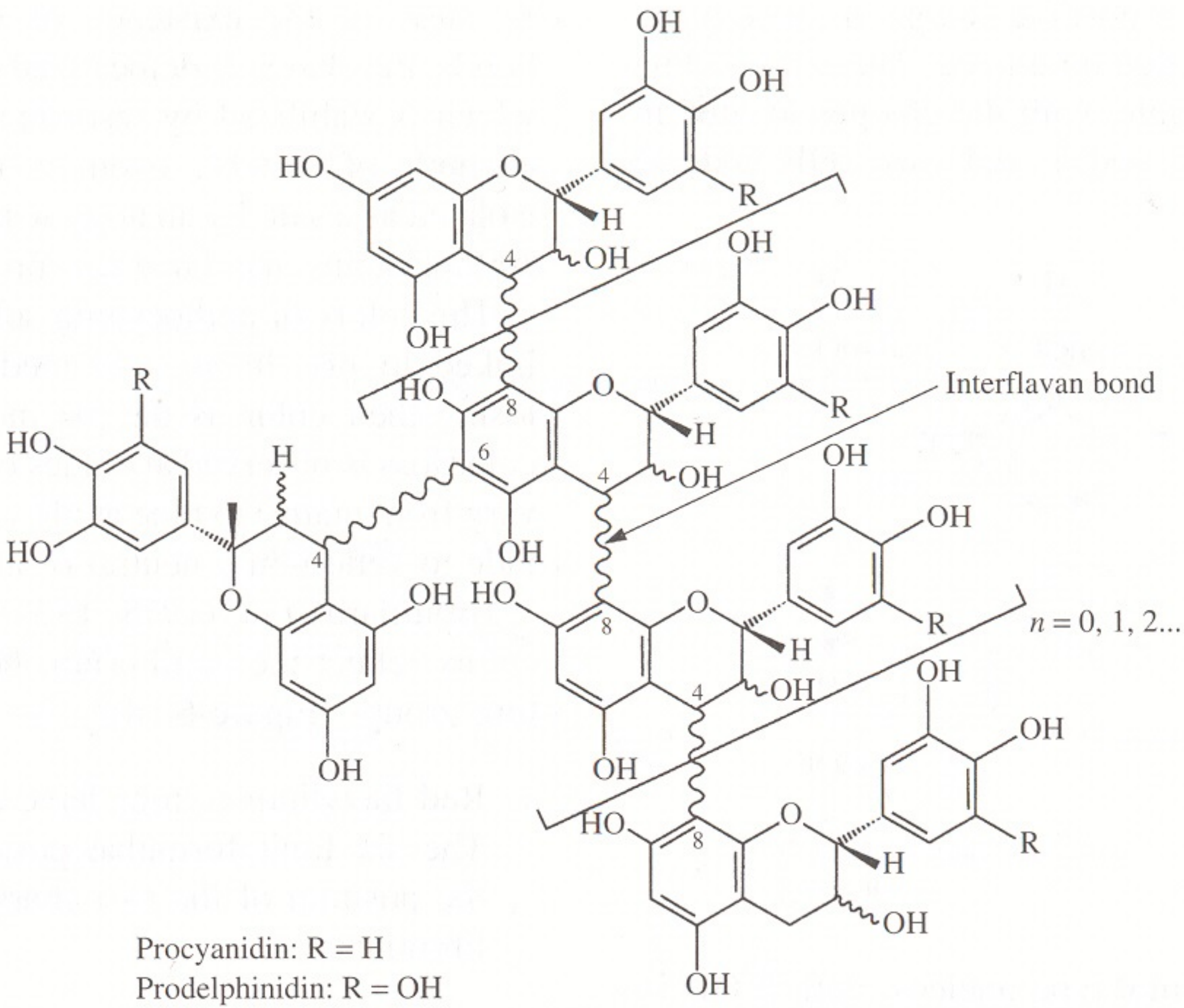
Background – phenols in wine

- Main phenols (flavonoids) in red wine
  - Anthocyanins responsible for red color
  - Flavan-3-ols (ex. catechin, epicatechin, epigallocatechin, epicatechin gallate)
    - Oligomers and polymers of flavan-3-ols, so called proanthocyanidins (PA) or condensed tannins Fig.1



Anthocyanin

Fig 1: Proanthocyanidins



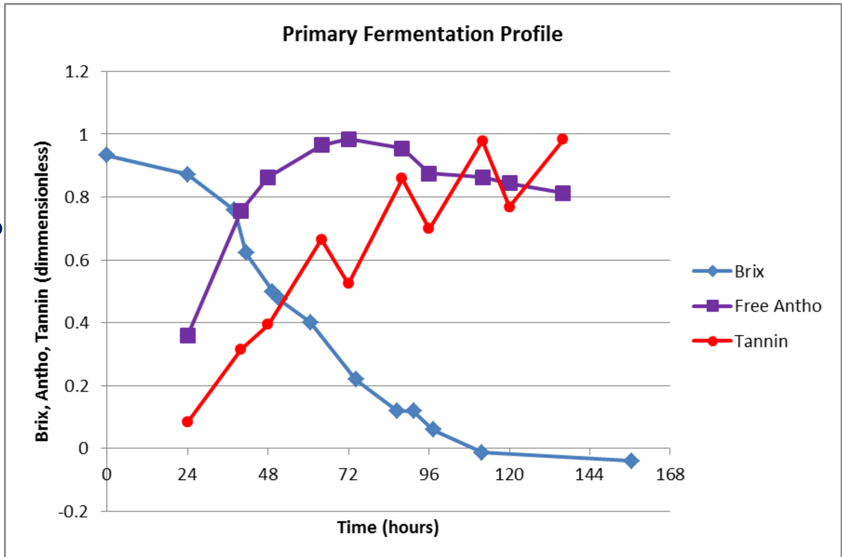
Procyanidin: R = H
Prodelphinidin: R = OH

Extension units

Terminal unit

Background – phenols in wine

- Extraction during wine making
  - Anthocyanins from skins
    - Early during fermentation (3-5 days)
  - Seed PA (mDP ~ 10), higher % galloylation
  - Skin PA (mDP ~ 30), also contain (epi) gallocatechin units
    - Increase extraction with temp, % EtOH
    - Polymerization reactions between anth and PA or between PA and PA



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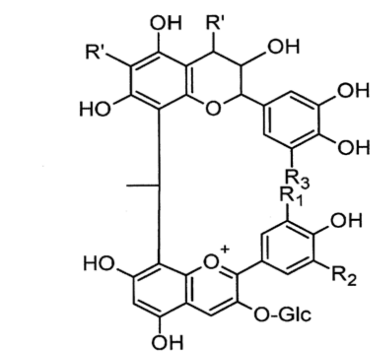
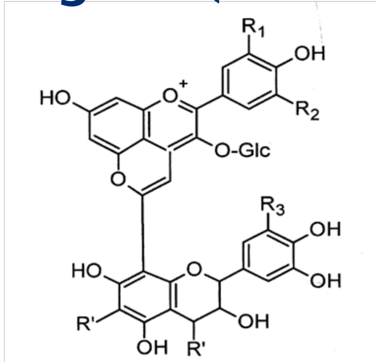
Background – phenols in wine

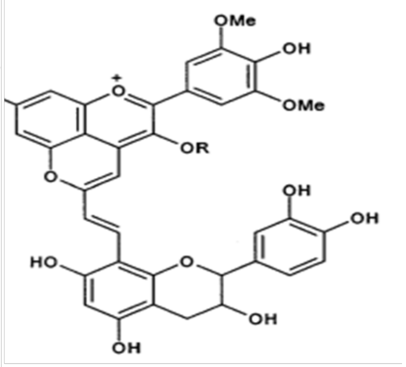
- **During wine maturation and ageing**
  - **Anthocyanins and PA polymerise with each other by different mechanisms**
  - **Reactions influenced by:**
    - **Grape composition**
    - **Phenol extraction**
    - **Presence of wood or oenological (commercial) tannin**
    - **Oxygen**



Flavan 3-ol-ethyl-anthocyanin (1)



Flavanylpyranoanthocyanin (4)



Del Ãlamo *et al*., (2010) Anal. Chim. Acta 660: 92-101 ; Cano-López *et al*., (2006) Am. J. Enol. Vitic. 57: 325-331; Cano-Mateus et

Sensory properties of phenols

- Tannins or proanthocyanidins
  - Main contributors to bitterness and astringency
  - Ratio of astringency to bitterness increase with mDP
  - ‘Coarseness’ and ‘dryness’ of astringency increase with galloylation
- Sensory properties of pigments
  - Anthocyanins have no taste or mouthfeel
  - Pol. Pigments add to astringency “dry”, “grippy”, “viscosity”, “fine emery”

Gawel *et al*. (1998) Austr. J. Grape Wine Res.(6) 74; Vidal *et al*. (2003) J. Sci . Food Agric. (83) 564; Oberholster, Francis, Iland, Waters (2009) Austr. J. Grape Wine Res. (15) 59-69

Micro-oxygenation (MOX)

- Aim to simulate barrel aging at low O_2 dosages
- Claim to:
    - Enhance color density and stabilization, similar effect to barrel maturation
    - Reduces vegetal aroma (enhances fruitiness)
    - Reduces tannin astringency

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Cejudo-Bastante et al. (2011) Food Chem. 124: 727-737; Cejudo-Bastante et al. (2011) Food Chem. 124: 738-748; Parker et al. (2007) Austr. J. Grape Wine Res. 13: 30-37; Perez-Magarino et al. (2009) J. Food Com. Anal. 22:204-211.

Micro-oxygenation (MOX)

- **Dosages:**
  - **Pre-MLF MOX MLF 10-30 mg/L/month**
    - **10-25 days**
  - **Post-MLF 2-5 mg/L/month**
    - **56-252 days**
- **O_2 penetration through the barrel estimated at 1.66 and 2.5 $ml.L^{-1}.month^{-1}$**
  - **Mostly used in conjunction with wood alternatives**
  - **↑ Color density, similar to barrel aging (Gómez-Plaza and Cano-López, 2011)**
- **Only one study compared barrel aging directly with MOX (Cano-Lopez et al., 2010)**

Cano-López (2010) Food Chem. 119: 191-195; Del Ãlamo et al., (2010) Anal. Chim. Acta 660:92-101; Gómez-Plaza and Cano-López (2011) Food Chem. 125: 1131-1140; Nevares and Del Ãlamo et al., (2008) Anal. Chim. Acta 621:68-78; Schmidtke et al. (2011) Crit. Rev. Food Sci. Nutr. 51:115-131

Barrel maturation, MOX and wood alternatives

Barrel maturation
BFM and BAM

vs

+ **MOX**

Stainless steel tank + O_2
MOX

+ **MOX** +

Stainless steel tank + O_2 + staves
MXS

+ **MOX** +

Stainless steel tank + O_2 + tannin
MXT

+ **MOX** +

Stainless steel tank + O_2 + chips
MXC

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Oberholster et al., (2014) J. Food Chem., DOI: 10.1016/j.foodchem.2014.10.043

Experimental protocol

- **Red Blend (63/27/10) Cab. Sauv., Merlot, Malbec)**
- **pH 3.77, 13.3 v/v EtOH, RS 1 g/L, 6.1 g/L TA**
  - SS Fermentation
  - Completed MLF prior to blending
  - Treatment 15°C
  - MOX 1 mg/L/month
  - DO measurements
  - Sampling 3 + 6 mths, 5 mths bottle aging

Enartis MicroOX

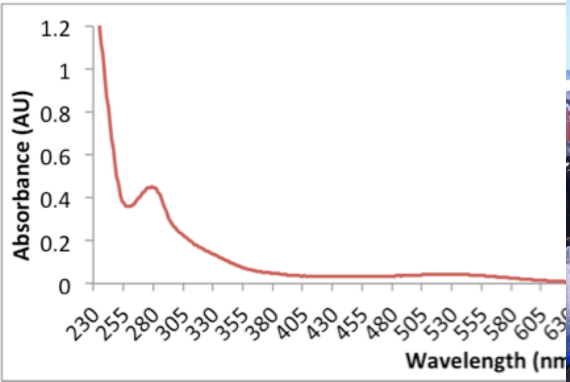
Oberholster et al., (2014) J. Food Chem., DOI: 10.1016/j.foodchem.2014.10.043

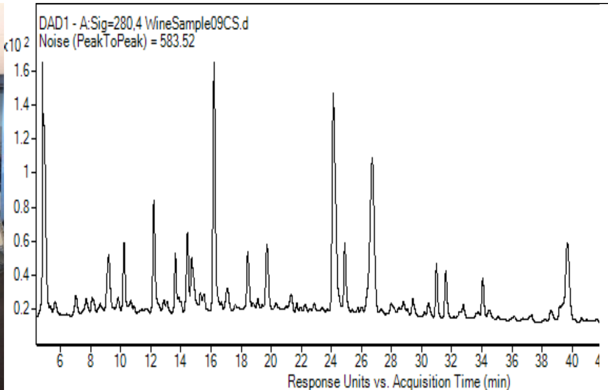
O_2 Monitoring During Treatments

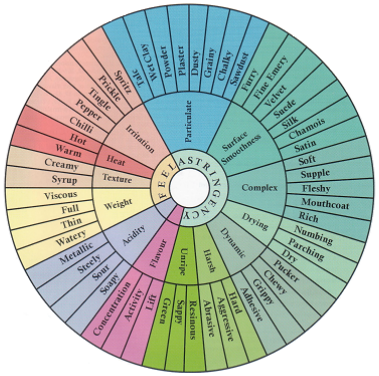
Oberholster et al., (2014) J. Food Chem., DOI: 10.1016/j.foodchem.2014.10.043

Chemical analyses

- UV-VIS and HA assay correlation
- Phloroglucinolysis
- LC-ESI-MS
- Descriptive analysis







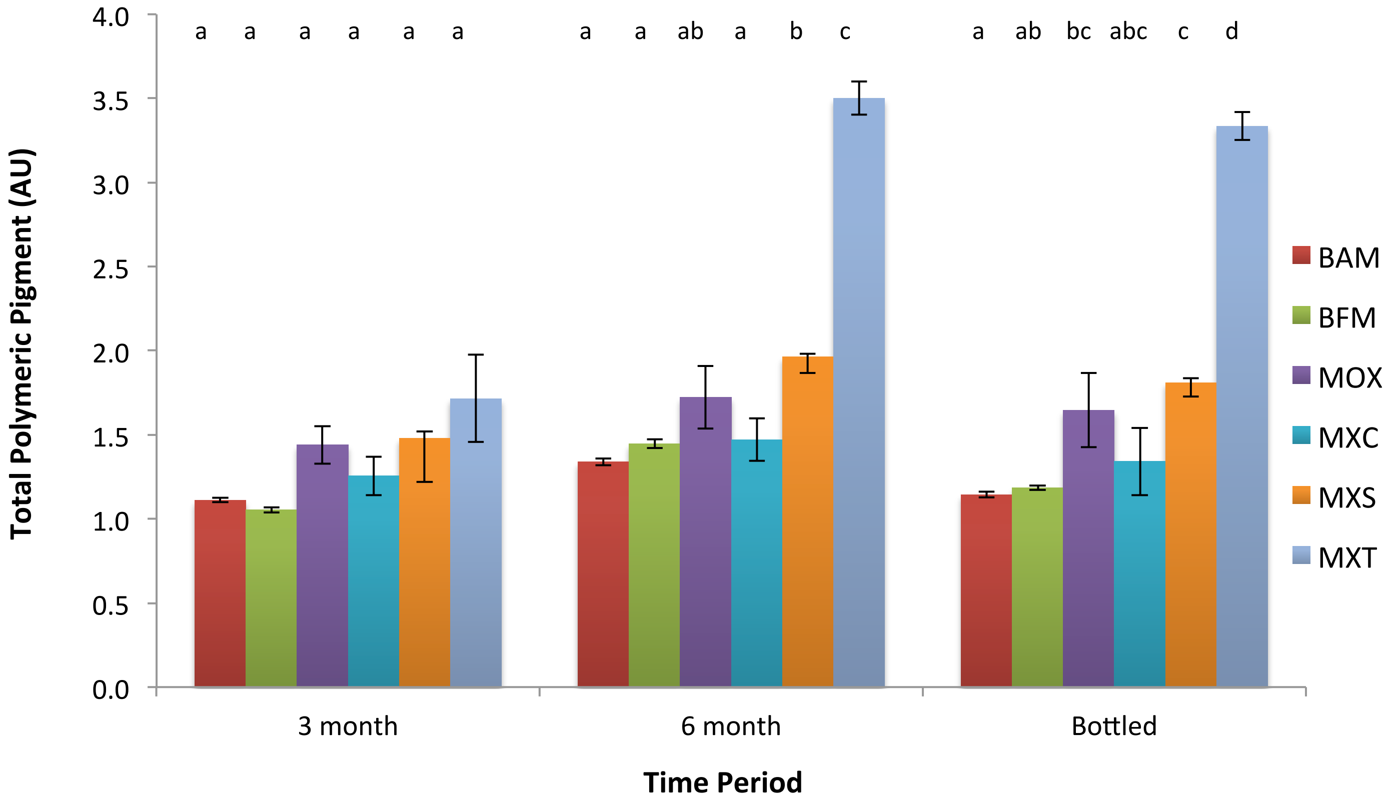
UV-VIS Results

Treatment	Color Intensity (AU)	Red color (520 nm, AU)	Hue (420/520 nm)
BAM	7.70 ± 1.03a	4.00 ± 0.51a	0.74 ± 0.02ab
BFM	8.01 ± 0.96a	4.00 ± 0.48a	0.76 ± 0.01b
MOX	9.36 ± 1.02b	4.75 ± 0.59b	0.74 ± 0.04ab
MXC	8.49 ± 1.03c	4.22 ± 0.56a	0.77 ± 0.03c
MXS	9.23 ± 0.68b	4.69 ± 0.33b	0.73 ± 0.02a
MXT	11.58 ± 1.31d	5.98 ± 0.75c	0.67 ± 0.05d

Mean values of color intensity, red color (520 nm) and hue for different wine treatments across all time points. Treatments sharing common letters within a color parameter do not differ significantly at $p<0.05$ (n=9).

Oberholster et al., (2014) J. Food Chem., DOI: 10.1016/j.foodchem.2014.10.043

UV-VIS Results



Total polymeric pigment levels as determined by correlation between UV-vis data and protein precipitation (BSA) assay for all treatments at 3 month, 6 month and post-bottling intervals. Treatments sharing common letters within a time period do not differ significantly at *p*<0.05 (n=3).

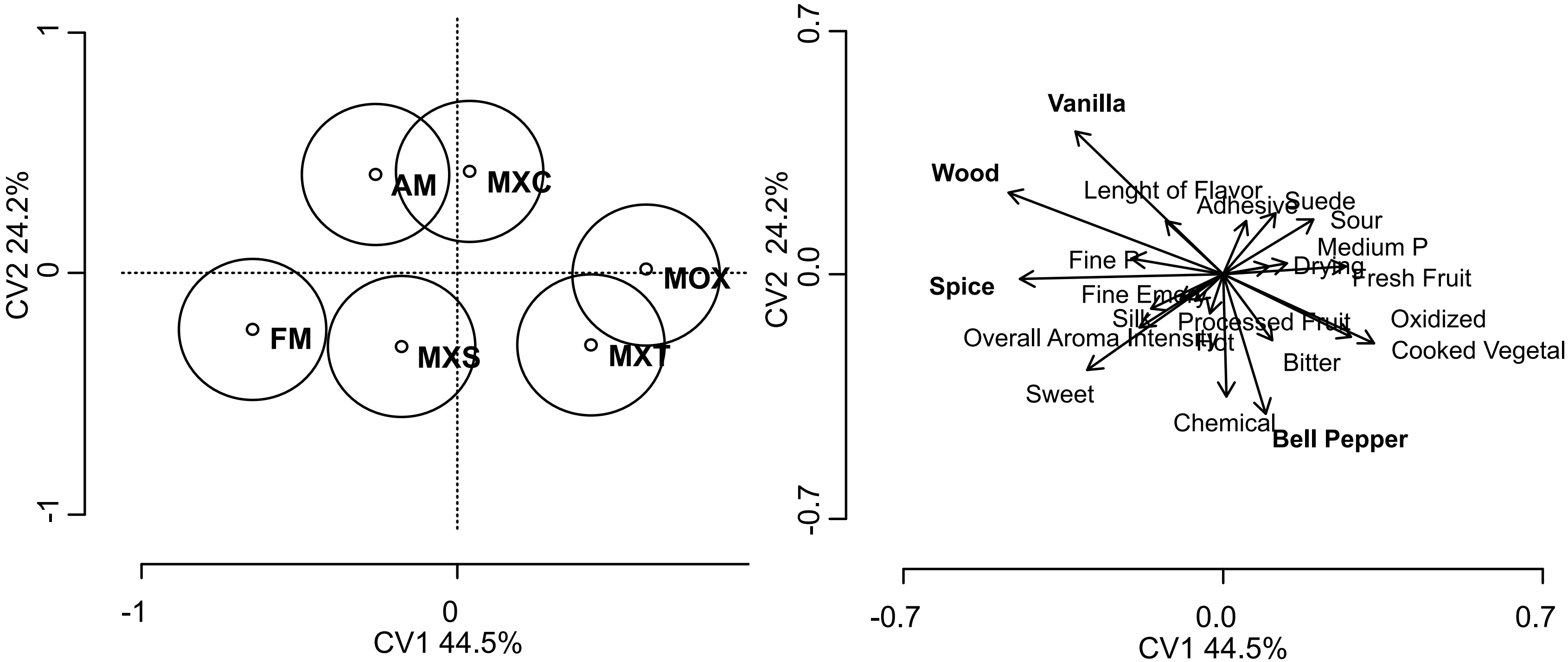
Oberholster et al., (2014) J. Food Chem., DOI: 10.1016/j.foodchem.2014.10.043

LC-ESI-MS results

- Polymeric pigment and phenol determination by HPLC confirm UV-VIS results
  - Only treatment MXT signf diffr from rest
- Total anth by UV-VIS and HPLC showed inverse correlation with pol pigm
- Cat, epicat and B1, B2 (dimers) signf lower in MXT after 5 months bottle aging
  - Inverse corr with pol phenols and pigment formed
- MOX-treatments ↑ acetaldehyde-mediated polymeric pigments (MXT>MXS~MOX>rest)

Oberholster et al., (2014) J. Food Chem., DOI: 10.1016/j.foodchem.2014.10.043

CVA biplot of sensory results



Canonical variate analysis (CVA) product space of the descriptive analysis with the 95% confidence interval circles around the product mean (A) and the variables plot with all attributes (B) (significant attributes are in bold) from the ANOVA at $p < 0.05$. Circles that overlap are not significantly different.

Oberholster et al., (2014) J. Food Chem., DOI: 10.1016/j.foodchem.2014.10.043

Summary

- In general, MOX increased CD
  - Due to increased formation of pol pigments and phenols
    - Mainly acetaldehyde mediated polymerization reactions
  - No significant mouthfeel differences
  - Oak additives did affect aroma profiles
  - MOX + wood additives similar to short-term barrel aging
    - MOX + Staves ~ French oak barrels
    - MOX + Chips ≅ American oak barrels

Further Work

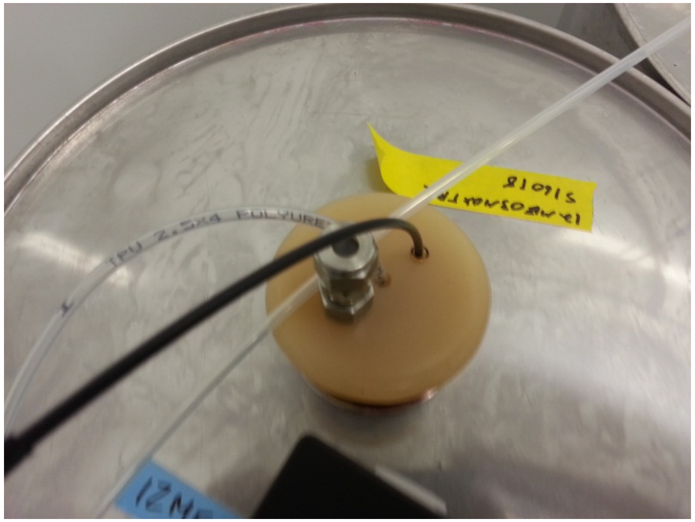
- Build a model: optimal MOX rates and amounts vs wine composition
  - Initial phenol content of wine + anthocyanin to tannin ratio are important
    - Little data available
  - Impartial method to follow MOX?
    - Frequent tastings
  - This work is currently under way in collaboration with Argentina (INTA)
    - 1*Merlot, 1*Malbec, 2* Cab Sauv

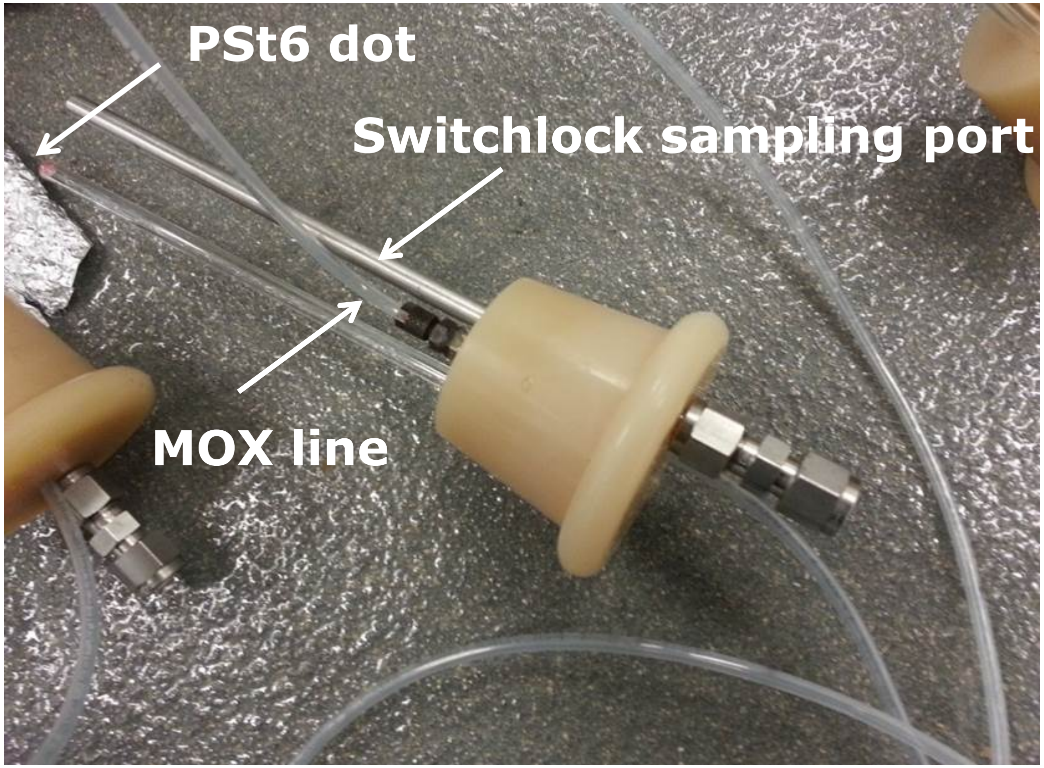
Post-MLF MOX at different rates

- 2012 Merlot from Oakville
  - pH 3.68, TA 6.22 g/L, free SO_2 27 mg/L, RS < 1 mg/L

Post-MLF MOX at different rates

- Experimental layout
  - 5 treatments @ 59 °F (15 °C)
  - 0, 1.5, 3, 4.5, 6 and 9 O_2 mg/L/month

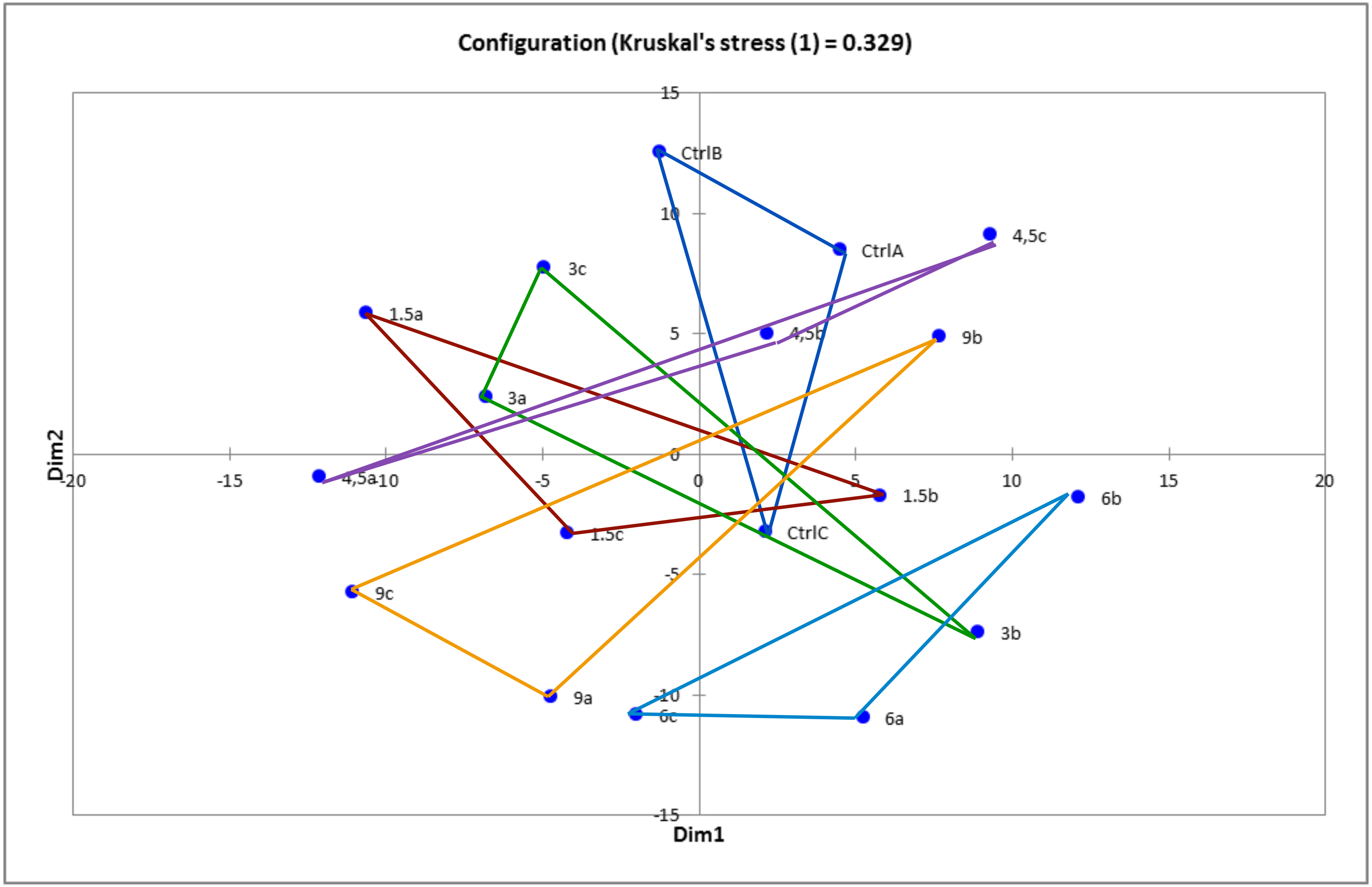




Post-MLF MOX at different rates

- Analyses
  - DO every 5 days
  - Pulled sample every 10 days
    - CH_3CHO analysis by GC-MS
  - Stopped treatment after 22 weeks
  - After treatment and 3, 6 and 12 months of bottle aging
    - UV-vis and HA-assay
    - Phenolic profile by RP-HPLC
    - Tannin profile by phloroglucinolysis and LC-ESI-MS
    - Sensory analysis

Multidimentional scaling (MDS)



Tasting notes: Summary

- 1.5 and 3 mg/L/month MOX were similar, more fruit on nose compared to control
- 3 – 4.5 mg/L/month MOX improved mouthfeel, 4.5 starting to soften
- 6 and 9 mg/L/month MOX significant decrease in astringency, aroma more candy then fresh fruit

Cab Sauv 2013/2014 MOX treatments

- **2013 Cab Sauv from Oakville (pH 3.64, TA 5.8 g/L, free SO_2 30 mg/L, RS <1 g/L, 15.23 v/v EtOH)**

Pre-MLF MOX	Post-MLF MOX
0 mg/L/month	0 mg/L/month
	4.5 mg/L/month
	9 mg/L/month*
	13.5 mg/L/month**
20 mg/L/month	0 mg/L/month
	4.5 mg/L/month
	9 mg/L/month*
40 mg/L/month	0 mg/L/month
	4.5 mg/L/month
	9 mg/L/month**

Acknowledgements: MOX

- **People**
  - **Byron Elmendorf**
  - **Larry Lerno**
  - **Hildegarde Heymann**
  - **Chik Brenneman**
  - **Anibal Catania**
  - **Natalia Owen**
- **Funding/gifts**
  - **American Vineyard Foundation**
  - **Wine Spectator Scholarship**
  - **Enartis Vinquiry for MicroOx unit**
  - **Laffort – wood alternatives**
  - **Cooperage 1912 – new oak barrels**

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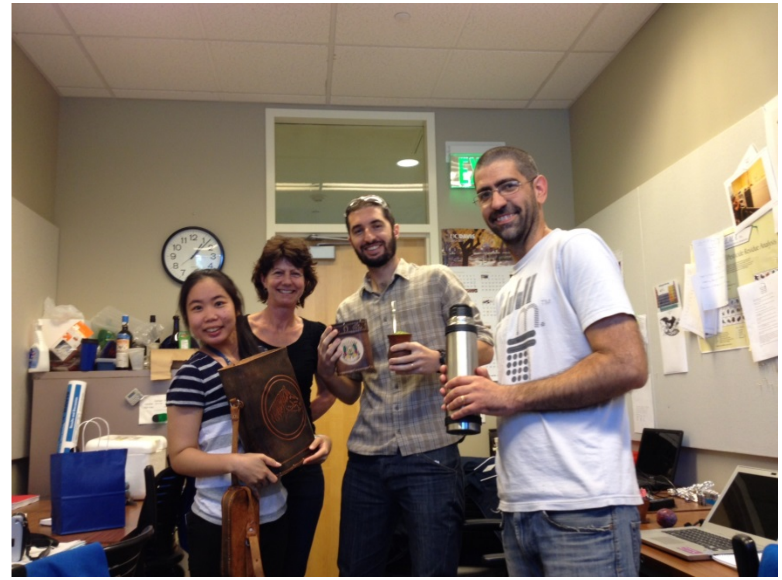

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