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**Wednesday, September 27, 2017**

**Who Will Win the #ChemNobel? Predicting the 2017 Nobel Laureate(s) in Chemistry**

Special Broadcast Co-produced with C&EN

- Carmen Drahl, Freelance Science Journalist
- Omar K. Farha, Northwestern University
- Marie Heffern, UC Davis
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**Thursday, September 28, 2017**

**Spinal Muscular Atrophy: Novel Approaches for Treatment**

Co-produced with the ACS Medicinal Chemistry Division and AAPS

- Kevin Hodgetts, Director of LDDN and Head of Medicinal Chemistry, Assistant Professor of Neurology at Brigham and Women’s Hospital and Harvard Medical School
- Alyson Weidmann, Managing Editor, ACS Chemical Biology, ACS Chemical Neuroscience, and Biochemistry

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The secret to great wine? Organic chemistry.

Wine chemist Andrew Waterhouse talks about teaching a generation of winemakers

By Bethany Halford

For Andrew L. Waterhouse, being tasked with wine selection when having drinks with family, friends, or inquisitive journalists is something of an occupational hazard. “It’s just part of the job,” the professor of viticulture and enology at the University of California, Davis, says.

It’s a good bet that Waterhouse will pick a winning wine. He’s widely respected for his expansive knowledge of wine chemistry and has educated a generation of winemakers during his 26 years teaching in UC Davis’s world-renowned program.

But Waterhouse hasn’t always been a wine connoisseur. With training in natural product synthesis, he started his career at a different school teaching organic chemistry primarily to premed students and researching conformational analysis of polysaccharides. One day, while paging through C&EN

http://cen.acs.org/articles/95/i24/Organic-chemistry-The-secret-to-great-wine.html
What Makes Wine Tick: Key Reactions that Create this Delightful Beverage

Andrew L. Waterhouse
The sugars in grapes include:

- sucrose
- maltose
- glucose
- aspartame

3-Mercaptohexanol (3-MH)

- A “grapefruity” thiol that defines NZ Sauvignon blanc
- There is Zero 3-MH in the fruit!
- Formation involves
  - Harvesting – fruit damage
  - Addition of sulfites “to prevent oxidation”
  - At least two fermentative transformations
- Each step reveals wine chemistry
Step One – Oxidation

- Video of mechanical harvesting
  - https://www.youtube.com/watch?v=AF8VMDX2FVo
  - 0:21-0:35

Oxidation Reaction

- The grape precursor: **linolenic acid**

- Result: **α,β unsaturated aldehyde**
  - Typical fatty acid auto oxidation

![Diagram of linolenic acid and α,β unsaturated aldehyde](image-url)
Step 2: Michael Addition to Hexenal

- **Glutathione, 40 mg/L**
  - Juice

- **Sulfites, HSO$_3^{-}$**
  - At hopper, ~50 mg/Kg

- **Other possibilities**
  - Cysteine
  - H$_2$S, formed in fermentation

- **Nucleophile inventory in wine?**

---

**Audience Challenge Question**

ANSWER THE QUESTION ON BLUE SCREEN IN ONE MOMENT

Which is a Nucleophile in Wine?

- Tartaric Acid
- Ethyl acetate
- Sulfur dioxide
- Gallic acid
Electrophiles and Nucleophiles

- Common reactive moieties
- Wine pH:
  - 3.0-4.0
- Slow is OK!

Acetaldehyde and “Phloroglucinol”

- Formation of modified tannins to make wine tannins via hydroxyalkylation
Thiol and Quinone

- Quinone formed by oxidation
- Rapid reaction with S nucleophile
- Formation of modified catechol

Audience Challenge Question

Which is a key intermediate in ethanol formation?

- acetaldehyde
- glycerol
- acetic acid
- Δ⁹-THC (delta-9-tetrahydrocannabinol)
Step 3: Aldehyde Reduction to Alcohol

- **Aldehyde to Alcohol**

- **Ethanol Fermentation**
  - All arises from Acetaldehyde

  \[
  \text{CH}_3\text{CHO} \rightarrow \text{CH}_3\text{CH}_2\text{OH}
  \]

---

Electron Acceptor Needed

- **Fermentation: glycolysis**
  - Hexose + 2 ADP → 2 Ethanol + 2 CO\textsubscript{2} + 2 ATP

- **Oxygen not available as e\textsuperscript{-} acceptor**

- **Need to convert NADH to NAD\textsuperscript{+}**

- **Acetaldehyde is reduced to EtOH**
Glycolysis Pathway

Yeast: Aldehyde Reduction

- **Vanillin Reduction**
  - Abundant in Bourbon

- **Yeast reduce vanillin to alcohol**
  - Barrel fermented wine
**Old Winemakers Trick**

- **After fermentation**
  - Rack off fresh wine *(decant)*
    - Yeast lees at bottom of tank
    - 50-100 lbs

- **Add old “oxidized” wine**
  - Methional *(cooked cabbage)*

- **Mix with yeast**
  - “New” wine

---

**Step 4: Thiol Formation**

- **Cleave sulfides to thiols**

- **New Ideas**
  - Sulfonate reduction
  - $H_2S$ addition to hexenal
**Thiolysis Pathway - Option 1**

1. GSH transporter encoded by OPT1 enables uptake of GSH-3-MH; 2. γ-glutamyltranspeptidase cleavage of glutamate and transport of Cysgly-3-MH; 3. general amino acid transporter encoded by GAP1 for uptake of Cys-3-MH; 4. metabolism of GSH-3-MH to 3-MH either directly, or step-wise via other precursors; 5. cleavage of 3-MH from Cys-3-MH by carbon-sulfur lyase; 6. acetylation of 3-MH by alcohol acetyltransferase (AAT) to afford 3-MHA; 7. unknown mechanism leads to volatile thiol release into wine.

**Sulfonate Reduction? Option 2**

- **Sulfonic Acids**
  - Not easily reduced

- **Sulfites at harvest**
  - Increase 3-MH 400%!
**H₂S Addition to Hexenal? Option 3**

- **Increase of 3-MH early in fermentation**
  - Yeast make H₂S
  - Hexenal not all reduced yet

- **Reduction of aldehyde to alcohol**

**Audience Challenge Question**

**ANSWER THE QUESTION ON BLUE SCREEN IN ONE MOMENT**

**During aging, esters:**

- Hydrolyze (decrease)
- Form (increase)
- Are stable
- All of the above
Step 5: Acetylation of 3-MH

- Alcohols are partially acetylated during fermentation
- Many acetate esters
  - Isoamyl acetate (banana)
  - Isobutyl acetate (cherry)
  - Hexyl acetate (apple)
  - 3-MHA (passion fruit, guava, tropical)

3-MHA is Important for NZ wines

- When new, wines have a notable tropical fruit aroma
  - Dissipates over time
  - 3-MHA is lost; negl 3-MH loss
  - How to preserve this aroma?
How to Prevent Ester Hydrolysis?

- Wine is pH 3.5
  - Any change will alter taste dramatically

- Current solution
  - Keep wine cold till shipped, slow rxn

Aging: Loss of Thiols to Oxidation

- General loss of fruity aroma

- Can be mitigated by addition:
  - $\text{SO}_2$, ascorbic acid or GSH
  - Basic wine preservatives

- What reactions occur?
General Wine Oxidation Pathway

- Both steps require **Fe/Cu catalysis**
- **Mechanism/s complex**
  - Numerous redox active compounds
- **Oxidation “prevented”** by scavenging initial products

![General Wine Oxidation Pathway Diagram](image)

Quinone Reaction Options

![Quinone Reaction Options Diagram](image)
Oxidation Defines Shelf Life

- **Loss of fruity aromas**
  - Quinones + 3-MH

- **Formation of aldehydes**
  - Ethanol to acetaldehyde
  - Strecker aldehydes

- **Phenolics-antioxidants**
  - React with quinones and aldehydes

Preservatives Recover from Oxidation

- **Preservatives**
  - SO₂
  - Ascorbic Acid
  - Wine tannin (phloroglucinol)

- **Scavenge quinones**
  - Prevent loss of aromatic thiols

- **Scavenge aldehydes**
Summary

- Lipid oxidation
- Sulfur nucleophiles
- Aldehyde reduction by yeast
- Thiol release
- Loss of thiols to oxidation
- Ester hydrolysis

Take Home

- Distinctive wine flavors
  - Complex formation
- Reactions
  - Reduction and oxidation
  - Acid catalysis slow; patience rewarded
- Classic reactions
  - Novelty is identifying importance
For More Information


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- American Vineyard Foundation
"What Makes Wine Tick: Key Reactions that Create this Delightful Beverage"

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