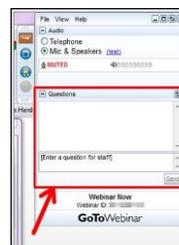
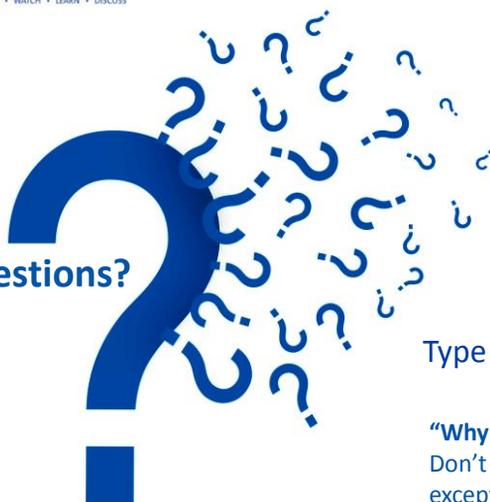




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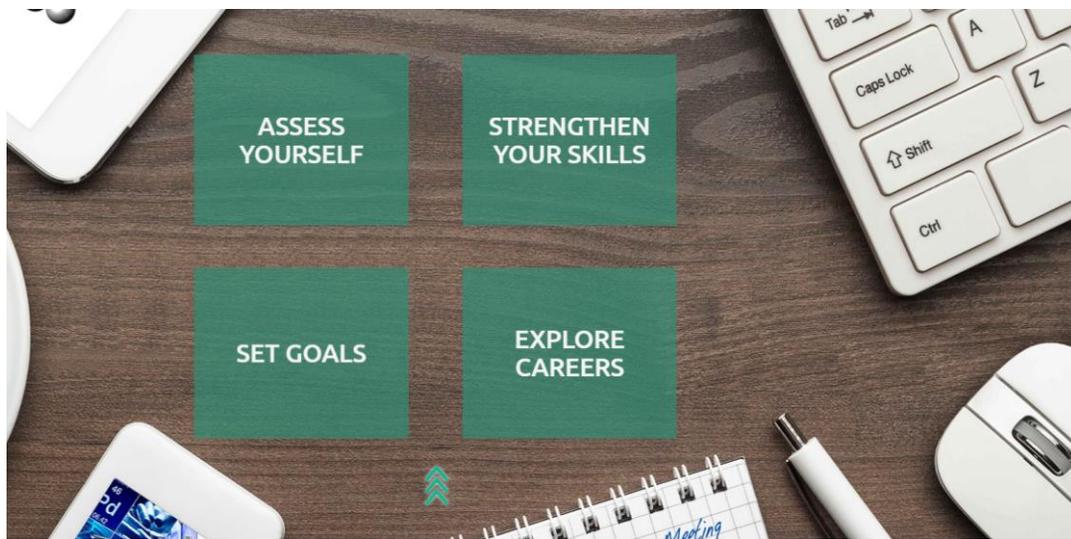
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What Makes Wine Tick: Key Reactions that Create this Delightful Beverage
Andrew Waterhouse delves into the two types of phenolic compounds that give wine much of its taste and health benefits.



How to Make Chocolate for your Special Valentine: Flowers Bloom, Chocolate Shouldn't
Rich Hartel is returning to share how to properly make chocolate and avoid the moldy looking "bloom" that can occur when it is done incorrectly.



Kitchen Chemistry: We've Got a Lot to Learn from Professional and Recreational Cooks
Join Matt Hartings a Professor of Chemistry at American University as he explains some of the intricate chemical transformations through various cooking techniques and food preparation.



Thanksgiving Chemistry for your Family's Feast
Guy Crosby returns to show how a little chemistry can improve your holiday meal.



Ice Cream Chemistry
Rich Hartel returns to explain the surprisingly complex chemistry of everyone's favorite summer treat.



Halloween Candy Chemistry: Caramels, Gummies, Jellies, and Candy Corn
Join us as Rich Hartel returns to dive deeper in to the chemistry of your favorite sweet treats!



Garlic and Other Alliums: The Lore and the Science
Eric Block explains the colorful history of alliums as well as the science of why they make us cry, give us horrible breath and taste so wonderful.



Color Chemistry: Red and White Beer for St. George's Day
Learn what determines the color of beer and how color is measured in the brewing industry.



The Chemistry of Cocktails: Bruising and Louching and Fire Oh My!
Dr. Darcy Gentleman discusses the chemistry of cocktails and quenches your thirst for knowledge.



Wine Science: Designing Great Wines
Join Dr. Susan Ebeler as she explains the chemistry of wine, from the vineyard to your palate.



Barrels of Chemistry: Decoding How Oak Affects Wine Flavor
Learn how the hints of cream, smoke, spice and vanilla that hide in your wine have less to do with the grape and more to do with the wood.



Sous Vide Cooking and Chemistry
Discover a form of cooking that can make the toughest cuts of meat come out tender, juicy and medium rare with Douglas Baldwin.

<https://www.acs.org/content/acs/en/acs-webinars/culinary-chemistry.html>

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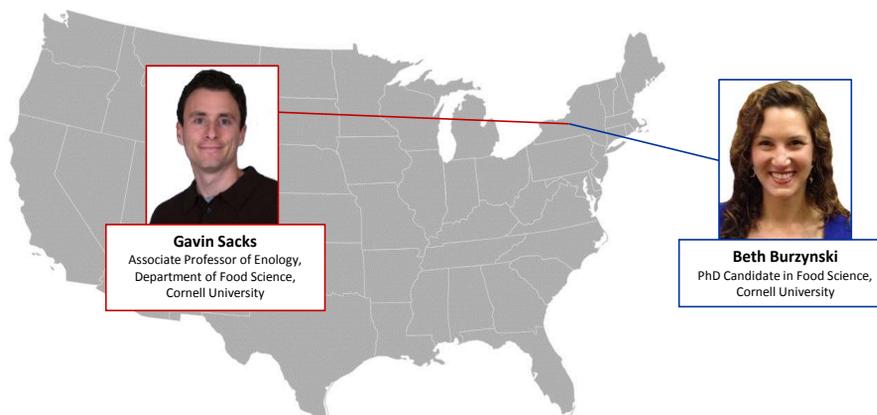
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10



“Ready to Drink Yet? The Chemistry of How Wine Flavor Changes During Aging”



Slides available now and an invitation to view the recording will be sent when available.

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This ACS Webinar is co-produced with ACS Division of Agricultural & Food Chemistry

11

“Ready to Drink Yet?”

The Chemistry of How Wine Flavor Changes During Aging

Gavin L. Sacks

Associate Professor of Enology
Department of Food Science
Cornell University

Moderator: Beth Burzynski, PhD Candidate in Food Science, Cornell University

Let's get started . . . consider the range of wine labels available to US consumers



This is a wine label



So are
all these

Wine labels can include info on

- Producer/brand
- Production region (e.g. Bordeaux)
- Grape variety (e.g. Chardonnay)
- Vintage year
- Alcohol content, "contain sulfites", government warnings

In the US, wine labels must be pre-approved prior to bottling or importation by the Tax and Trade Bureau (TTB)



Audience Challenge Question

ANSWER THE QUESTION ON BLUE SCREEN IN ONE MOMENT



How many different wine labels are approved for sale each year in the United States?

- 2,000 to 4,000
- 6,000 to 10,000
- 15,000 to 30,000
- 40,000 to 60,000
- 75,000 to 125,000



Premium wine is a “craft” product, not a “commodity” Variation in sensory (and thus chemistry) is expected



Taste (Gustation)



salty, **bitter**, **sweet**,
acidic, and umami
compounds

Touch (Chemesthesis)



Compounds responsible for
pungency, cooling, **astringent**,
viscous and related tactile
sensations

Smell (Olfaction)



Volatile compounds, of
which 50-75 create most
wine-like aromas

Appearance



Pigments (mostly red and
yellow) or light-scattering
haze particles

Popular appeal of wine - Explanations

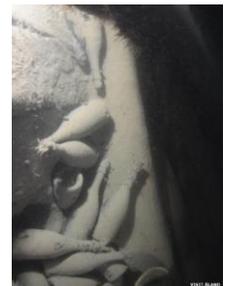


- Its variation
- Its deliciousness, particularly with food
- Its sense of place
- It contains ethanol
- Its mystique, including its longevity



The reputation for “age-ability” persists even though the majority of wines are meant to be, and are, consumed within 0.5-2 years of production

(the occasional bottle of 170-year old shipwrecked Champagne excepted)



“Age-worthy” does not have a well agreed upon definition among enologists



Working definition: “assuming two wines (A and B) are equally liked at some time point, Wine A ‘ages better’ if it is better liked than Wine B at a later time point.”

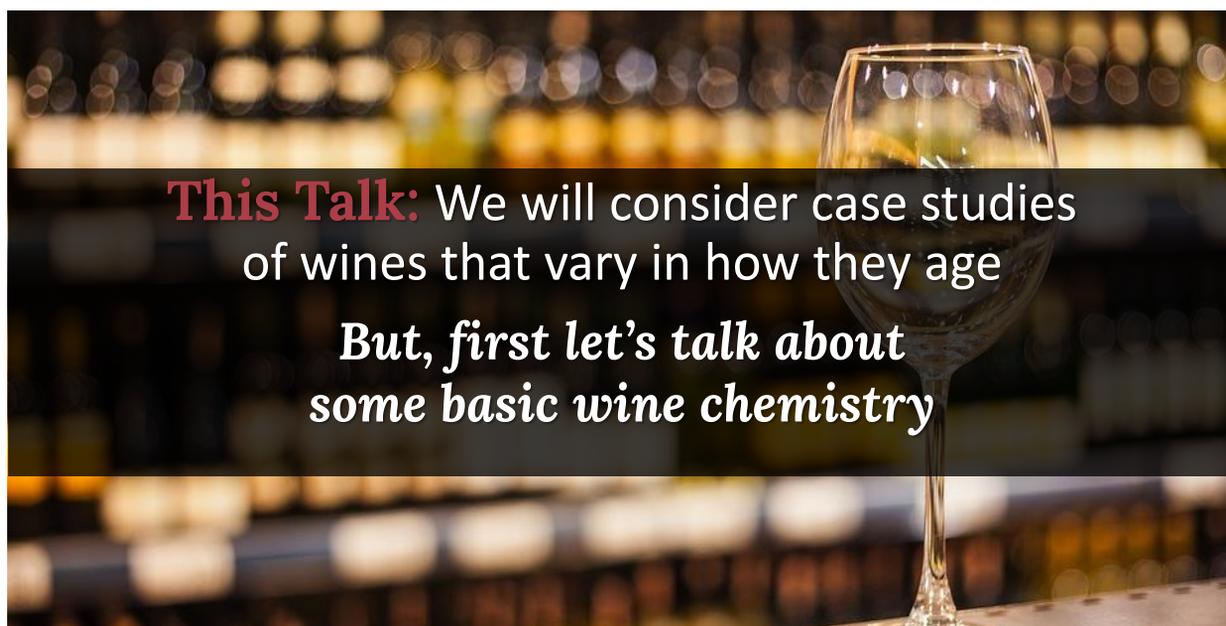
Maybe, youthful characteristics are preserved in Wine A

- Desirable sensory compounds could be more stable
- Fewer undesirable compounds could form

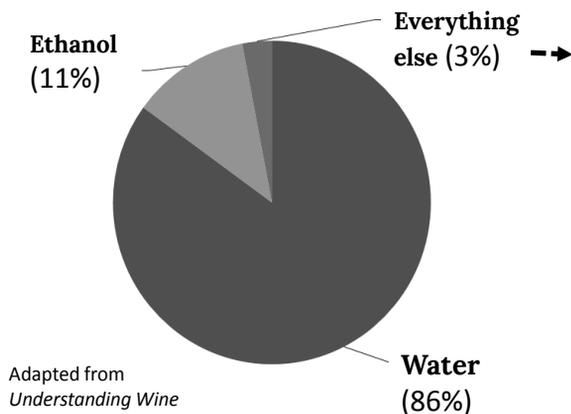


Or, new “aged” characteristics appear in Wine A

- Undesirable sensory compounds could be lost more rapidly during storage
- More desirable compounds could form



Chemically, what's in a typical dry red wine?



Adapted from
Understanding Wine Chemistry; Waterhouse,
Sacks, and Jeffery. 2016

Everything else, a non-comprehensive list

- Glycerol (6-12 g/L)
- Organic acids (5-8 g/L) → **wine pH is 3-4**
- Hexose sugars (0.5-3 g/L)
- Minerals, e.g. K^+ (0.5-2 g/L)

- Important odorants (ng/L to mg/L)

- Phenolics (0.5-2 g/L)
 - Anthocyanins [color]
 - Tannins [astringency]
- Sulfur dioxide (20-40 mg/L)
- Glutathione (15-100 mg/L)

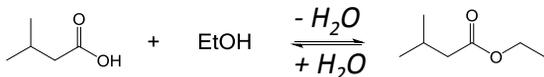
Reducing compounds
(nucleophiles)

What reactions can happen at pH 3-4, 10-12% EtOH, reducing conditions, 20 °C, over 6-24 months?

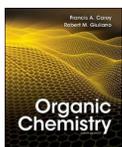


Reactions involving water or ethanol, often acid catalyzed

- Hydrolysis, ethanolysis (below)
- $H_2O/EtOH$ addition or elimination

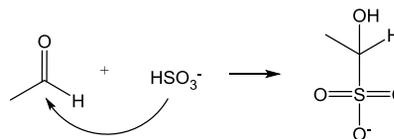


Other textbook reactions, e.g. Grignard?
Not likely ☺



Reactions between wine nucleophiles and electrophiles

- Example nucleophiles = SO_2/HSO_3^- , H_2S , thiols, polyphenols
- Example electrophiles = carbonyls (e.g. acetaldehyde); tannin hydrolysis products; quinones





Case Study 1: Varietal wines “not aging well” due to loss of desirable compounds



Muscat-type wines vs. Gewürztraminer



*Both types of wines have floral aromas when young,
but they have different reputations for aging*

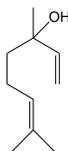
Consider two monoterpene-rich, “floral” smelling grape varieties, with dissimilar fates during aging



Muscat-type grapes,
e.g. Moscato bianco from Asti



*“Serving recommendations [for Moscato d’Asti]
. . . drink it young and fresh!” - winefolly.com*

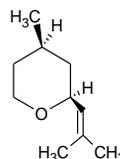


Key odorant = **linalool**
 (“lily-of-the-valley”)

Gewürztraminer

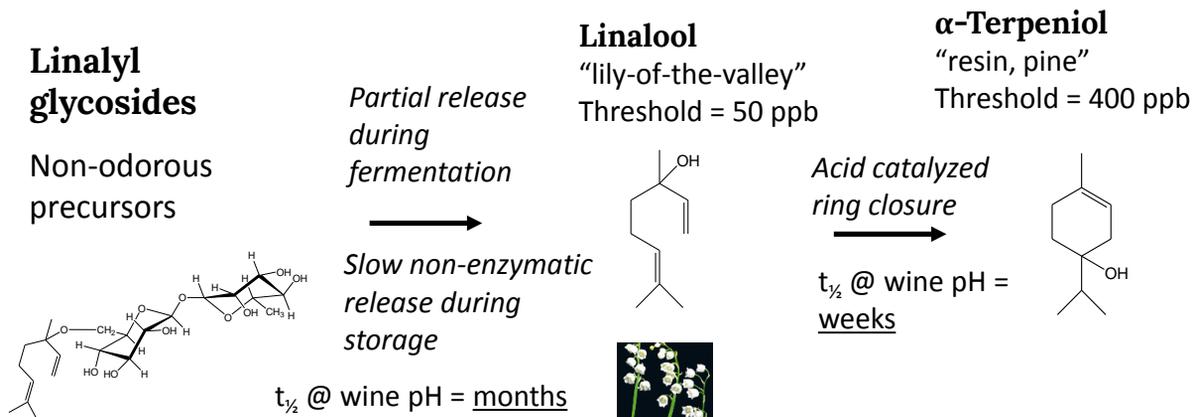


*“While you often can drink
Gewürztraminers young, some benefit from
2-4 years worth of aging.” - wineintro.com*

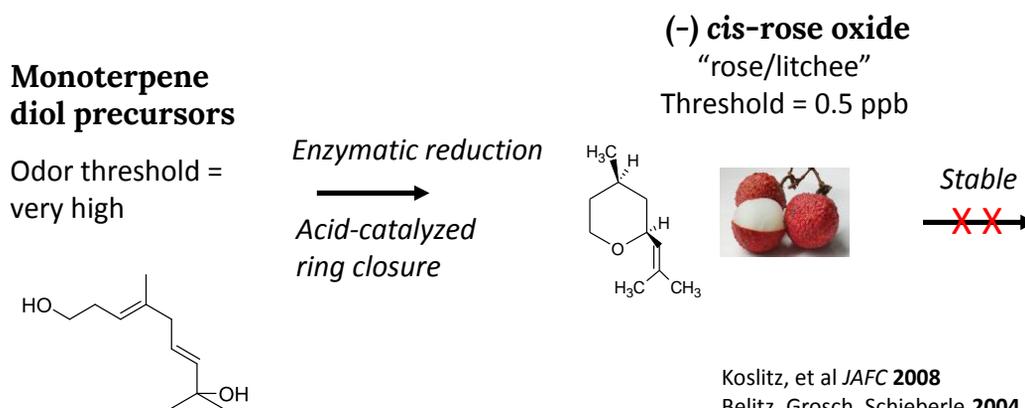


Key odorant =
(-) cis-rose oxide
 “rose/lychee”

The key “floral” monoterpenes in Muscat-type wines, e.g. linalool, are unstable in wine matrix



By comparison, the key **Gewürztraminer** monoterpene is stable or increases during storage



Recap: Wines with strong floral aromas often do not “age well” if you desire the odor to stay floral



- **Monoterpenes, particularly linalool, contribute “floral” aromas, but are not stable in aqueous acidic matrices (WINE!)**
 - In particular, Muscat-type varieties (e.g. Muscat bianco)
 - Stonefruit notes of some wines (e.g. Viognier) do not persist
- **A monoterpene exception: *cis*-rose oxide**
 - Gewürztraminer can continue to have “litchee” aromas, even with age



Case Study 2: Production practices lead to desirable odorants that are readily lost during storage

Beaujolais Nouveau* vs. *Standard red wines

Beaujolais Nouveau is known for intense “cherry, banana” type aromas and is intended for sale within weeks of fermentation

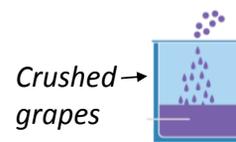


Red winemaking: The 30 second story



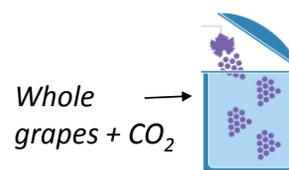
Standard Red Wine Maceration

Grapes are crushed and fermented by yeast in the presence on skins and seeds

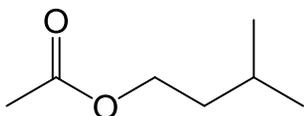


Carbonic Maceration (common for Beaujolais Nouveau)

Whole grape clusters are blanketed in CO₂, grapes auto-ferment to ~2% alcohol. Then, grapes are pressed, and juice is fermented to dryness by yeast



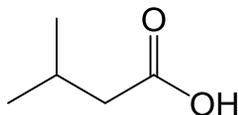
Several differences in **odorant concentrations** between carbonic (CM) and standard maceration, including...



Isoamyl acetate
 "Cherry/banana"



Higher in CM wines



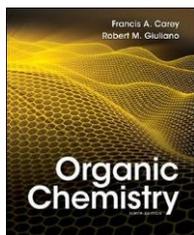
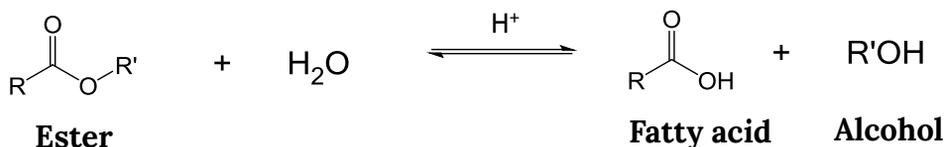
Isovaleric acid
 "Cheesy, sweaty"



Lower in CM wines

(although, below sensory threshold in most wines)

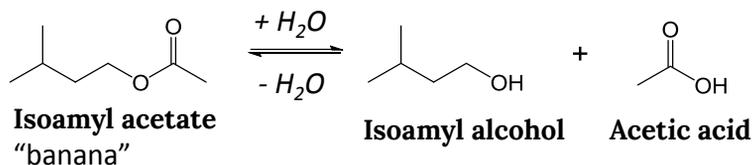
Ester hydrolysis / Esterification in Wine Just like in your Organic Chem I Class



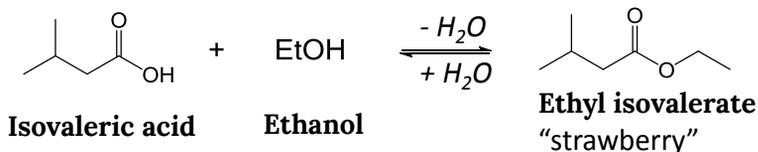
$$K_{\text{eq}} = \frac{[\text{alcohol}][\text{fatty acid}]}{[\text{ester}][\text{H}_2\text{O}]} \sim 0.25$$

Literature estimate

Working through the math...and assuming $[\text{EtOH}] = \sim 2\text{M}$ or 12% v/v, acetic acid = $\sim 5 \text{ mM}$, $[\text{H}_2\text{O}] = \sim 50\text{M}$

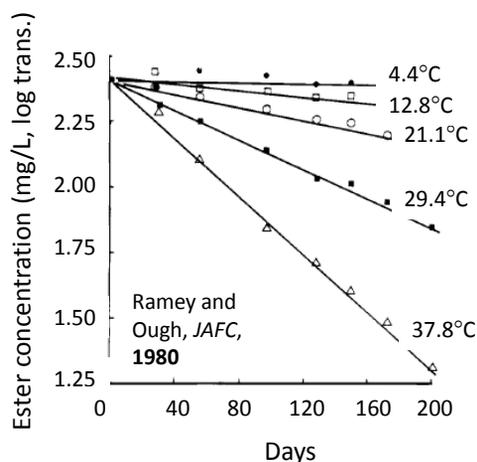


Isoamyl acetate and other acetate esters decrease during storage



Ethyl isovalerate and some other ethyl esters can increase during storage

Organic Chem I, cont., kinetics



Ester hydrolysis/esterification follow pseudo-first order kinetics in wines

At pH 3.6, T=25°C,

$t_{1/2}$ for hydrolysis of an ester is **3-5 months**

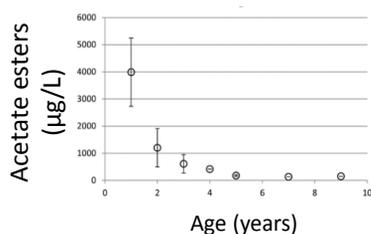
$t_{1/2}$ for esterification of a fatty acid is **1-2 yrs**

How to slow down ester reactions?

- Raise pH (causes other problems)
- Store cold, especially during transit
- **Drink quickly!**
 - *Beaujolais on Thanksgiving*

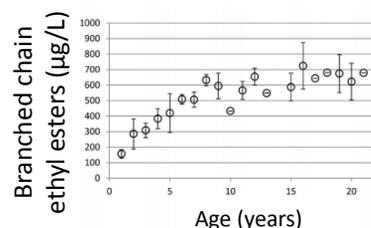


Recap: wines which rely heavily on acetate esters will likely “not age well”



Examples of wines with high acetate esters

- Beaujolais Nouveau and other carbonic wines
- ‘Tropical fruity’ whites, e.g. many Pinot Grigio, Sauvignon blanc, and stainless steel Chardonnay



Standard red winemaking

- = more branched chain fatty acids
- = more branched chain ethyl ester formation during storage

Fruity or other aromas? ↑



Audience Challenge Question

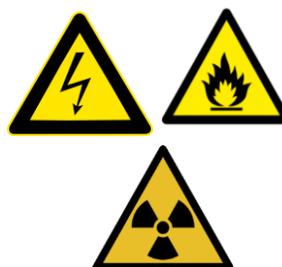
ANSWER THE QUESTION ON BLUE SCREEN IN ONE MOMENT



Which of these approaches to accelerated aging have been patented?

More than one correct answer may exist

- Agitation
- High-temperature
- Ionizing radiation
- Ultrasound
- Electric Currents



“Rapid aging” approaches do not appear to duplicate conventional aging (say, in a 12 °C cellar)



Example 1: UV or gamma ray irradiation generates free radicals
 → volatile sulfur compound formation → “burnt hair” aromas



Example 2: High temperature storage promotes different reactions at different rates

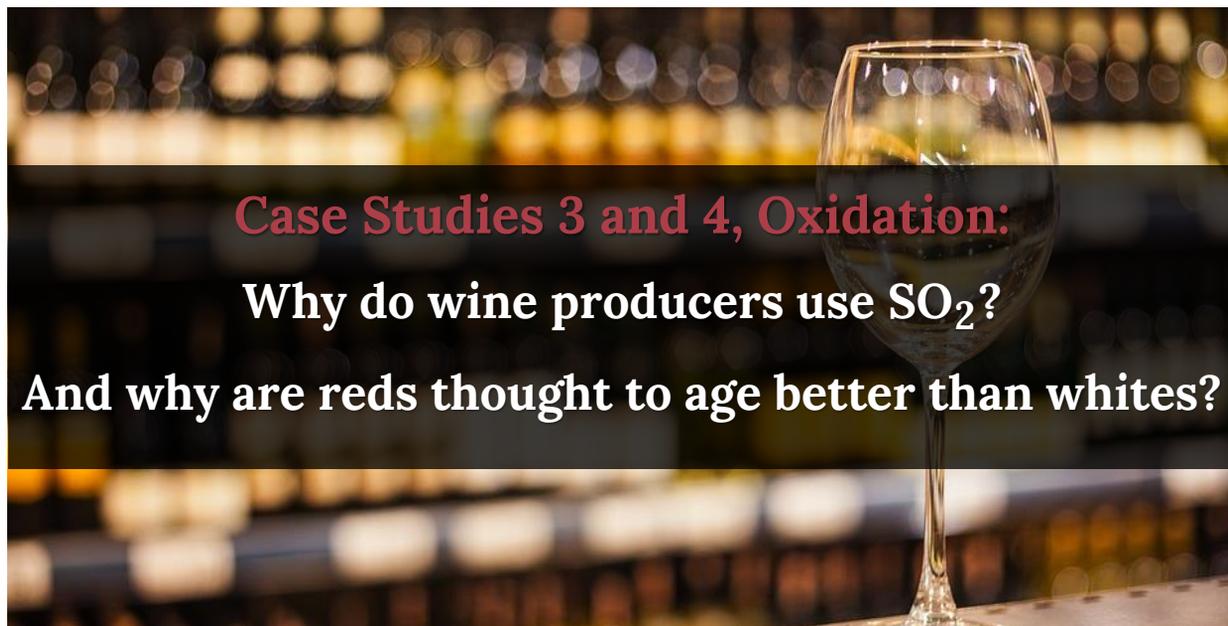
→ Wine reactions differ in activation energies



Unfortunately, higher temperatures often accelerate unwanted reactions to a greater extent!



Reaction in beverage model system	Activation energy, E_a (kJ/mol)	Fold-increase in reaction rate compared to 12 °C		
		At 30 °C	At 50 °C	
Acid hydrolysis of proanthocyanidins (tannins)	45	3	9	} Possibly desirable
Esterification or ester hydrolysis	62	5	22	
Hydrolysis of SMM to DMS	186	106	10250	
Acid hydrolysis of anthocyanin pigment	118	19	350	} Unlikely to be desirable
Formation of ethyl carbamate from urea and ethanol	118	19	350	



Audience Challenge Question

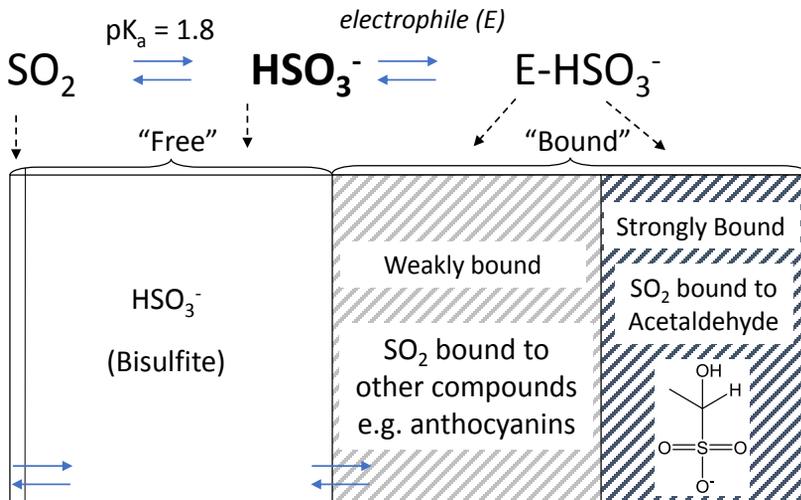
ANSWER THE QUESTION ON BLUE SCREEN IN ONE MOMENT



In the current model of wine oxidation, which wine component directly reacts with O₂?

- [Fe(II)] complexes
- SO₂ (in the form of bisulfite, HSO₃⁻)
- Polyphenolics, particularly condensed tannins
- Glutathione and related sulfhydryls
- Alcohols, particularly ethanol

Distribution of SO₂ species in wine

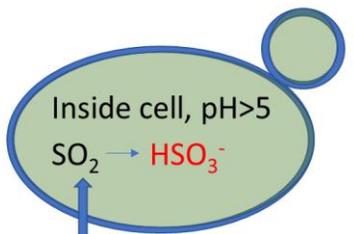


- At wine pH, most SO₂ in exists as bisulfite
- Smaller portion (<5%) exists as 'molecular' SO₂
- Almost no sulfite, SO₃²⁻
- Some bisulfite is covalently bound to wine electrophiles like acetaldehyde

Role of sulfur dioxide (SO₂) in wine



Anti-microbial: neutral, "molecular" form can cross the cell membrane

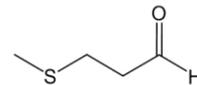


Lower pH favors molecular form

Anti-oxidant: Bisulfite (HSO₃⁻) reacts with products of oxidation

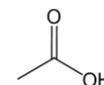


Best predictor of aroma quality = low levels of off-odorants from spoilage organisms or oxidation (San Juan, et al; *JAF* 2012)



Methional, "baked potato"

Via abiotic oxidation



Acetic acid

Via microbial spoilage

Focus on abiotic oxidation during aging

How is O₂ getting into a bottled wine?



Same Semillon wine with one of 14 closures

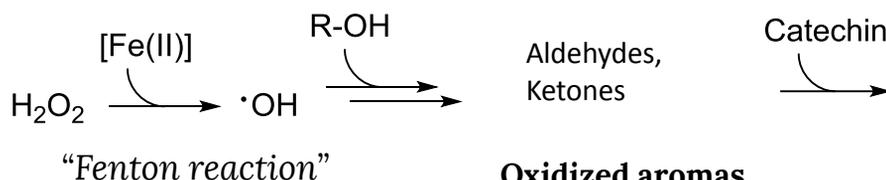
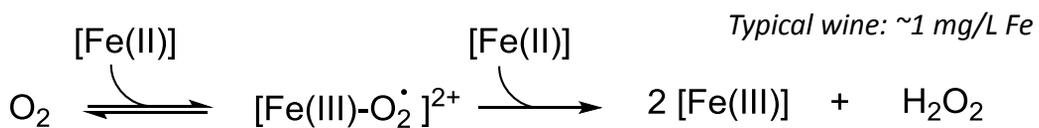


Adapted from P. Godden, et al, AJWGR 2001

Oxygen can . . .

- Be present in headspace during bottling
- Migrate through or around the closure

Wine Oxidation – Production of H₂O₂



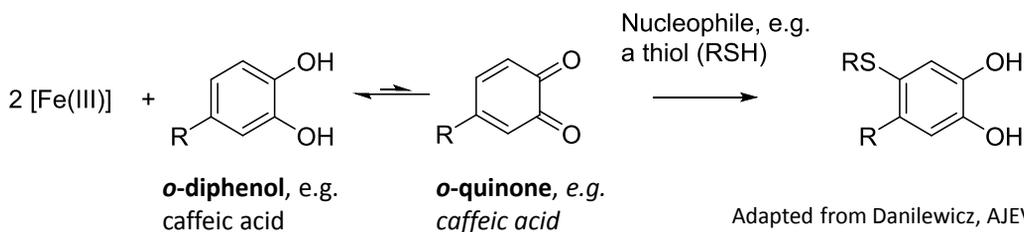
Oxidized aromas
 (“baked potato, bruised apple, cardboard”)

Catechin



Browning

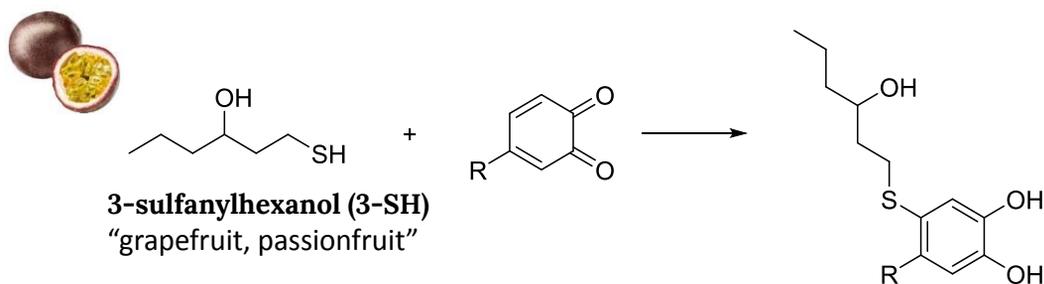
Wine Oxidation – Formation of Quinones



- Oxidation of diphenols to quinones by [Fe(III)] is not thermodynamically favorable in wine
- Wine nucleophiles “trap” quinones and drive oxidation forward
- By comparison most distilled spirits are low in nucleophiles (and often transition metals and phenolics, too) . . . Oxygen consumption is very slow



Quinones can react with many nucleophiles, including desirable “fruity” smelling thiols



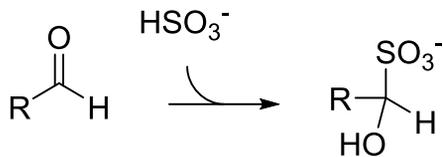
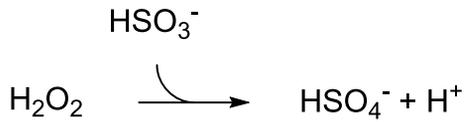
- 3-SH is critical for the fruitiness of many wines, particularly Sauvignon blanc
- Result: loss of quality, unless another nucleophile is present (enter SO_2)

Nikolantonaki and Waterhouse, JAFV 2012

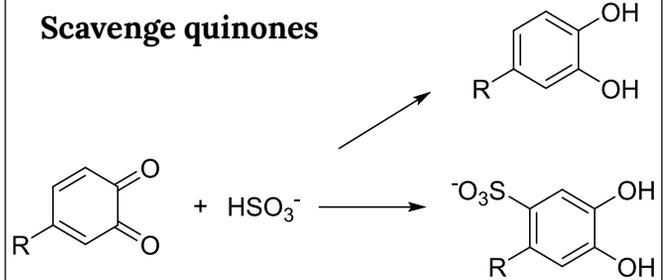
The role of SO₂ as a wine antioxidant - Scavenge wine oxidation products



Scavenge H₂O₂ and aldehydes



Scavenge quinones



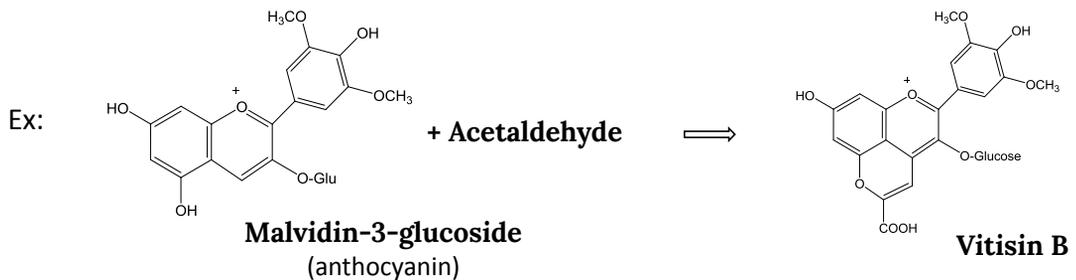
The ability to rapidly scavenge H₂O₂ is unique to HSO₃⁻

Once HSO₃⁻ is mostly depleted (< 10 mg/L), oxidation products accumulate

So why would red wines potentially age better than white wines?



- In part, red wines are less dependent on thiols as key aroma compounds
- Also, polyphenols (anthocyanins, tannins) can react with oxidation products, e.g. malodorous carbonyls, or quinones



Recap: Antioxidants like SO_2 and/or polyphenols may help a wine age better, but not because they directly react with O_2



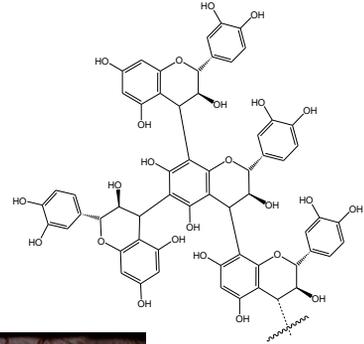
- Oxidation of wine is catalyzed by the presence of transition metals like Fe(II)
- Oxidation generates H_2O_2 and polyphenol quinones.
 - These species can result in loss of desired aroma compounds, production of oxidized aroma compounds (mostly carbonyls), and browning
 - SO_2 (as bisulfite) can react directly with H_2O_2 , quinones, and carbonyls
 - Polyphenols can react with quinones and carbonyls
- Counterintuitively, the presence of SO_2 and polyphenols increases the rate at which O_2 is consumed



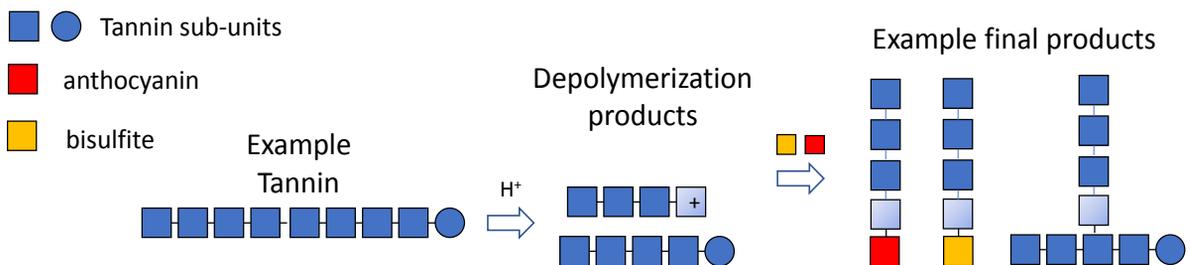
Ongoing Studies: What happens to condensed tannins (chemically, sensorially) during aging?



- **Condensed tannins, aka proanthocyanidins**
 - Polymers of flavan-3-ols, e.g. catechin
 - Present in grape skins and seeds – at higher concentrations in red wines
- **Responsible for “astringency” (drying, puckering sensation) in wines**
 - Mechanism = non-specific covalent binding of proteins, including salivary proteins



During storage, tannins can undergo both acid-catalyzed and electrophile/nucleophile reactions



- **How do these reactions affect tannin sensory attributes?**
 - Decrease in astringency, most likely?
 - Other changes, i.e. decrease in in-mouth persistence (“stickiness”)?

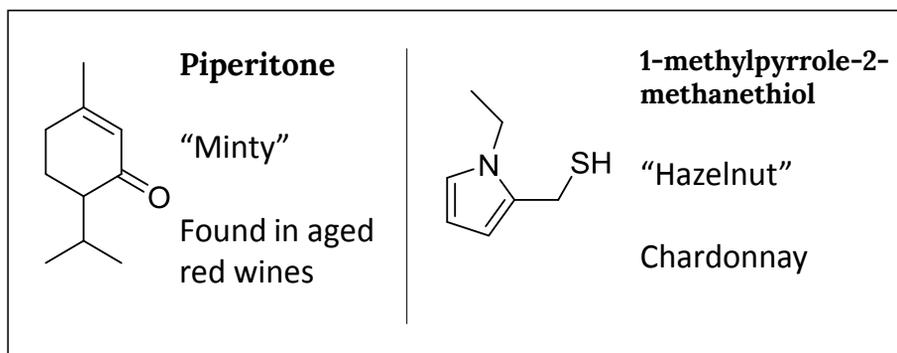
Ongoing Studies: What else forms during storage and contributes to the “bouquet” of aged wines?



- From before: certain ethyl esters, TDN, DMS
- Recent papers using **GC-O/MS** have suggested additional candidates



GC-Olfactometry
(GC-O)



Ongoing Studies: Why do wines differ in relative amounts of key malodorous compounds following oxidation?

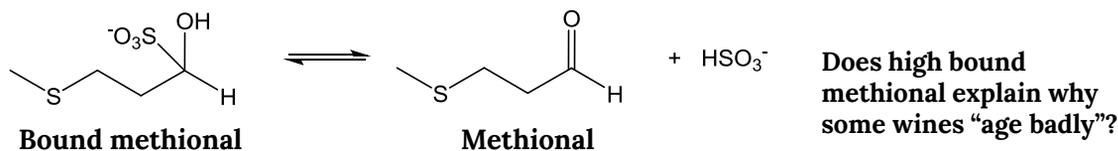


Methional (“baked potato”) and phenylacetaldehyde (“honey”) have been implicated as key wine oxidation odorants

- Low sensory thresholds
- Relatively weak SO₂ binders as compared to other aldehydes



Wines can differ by over an order of magnitude in the amount of these aldehydes formed during oxidation and HSO₃⁻ loss





Wrapping Up: Take-Home Messages



- **“Aging well” is a not single concept**
 - New desirable compounds could be formed; or else lost more slowly
 - Or, new undesirable compounds could be avoided; or else lost more quickly
 - And, what’s desirable to one consumer may not be to another
- **A limited number of types of reactions can occur in aging. Key classes**
 - Solvent-mediated, such as ester hydrolysis/esterification
 - Reactions between nucleophiles and electrophiles, e.g. addition of bisulfite to oxidation products
- **There’s much to learn still:** Tannin changes, odorants responsible for aged wine aroma, differences in observed oxidation products among wines

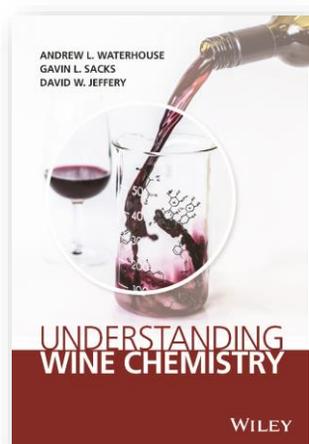
Still Thirsty?: If you like this talk, and want to learn more, consider the textbook



Understanding Wine Chemistry

Andrew L. Waterhouse, Gavin L. Sacks, and David W. Jeffery

Published in 2016 by John Wiley & Sons

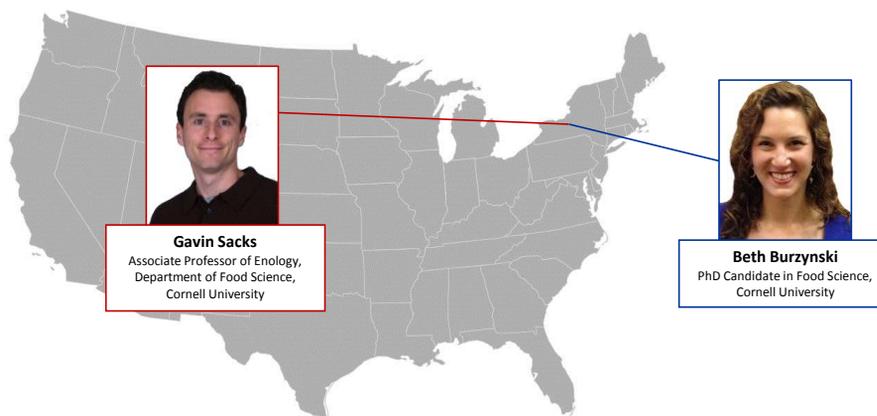


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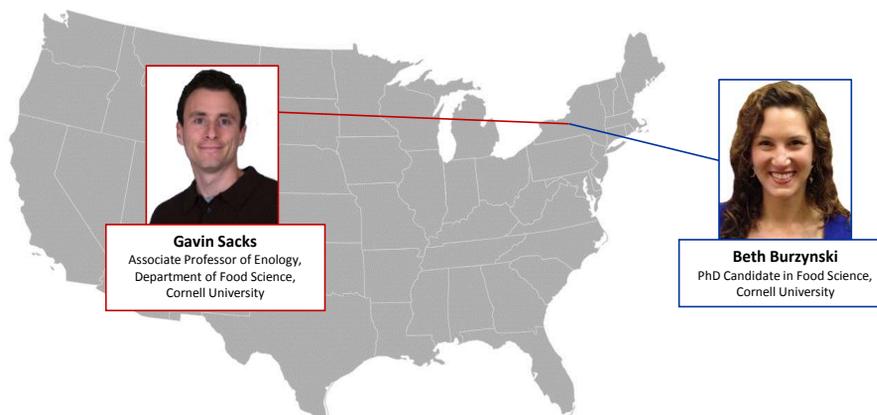
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Gavin Sacks

Associate Professor of Enology,
Department of Food Science,
Cornell University

Beth Burzynski

PhD Candidate in Food Science,
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