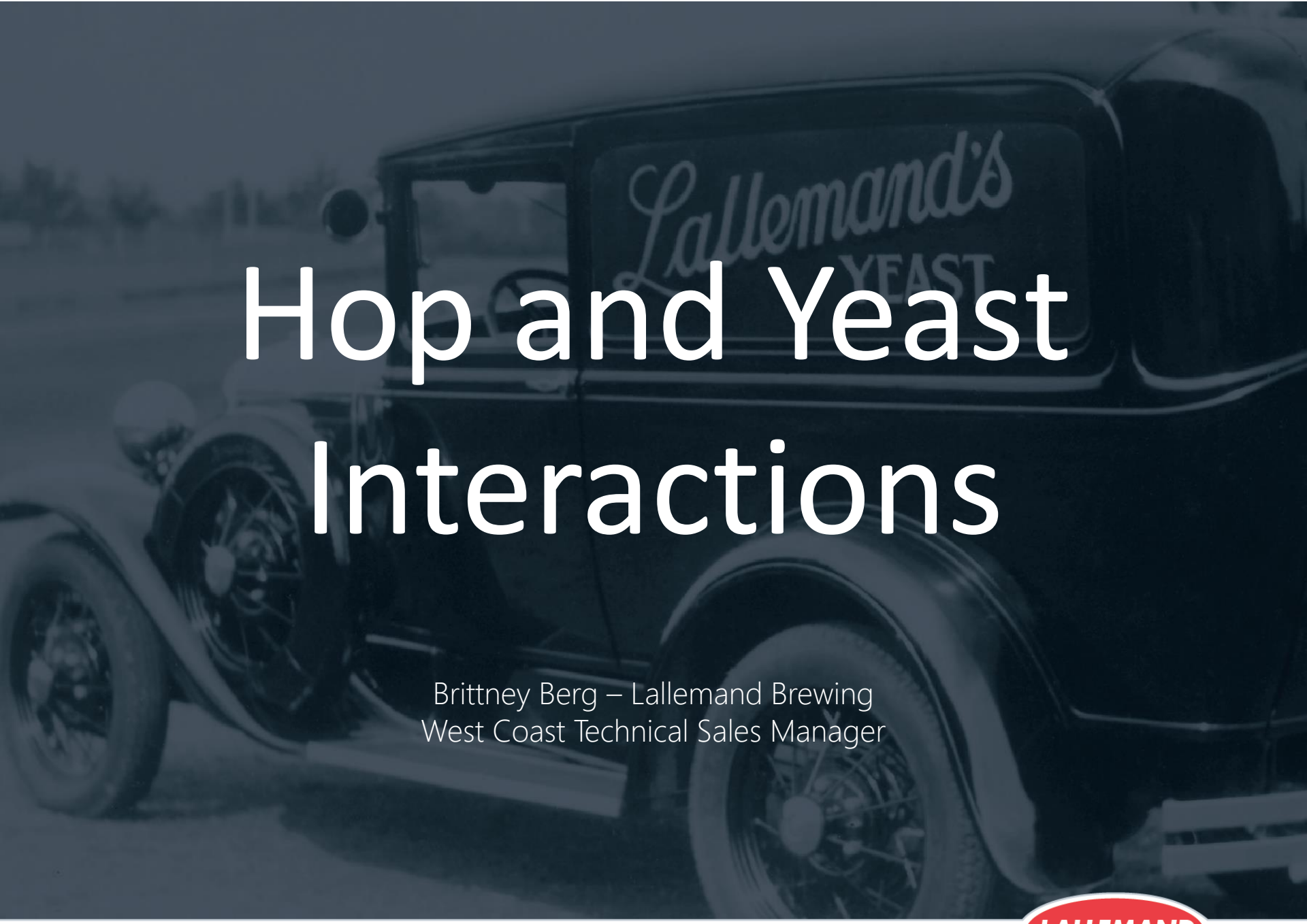
CA CRAFT BEER SUMMIT 2019

CALIFORNIA CRAFT BREWERS ASSOCIATION CCBA 30th ANNIVERSARY



Hop and Yeast Interactions

Brittney Berg – Lallemand Brewing
West Coast Technical Sales Manager

Lallemand's Core Activity

Development, production and marketing of yeast and bacteria…. and their derivatives

Overview

- A brief review of studies regarding hop derived compounds and how they are modified by yeast during fermentation

- Starting off simple: Hop composition & yeast factors
- Known Interactions
- Hop Derived Compounds:
  - Carbonyl Compounds
  - Esters
  - Monoterpene Alcohols
  - Glycosidically bound precursors
  - Hop Degradation Acids
  - Thiol precursors
- Trials

Background

What is “Biotransformation’?

- Biotransformation = “alteration of organic compounds by organisms or enzymes ”
- “an array of complex chemical processes during which yeast cells transform hop components into (new), often boldly aromatic compounds”
- “oil components that yeast have modified”
- “Yeast derived impact or modification of hoppy aroma”

Why “Biotransformation” ?

It’s a small (but important!) part of hoppy aroma in beer

We know that fresh/processed hop aromas are different then that of the final beer aroma

- Disproportionate extraction
- Losses by e.g. evaporation or adsorption
- Modification of hop derived volatiles by yeast enzymes

Hop Composition

POLYPHENOLS

RESINS

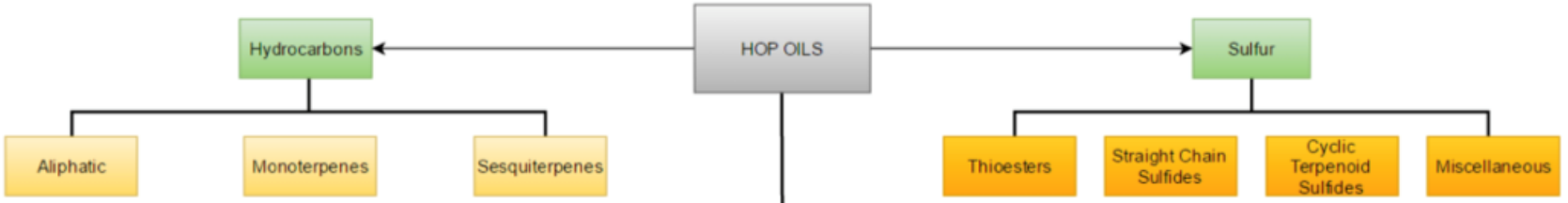
ESSENTIAL OILS

Hop Composition

ESSENTIAL OILS

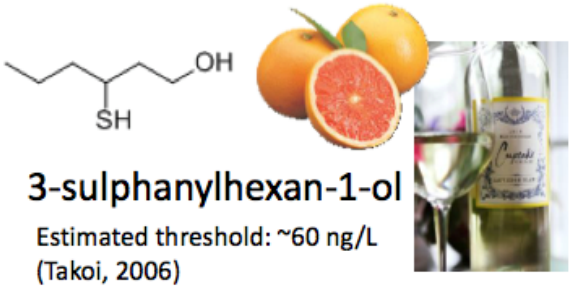
- Hydrocarbon fraction (50-80%)
  - Myrcene, Caryophellene, Farnesene, Humulene, …
- Oxygenated fraction (20-50%)
  - Linalool, Geraniol, Nerol, …
- Sulphur fraction (<1%)

Hop oil fractions



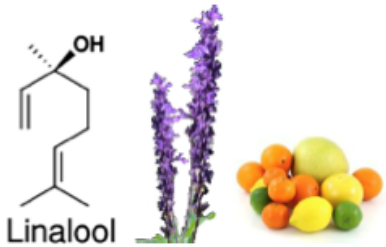
Myrcene

Estimated threshold: ~30 ppb in beer (Hieronymus, 2012)



3-sulphanylhexan-1-ol

Estimated threshold: ~60 ng/L (Takoi, 2006)

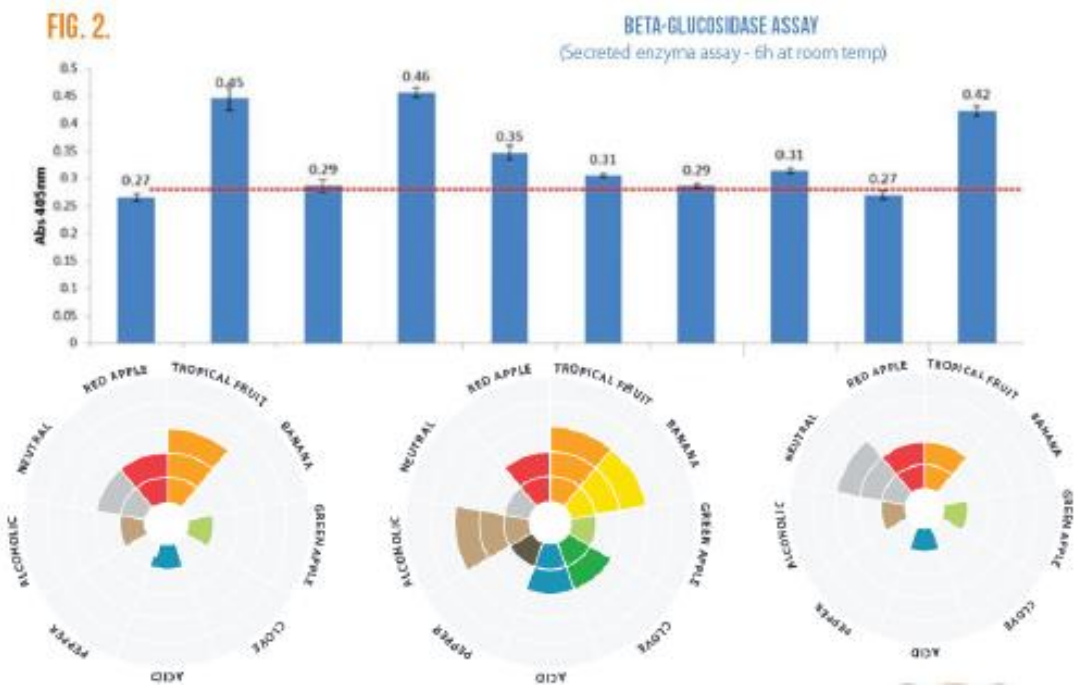


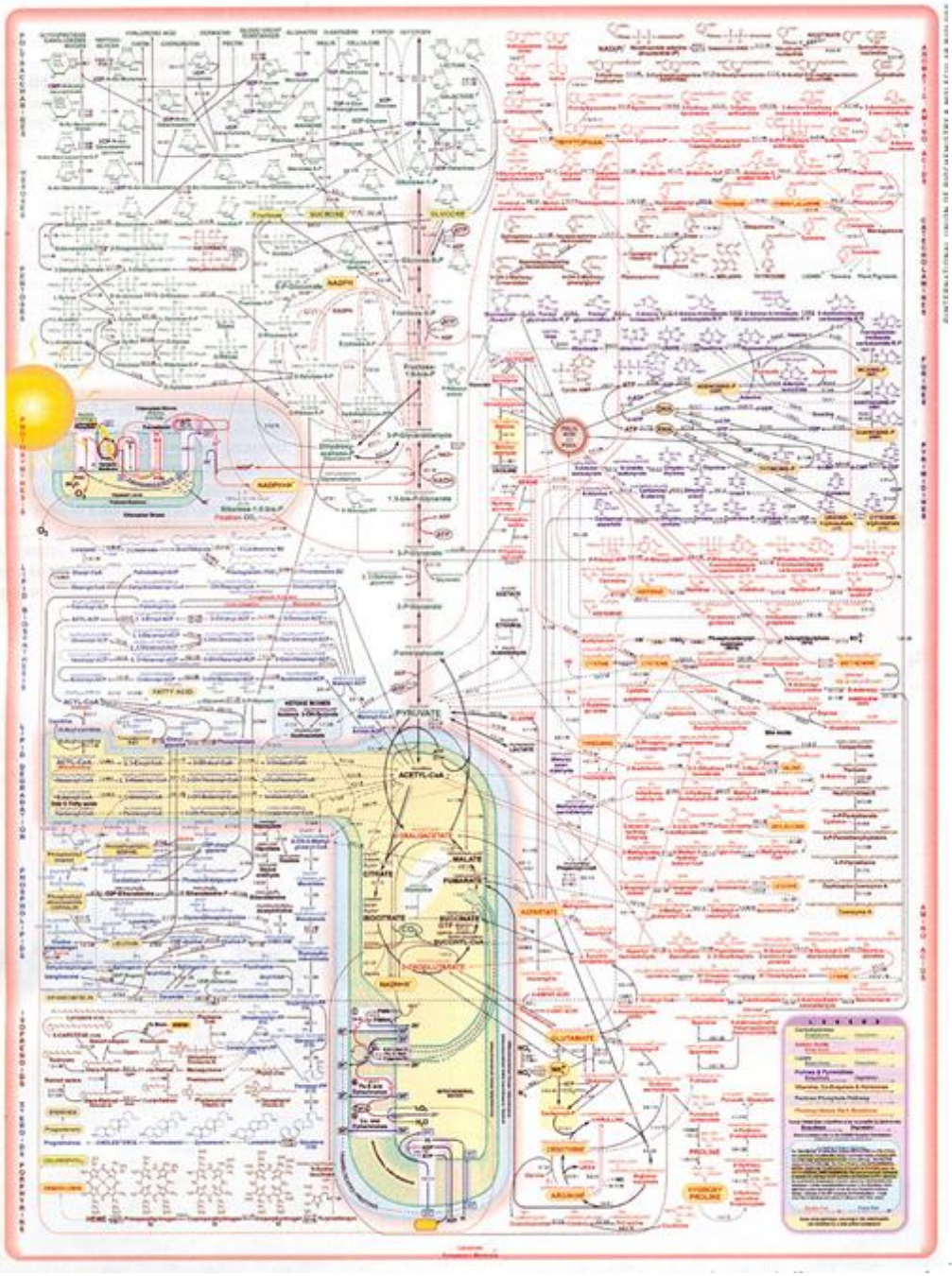
Linalool

Estimated threshold: ~10 ppb in beer (Almaguer, 2014)

Yeast Factors

- Yeast are complex
- Many factors influence how yeast behaves





Yeast Factors: DH during late primary / early secondary

Reasons to dry hop with yeast:

- dissolved oxygen protection
- natural mixing by convection
- biotransformation of hop oil compounds

Things to consider:

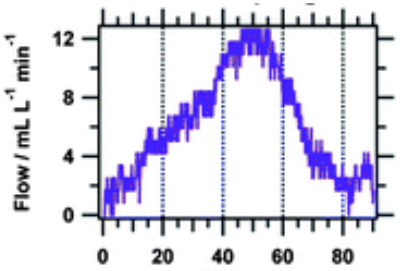
- stripping of aroma
- loss of volatiles due to adsorption onto biomass

Commonly Known Interactions

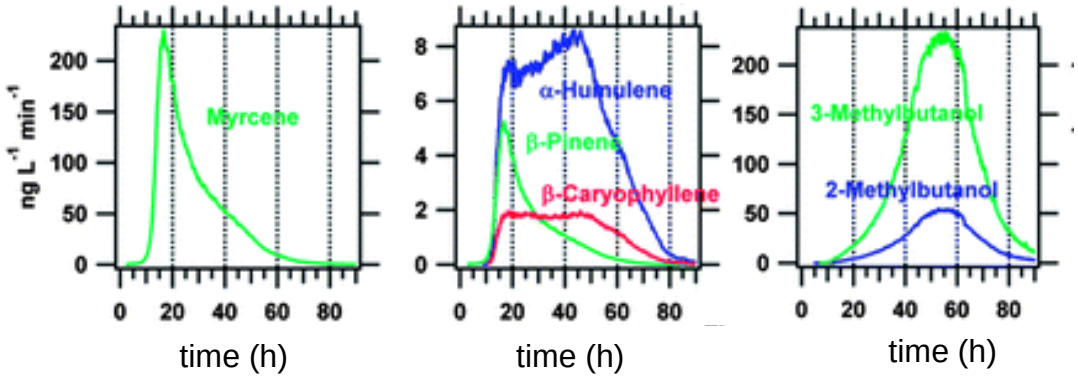
- Stripping compounds during fermentation(1,2)
  - CO2 production/Stripping
  - Adsorption
- Masking?
- Biotransformation

Volatile compounds are lost by stripping

carbon dioxide evolution rate



release curves of aroma compounds



Haefliger and Jeckelmann, Anal. Methods, 2013, **5**, 4409-4418

Influencing Factors (not discussed here)

- Yeast strain
- Cell count
- Temperature
- Point of hop addition
- Contact time

Various Studies Review

Hop Derived Compounds

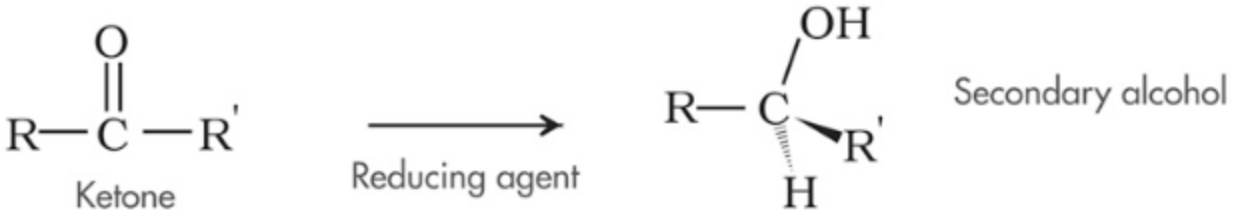
- Carbonyl compounds (also from derived from malt, mashing, boiling)
- Esters (branched chain esters, not found in unhopped beer)
- Monoterpene alcohols
- Glycosidically bound precursors
- Acids
- Polyfunctional thiols

Carbonyl Compounds

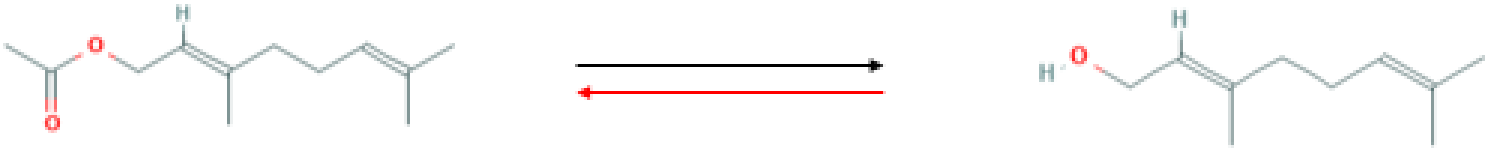
Carbonyl → Alcohols

Dehydrogenases and reductases

Example: methyl ketones are partially reduced to the corresponding secondary alcohols(3)



Esters



Geranyl acetate

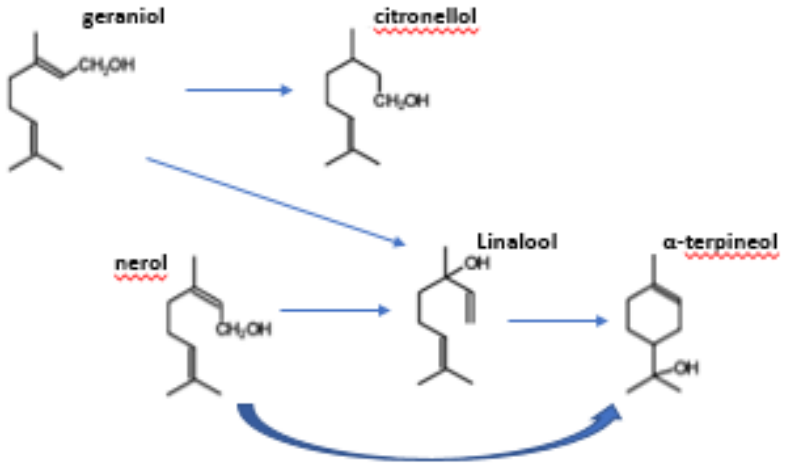
Geraniol

Esters can be hydrolyzed or trans-esterified

- Geranyl and citronellyl acetate esters are formed by lager yeast, but not by ale yeast [4]
- Esterase activity?
- Chemical esterification during beer ageing alters flavor

Monoterpene alcohols

- Responsible for spicy/floral/hoppy aromas
- Do not transform spontaneously, but are catalyzed by yeast (or low pH)
  - *Saccharomyces cerevisiae* can reduce, translocate, and isomerize monoterpene alcohols (4)

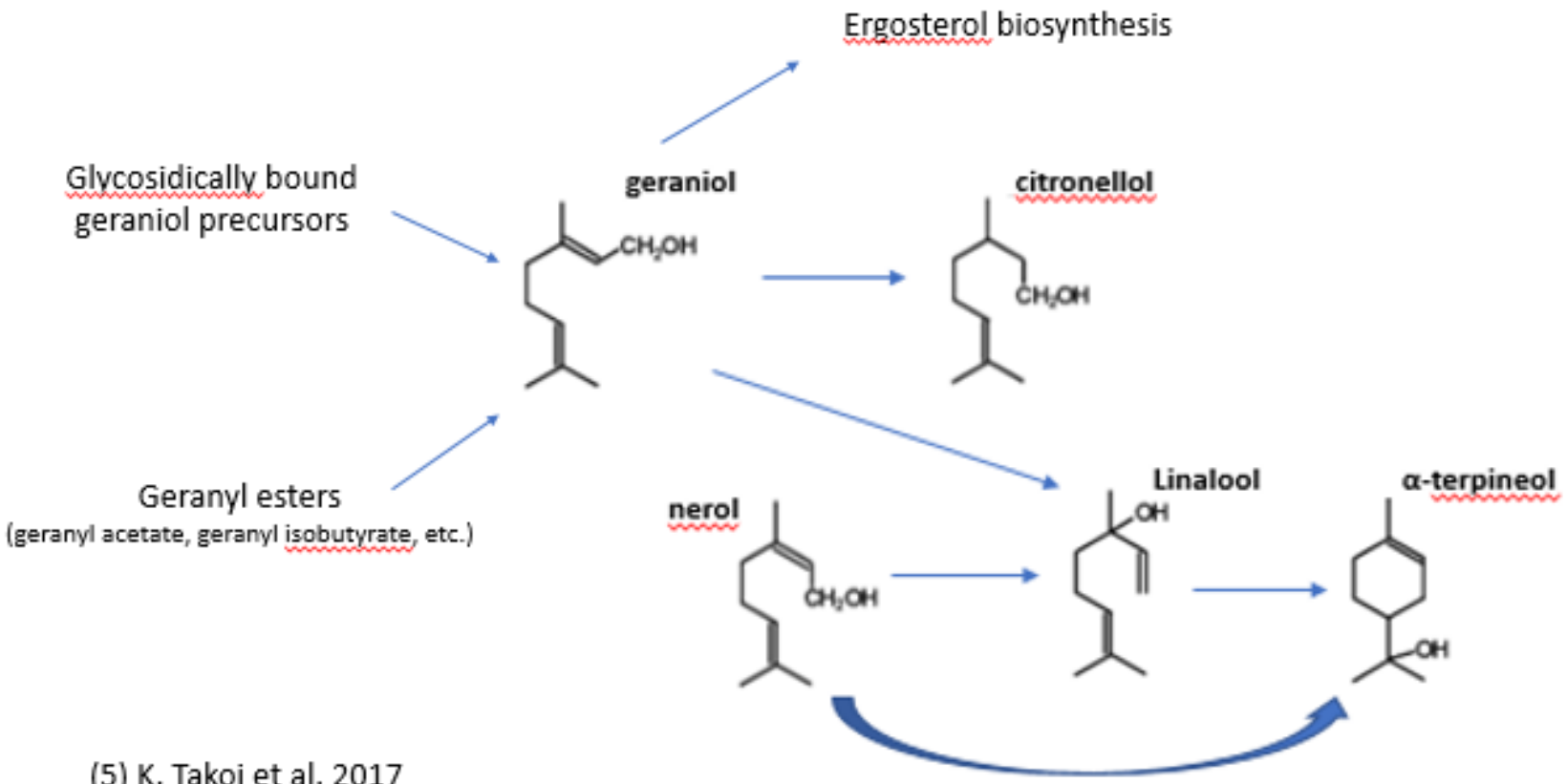


Monoterpene alcohols - Geraniol

- Research from e.g. Takoi et al. classified hops into two categories:
  - Free geraniol dominant hops
  - Geraniol precursor dominant hops

- Sources of geraniol: free geraniol, geraniol precursors, and geranyl acetate(5)

- Geraniol decreases during first 3 days of fermentation – is used for ergosterol biosynthesis (5)



(5) K. Takoi et al. 2017

Glycosidically bound precursors

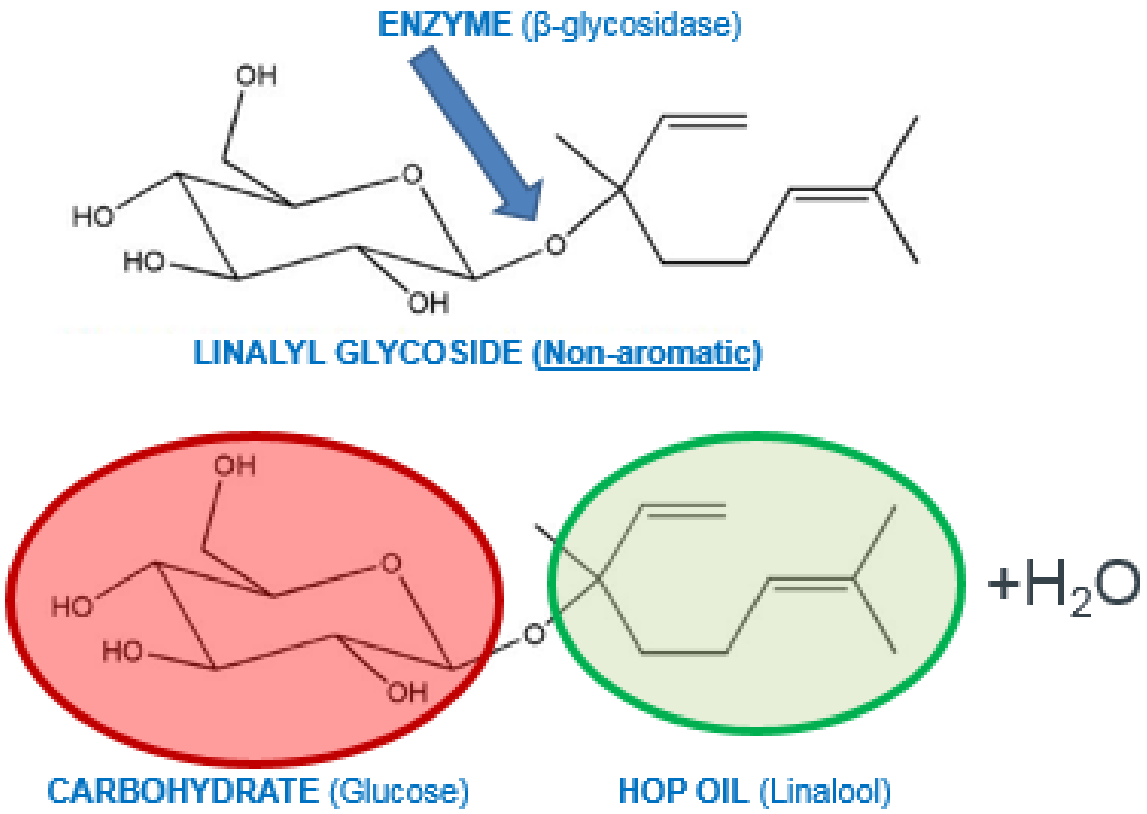
What are glycosides?

- Sugar bound molecules
- Non-volatile
- Found in hops[2]

Research has shown that glycosidically bound aroma precursors are hydrolyzed.[2]

- Non-aromatic compounds are hydrolyzed: releasing one aromatic compound, one glucose, and one molecule of water
- β-glucosidase enzyme

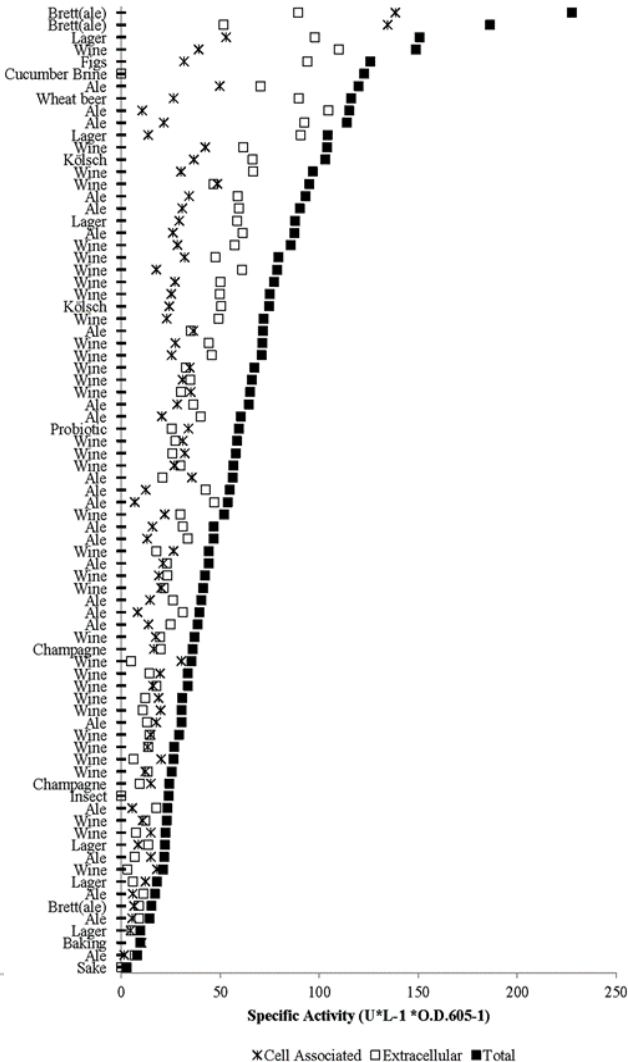
Glycoside Hydrolysis



Glycosidically bound precursors

Researchers from OSU have done significant research in this area:

- Found evidence that hops contain substantial amounts of glycosidically bound volatiles
- Brewing yeast exhibit wide range of glycosidase hydrolysis activity
- Maximum hydrolysis occurs within 3 days of primary fermentation
- Since glycoside concentration in wort are low, yeast B-glucosidase activity makes small contributions to hop aroma



Sensory impacts

Enzymatic hydrolysis ß-Glucosidase, pH 5, 24 h, 40 °C	Addition of enzyme	Without enzyme
3(Z)-Hexenol	9	0
1-Octen-3-ol	484	0
1,5-Octadien-3-ol	39	0
Linalool	9	0
α -Terpineol	17	0
8-Hydroxy-linalool I	6	0
8-Hydroxy-linalool II	32	0
Benzylalcohol	82	15
3-Hydroxy-7,8-dihydro-β-ionol	10	0

Aroma	Mostly grapefruit and pine with some tropical pineapple, orange and caramel backin' it up	Mostly pine with some **citrus, orange and grapefruit**, followed by **tropical pineapple** aroma as well, slight caramel and isoamyl acetate

Kollmannsberger et al, 2006

Hop degradation acids

Esterification of short chain hop derived acids

Hop degradation products → ethyl esters (fruity esters)[6]

Researchers found that ester concentration in beer can increase by the use of aged hops[6]

This conversion is not particularly clear, but there are probably many factors that play into this

Polyfunctional thiols

What are Thiols?

- Sulfur containing compounds – highly potent

Free and bound forms available

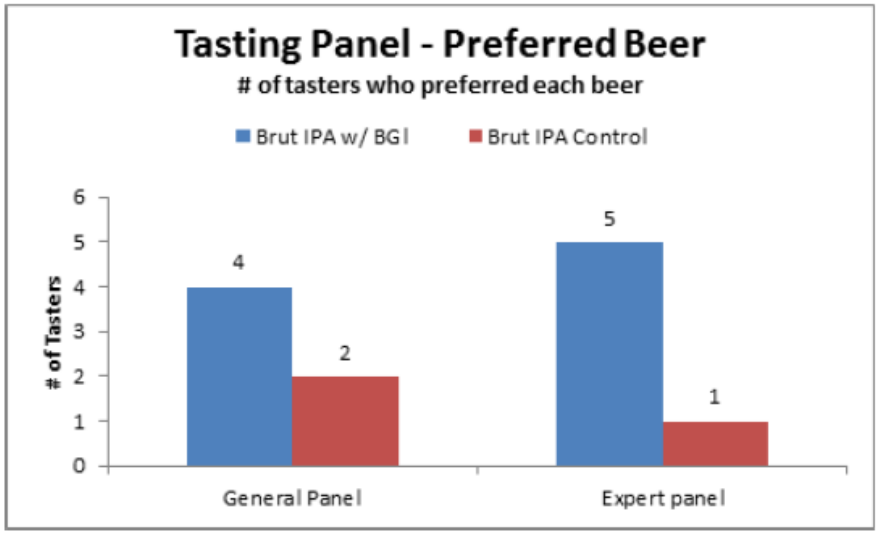
Bound: Cysteinylated and Glutathionylated thiol precursors are found in hops

Non-volatile

Possible β-lyase activity catalyzing a release of aromatic thiols[7]

Trials

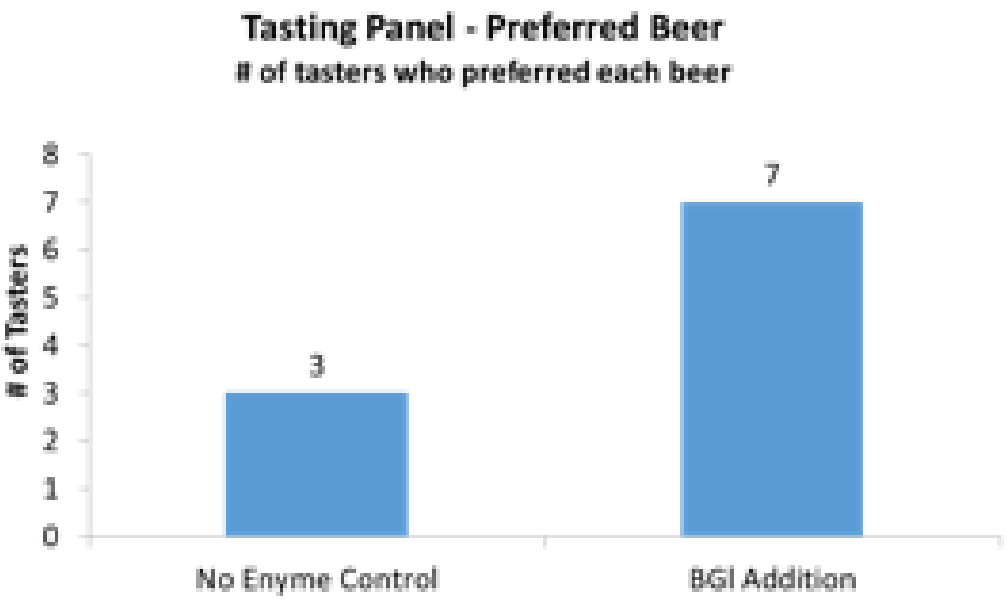
Lallemand Trials - NaparBier



NAPARBIER

- Commercial production of a Brut IPA at Naparbier
- Wort split into two separate fermentations: BGl enzyme 1 addition vs. control
- First dry hopping was at day 0, with addition of Chinook and Centennial hops; fermentation held at 18°C
- A 2nd dry hop was added at day 12 using the same hop regime with Chinook and Centennial; temperatures lowered to 16°C.

Lallemand Trials – Garage Beer Co.



- Brewed their house IPA, 100g/hL dried yeast pitch
- Control vs Addition of BGl enzyme

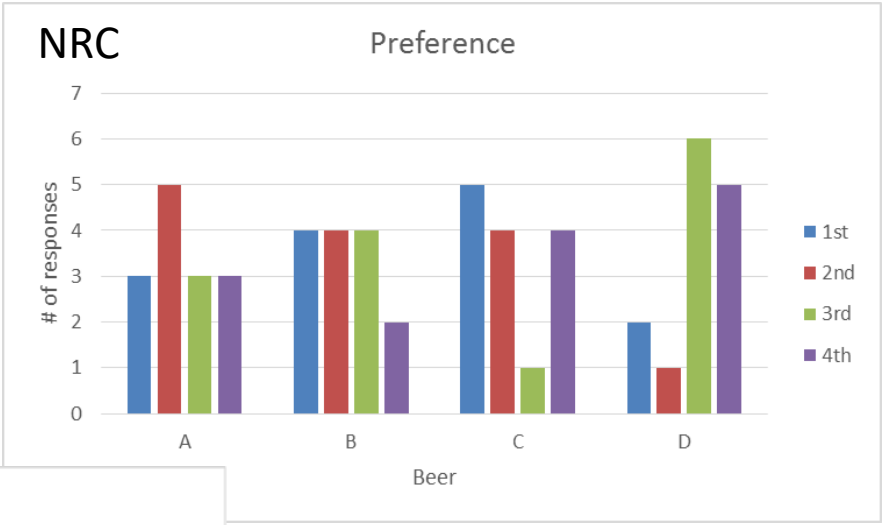
Glen Affric Beers – tasting Preference

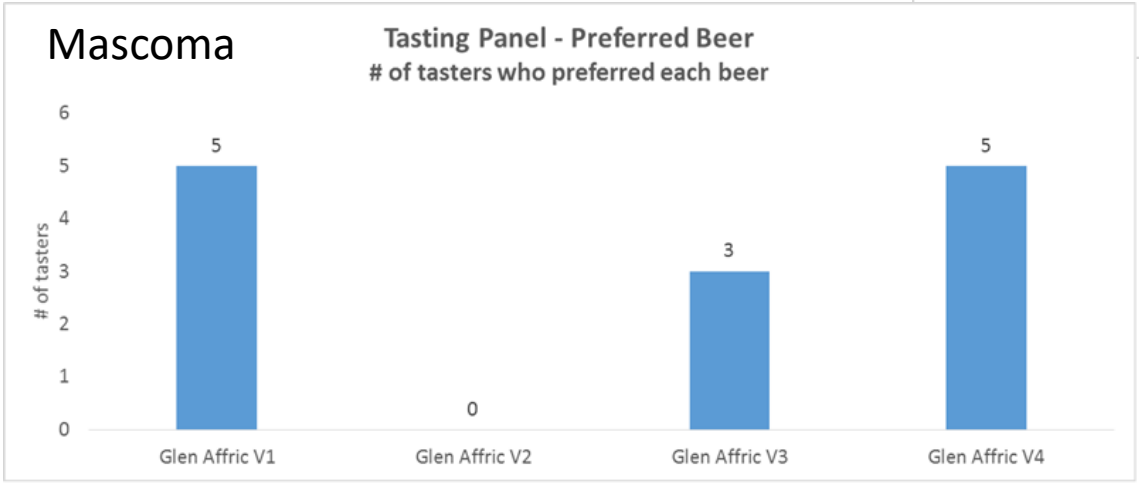
A: Enzyme added at yeast pitch

B: No enzyme added

C: Enzyme added at yeast pitch + 25% of the dry hop

D: Enzyme added with the dry hop on day 4





Summary

- Aroma of fresh/processed hops ≠ aroma of final beer
- Changes of fermentation parameters or hopping regime can effect beer flavor
- Biotransformation is complex and there is still a lot unknown
- Room for exploration, creativity and research!

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& more:

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Special thanks…….

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Thank you!!