"Dude, You're Bound for Trouble:" Life in detox with Riesling aroma precursors

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Projects supported by NYWGF

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FINAL EXAM, QUESTION 1

From a chemical perspective, what makes Riesling recognizable as Riesling?

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Quick way to approximate relevance of odorant(s): Odor Activity Value or Aroma Value

$$\text{Odor activity value (OAV)} = \frac{\text{Concentration}}{\text{Sensory Threshold}}$$

Adapted from Belitz, Grosch, Schieberle, "Food Chemistry"

Useful rule of thumb for odorants or odorant family:

If OAV > 1, more likely to be relevant
If OAV < 1, unlikely to be relevant

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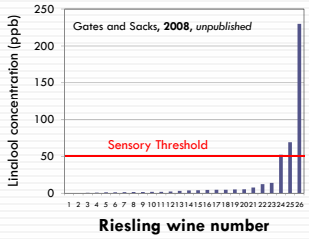
The popular explanation, "monoterpenes", have OAV ≤ 1 in most Riesling wines



Concentrations of **linalool** ("floral") in 2005 and 2006 New York State Riesling, measured in early 2008

Only 3 of 26 wines above sensory threshold (OAV>1)

Even lower OAV (<0.1) of other monoterpenes (e.g geraniol)

By comparison, monoterpenes have OAV>10 in Muscat-type wines

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Riesling aroma: possibly, a "balance" of many compounds with modest OAV?

Odorant or odorant family	Aroma	Odor activity value range in Riesling
Acetate esters	Banana, tropical	2-40
TDN	Petrol, kerosene	0.1-10
Monoterpenes	floral	0-5
Volatile thiols	Citrus, sweaty	6-12
Phenols (e.g. vinylguaiacol)	Spicy, woody	0-2
And other culprits, not necessarily specific to Riesling: molecular SO_2, ethyl esters, furaneol (in late harvest), β-damascenone, lactones		

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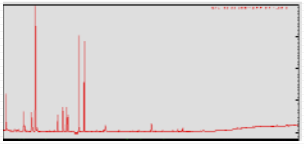
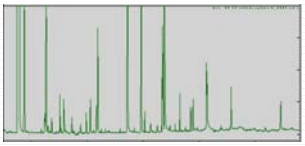
Winemaking results in both *de novo* odorant production and release of "bound" volatiles



Riesling juice by GC-MS
(~100 compounds)



Riesling wine by GC-MS
(>1000 detectable compounds)

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Riesling aroma: derived mainly from precursors "bound-volatiles"

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Compounds in bold are derived partially or fully from grape-derived precursors

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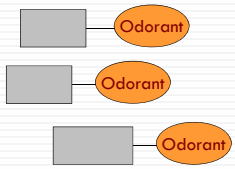
** from Tominaga, AJEV, **2000**. All other from measurements on NYS wines*

Majority of grape-derived aroma compounds in wine were initially "bound"



"Bound" volatiles

Not volatile
Non-odorous

= Sugar, cysteine/glutathione

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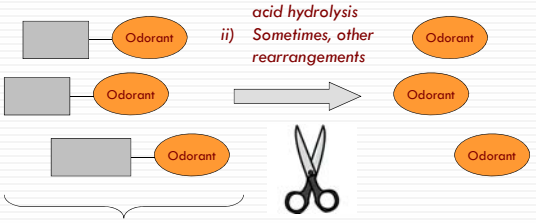
Precursors are "potential aroma" Can be released during fermentation



"Bound" volatiles, not volatile or odor-active

"Free" volatiles, with odor-activity

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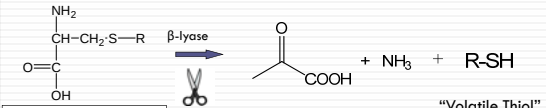
Non-odorous aroma precursors in grapes, i.e. "bound volatiles", Part 1

- **S-cysteine / S-glutathione conjugates,** i.e. volatiles bound to cysteine (amino acid) or glutathione (tri-peptide)
  - Form tropical, cat-pee, grapefruit-smelling **volatile thiols**
  - Key to Sauvignon blanc, but above threshold in many varietals



S-cysteine conjugate precursor

"Volatile Thiol"

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Non-odorous aroma precursors in grapes, i.e. "bound volatiles" , Part 2

- **Glycosides,** i.e. volatiles bound to sugars
  - Over 200 aglycones identified following enzymatic and/or acid-catalyzed hydrolysis
- Several compound classes represented
  - Monoterpenes
  - C13-norisoprenoids
  - Phenols
  - Lactones, and others
- "floral", "fruity", "petrol" and other aromas

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The potent volatiles in Riesling wines exist mostly in their bound form in musts

Typically, >90% as bound

Low levels of free odorants

Cultivar dependent

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Today's thesis

Riesling flavor is a complex machine with many levers. We must understand what controls those levers

(as opposed to, "let's pull leaves again and see what happens")

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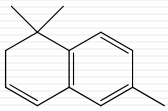
1,1,6-Trimethyldihydronaphthalene (TDN)



C_{13} norisoprenoid

Recognition in model wine: 20 ng/mL
Typical conc. (most wines) < 10 ng/mL
(Riesling) up to 200 ng/mL

Petrol, kerosene aroma

Several previous studies: Potential TDN increases with greater cluster light exposure

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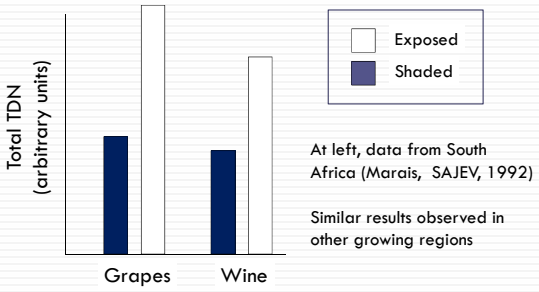
Total TDN (free + potential) increases with cluster exposure



At left, data from South Africa (Marais, SAJEV, 1992)

Similar results observed in other growing regions

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Strong evidence that precursors of TDN and other C_{13}-norisoprenoids are carotenoids

Carotenoids in Photosystem II are implicated with
1. Assisting in light harvesting ("antenna pigments")
2. Dissipating excess energy ("xanthophyll cycle")

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Proposed pathway for C_{13} norisoprenoid precursor formation

Carotenoids

↓ *Enzymatic or abiotic degradation after veraison*

C_{13}-norisoprenoid precursors (in grape)

↓

Glycosylated C_{13}-norisoprenoid precursors in ***grapes***

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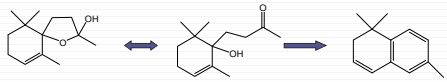
Adapted from Baumes, et.al. *An. Chim. Acta* 2002

Glycosides then hydrolyzed during or after winemaking, eventually yielding C_{13} norisoprenoids

Carotenoids → *Glycosylated C_{13}-norisoprenoid precursors in grapes*

Hydrolysis during winemaking, storage; Acid-catalyzed rearrangements



2,6,10,10-tetramethyl-1-oxaspiro[4.5]dec-6-ene-2,8-diol

Winterhalter, et.al. (J. Ag Food Chem, 1991)

TDN

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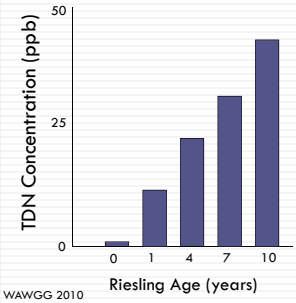
TDN – increase during storage



TDN precursors will slowly hydrolyze and rearrange to form free TDN during storage

In aged Riesling can exceed 200 ng/mL (sensory threshold = 20 ng/mL)

Adapted from Rapp, Nahrung, 1998

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The practical question: Is there a critical window where light affects TDN precursors?

Increase in TDN ("petrol") associated with sun-exposed clusters

Meyers, Sacks, Vanden Heuvel, *ASEV, Napa CA*, **2009**
Marais, et.al. *South Afr. JEV*, **1992**
Lee, et.al. AJEV, **2007**
and others

Cluster exposure during growing season is often desirable

Ex: Decrease malic acid, disease pressure and increase spray effectiveness

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Is there a critical time for removal? Leaf Removal Treatment Timings (2009)

Control

Berry-set

Pre –veraison (Pre-V)
33 days post-set

Post –veraison (Post-V)
50% fruit softened

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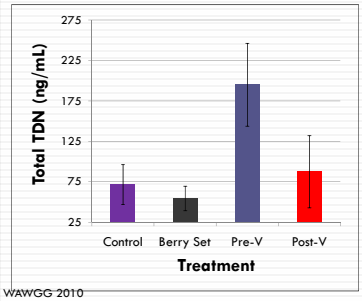
Pre-veraison leaf removal → **significant increase in TDN** compared to control and other timings



Pre-veraison leaf removal resulted in higher total TDN in juice (left)

Higher free and total TDN in wine also observed

Kwasnieski, Pan, Vanden Heuvel, Sacks
JAFC, *submitted in 2009*

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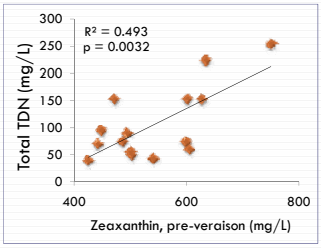
Correlation of zeaxanthin, pre-veraison, and TDN concentration at harvest



Zeaxanthin, pre-veraison, is positively correlated with TDN concentration

No other carotenoid (pre-veraison or harvest) significantly correlated with TDN concentration

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Summary

- Riesling aroma can have several compound classes all close to or above threshold
  - TDN, monoterpenes, volatile thiols, phenols, acetate esters, and others
  - Mostly "bound" compounds, which appear to derive via detoxification pathways in grapes
- "What are the levers?". Must improve understanding of how growing conditions influence aromas
  - Sun exposure just prior to veraison = TDN precursors
  - Other examples: botrytis

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