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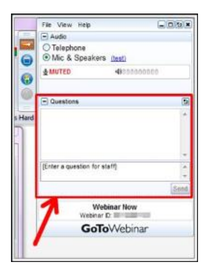

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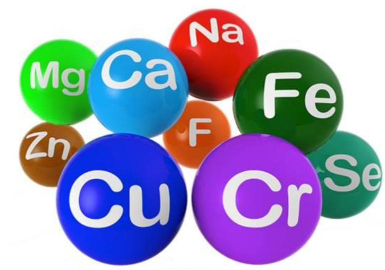

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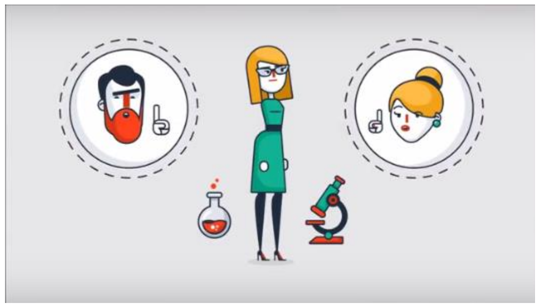

- Know your career options
- Develop strategies to strengthen your skills
- Map a plan to achieve your career goals

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Alyson Weidmann, Managing Editor, *ACS Chemical Biology*, *ACS Chemical Neuroscience*, and *Biochemistry*

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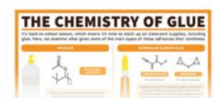

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Chemical educator and Compound Interest blogger Andy Brunning untangles the molecular components of various adhesives

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These female scientists should have won the Nobel

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Volume 95 Issue 24 | pp. 22-23 | C&EN Talks With
Issue Date: June 12, 2017 | Web Date: June 6, 2017

The secret to great wine? Organic chemistry.

Wine chemist Andrew Waterhouse talks about teaching a generation of winemakers

*By **Bethany Halford***

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Waterhouse Credit: Eleni Kardaras Photography

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

Vitals

- **Hometown:** Davis, Calif.
- **Education:** Ph.D., synthetic organic chemistry, University of California, Berkeley
- **Professional highlight:** Honorary doctorate from the University of Bordeaux, a school with a wine program that dates back to 1880, the same year the viticulture and enology program started at the University of California
- **Favorite molecule:** Acetaldehyde, which is a key wine oxidation product
- **Favorite way to enjoy a glass of wine:** Barrel sampling with friends
- **Favorite city:** Ljubljana, Slovenia. "The food is wonderful; things are organized; there are many excellent local wines to taste and not too many tourists."

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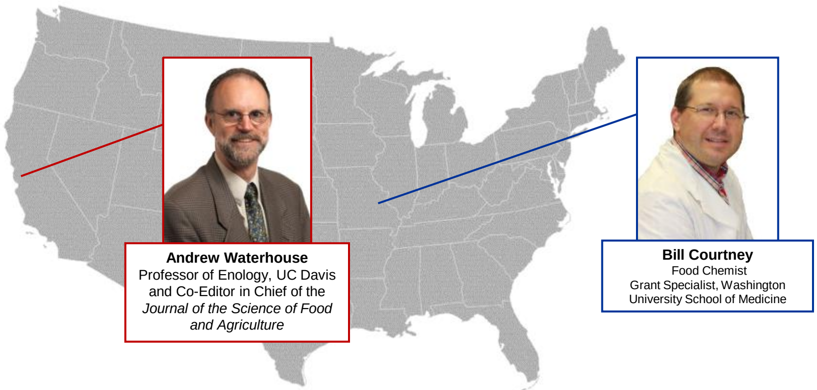
*“**What Makes Wine Tick:** Key Reactions that Create this Delightful Beverage”*



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What Makes Wine Tick:
Key Reactions that Create this Delightful Beverage

Andrew L. Waterhouse

VITICULTURE & ENOLOGY
UNIVERSITY OF CALIFORNIA DAVIS

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Audience Challenge Question

ANSWER THE QUESTION ON BLUE SCREEN IN ONE MOMENT

The sugars in grapes include:

- sucrose
- maltose
- glucose
- aspartame

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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

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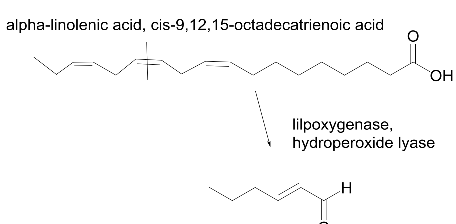
Step One – Oxidation

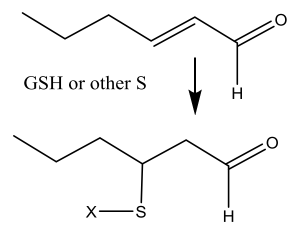
- Video of mechanical harvesting
- https://www.youtube.com/watch?v=AF8VMDX2FVo
- 0:21-0:35

Oxidation Reaction

- The grape precursor: **linolenic acid**
- Result: **α,β unsaturated aldehyde**
  - Typical fatty acid auto oxidation



Step 2: Michael Addition to Hexenal



- **Glutathione, 40 mg/L**
  - Juice
- **Sulfites, HSO_3^-**
  - At hopper, ~50 mg/Kg
- **Other possibilities**
  - Cysteine
  - H_2S, formed in fermentation
- **Nucleophile inventory in wine?**

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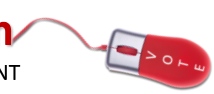

Which is a Nucleophile in Wine?

- Tartaric Acid
- Ethyl acetate
- Sulfur dioxide
- Gallic acid

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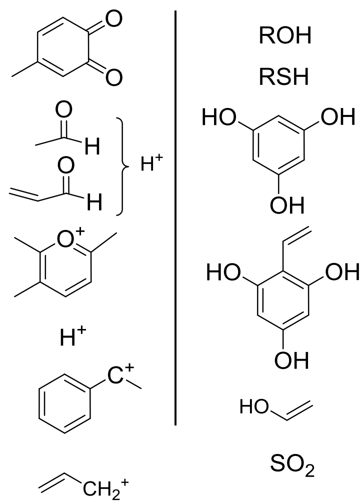
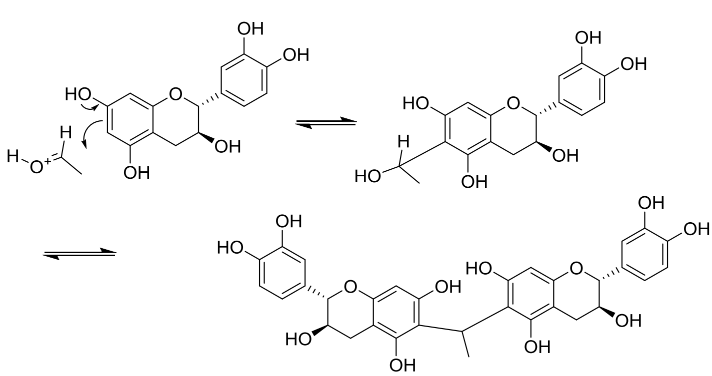
Electrophiles and Nucleophiles

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

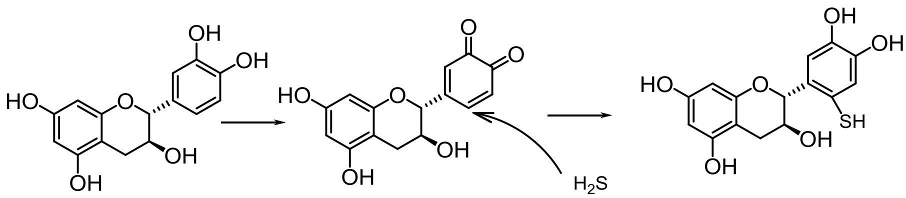


Acetaldehyde and "Phloroglucinol"

- 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

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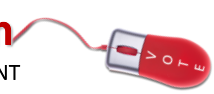

Which is a key intermediate in ethanol formation?

- acetaldehyde
- glycerol
- acetic acid
- Δ^9-THC (delta-9-tetrahydrocannabinol)

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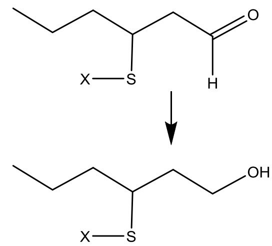
Step 3: Aldehyde Reduction to Alcohol



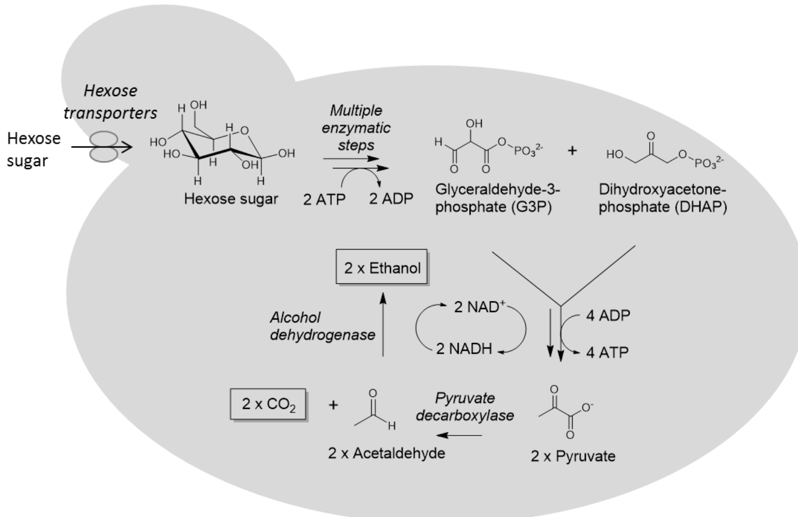
- **Aldehyde to Alcohol**
- **Ethanol Fermentation**
  - All arises from Acetaldehyde

$$CH_3CHO \longrightarrow CH_3CH_2OH$$

Electron Acceptor Needed

- **Fermentation: glycolysis**
  - Hexose + 2 ADP → 2 Ethanol + 2 CO_2 + 2 ATP
- **Oxygen not available as e^- acceptor**
- Need to convert **NADH to NAD^+**
- Acetaldehyde is reduced to **EtOH**

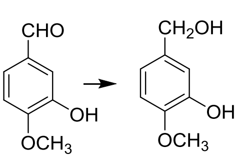
Glycolysis Pathway



- Waterhouse, Sacks & Jeffery, Understanding Wine Chemistry, Wiley, 2016

Yeast: Aldehyde Reduction

- **Vanillin Reduction**
  - Abundant in Bourbon
- **Yeast reduce vanillin to alcohol**
  - Barrel fermented wine



Old Winemakers Trick

$CH_3SCH_2CH_2CHO$

↓

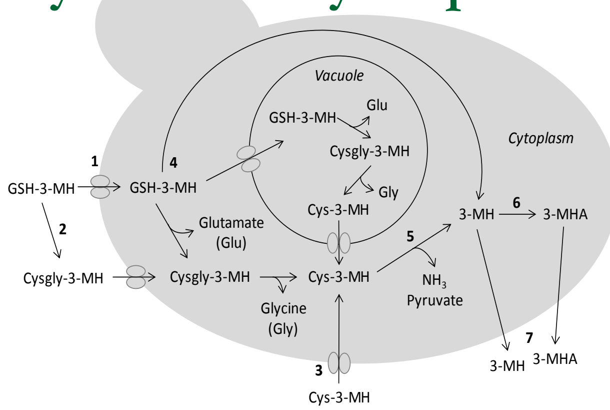
$CH_3SCH_2CH_2CH_2OH$

- **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

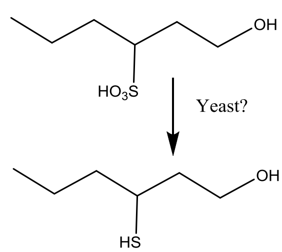
Thiolysis Pathway - Option 1



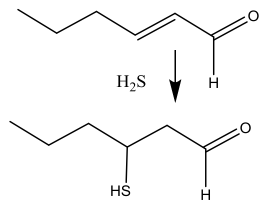
- 1, GSH transporter encoded by OPT1 enables uptake of GSH-3-MH; 2, γ-glutamyltranspeptidase cleavage of glutamate and transport of Cysgly-3-MH; 3, general amino acid transporter encoded by GAP1 for uptake of Cys-3-MH; 4, metabolism of GSH-3-MH to 3-MH either directly, or step-wise via other precursors; 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%!



H_2S Addition to Hexenal? Option 3



- **Increase of 3-MH early in fermentation**
  - Yeast make H_2S
  - Hexenal not all reduced yet

- **Reduction of aldehyde to alcohol**

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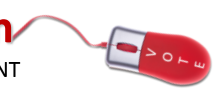


During aging, esters:

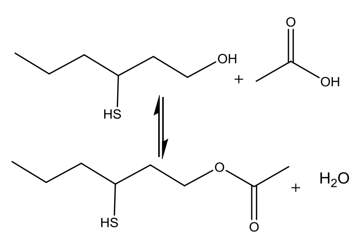
- Hydrolyze (decrease)
- Form (increase)
- Are stable
- All of the above

Step 5: Acetylation of 3-MH

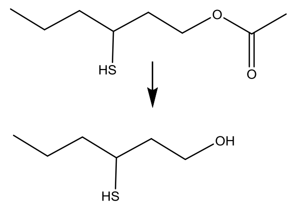
- **Alcohols are partially acetylated during fermentation**
- **Many acetate esters**
  - Isoamyl acetate (banana)
  - Isobutyl acetate (cherry)
  - Hexyl acetate (apple)
  - **3-MHA** (passion fruit, guava, tropical)

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

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Aging: Loss of Thiols to Oxidation

- **General loss of fruity aroma**
- **Can be mitigated by addition:**
  - SO_2, ascorbic acid or GSH
  - Basic wine preservatives
- **What reactions occur?**

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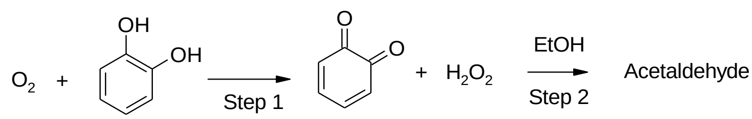
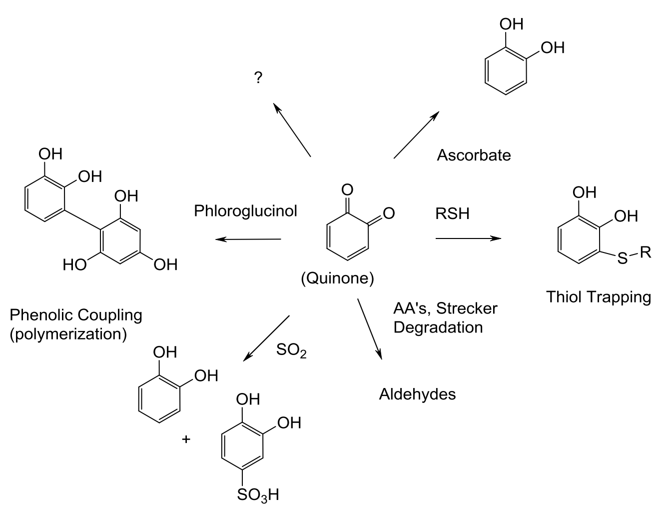
General Wine Oxidation Pathway



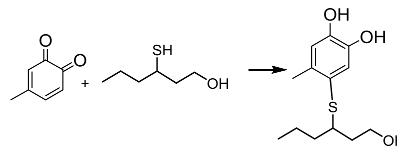
- Both steps require **Fe/Cu catalysis**
- **Mechanism/s complex**
  - Numerous redox active compounds
- **Oxidation "prevented"** by scavenging initial products

Quinone Reaction Options

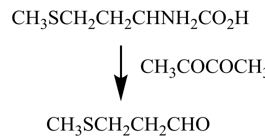


Oxidation Defines Shelf Life

- **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**
  - SO_2
  - 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

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Take Home

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

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For More Information

- **Understanding Wine Chemistry**, Waterhouse, Sacks & Jeffery, Wiley, 2016
- **The Science of Wine: From Vine to Glass**, Jamie Goode, UC Press, 2014
- **Principles and Practices of Winemaking**, Boulton et al, Springer, 1999

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Acknowledgements

- **David Jeffery**, University of Adelaide
- **Gavin Sacks**, Cornell University
- **Maria Nikolantonaki**, University of Burgundy
- **Ryan Elias**, Penn State University
- Many others
- American Vineyard Foundation

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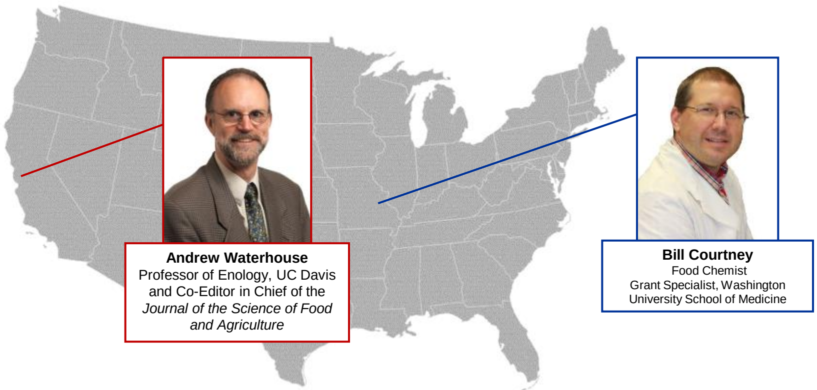

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Wine chemist Andrew Waterhouse talks about teaching a generation of winemakers

By ***Bethany Halford***

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Waterhouse Credit: Eleni Kardaras Photography

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Vitals

- **Hometown:** Davis, Calif.
- **Education:** Ph.D., synthetic organic chemistry, University of California, Berkeley
- **Professional highlight:** Honorary doctorate from the University of Bordeaux, a school with a wine program that dates back to 1880, the same year the viticulture and enology program started at the University of California
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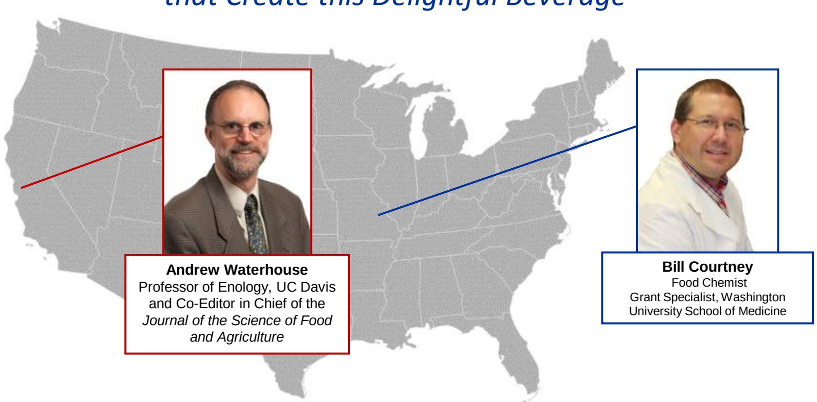

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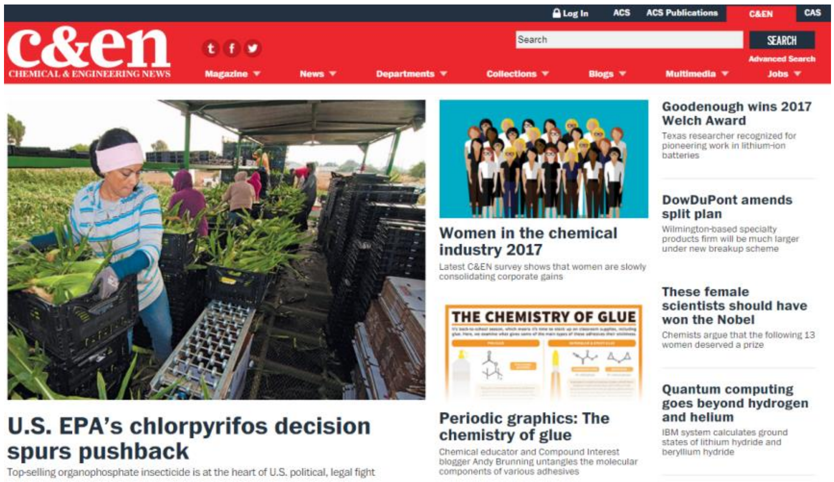

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Spinal Muscular Atrophy: *Novel Approaches for Treatment*

Co-produced with the ACS Medicinal Chemistry Division and AAPS

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