

Hop Flavor Paradigm

What we think we know.....

Pattie Aron
June 15, 2015
ASBC
La Quinta, CA

Hop Flavor

- Spicy, floral, citrus aroma and flavor, and “mouthfeel”
- Early extensive investigations were conducted to correlate the hop oil compounds to various hoppy flavors in beer.

Chapman's early studies (1895-1929)

Howard (1956)

Howard and Stevens (1959)

Irwin (Labatt)

Fukuoka and Kowaka (Kirin)

Peacock and Deinzer (Oregon State)

Tressl (Technischen University, Berlin)

Harley and Peppard (BRF)

Lam, Foster II, and Deinzer (Oregon State)

And many others.....

Old World Hops vs. New World Hops

- European “Noble Aroma” hops
 - Hallertauer Mittelfrueh, Tettnanger, Saazer
 - Growing in US with low yields
- American-European noble type hops
 - Hallertauer Mittelfrueh: Mt. Hood, Liberty, Crystal, Ultra
 - Tettnanger: Santiam
 - Saazer: Sterling
- American characteristic hops
 - Cascade, Willamette, Fuggle, Simcoe, Amarillo, Millennium, Citra.....

Classification of American hops by Aroma



(floral/fruity/ester)

- Chinook
- Mt. Hood
- Cluster
- Super Galena
- Sterling



(citrus/orange)

- Citra
- Amarillo
- Simcoe
- Summit
- Centennial
- Apollo
- Cascade



(piney/spicy/noble hop)

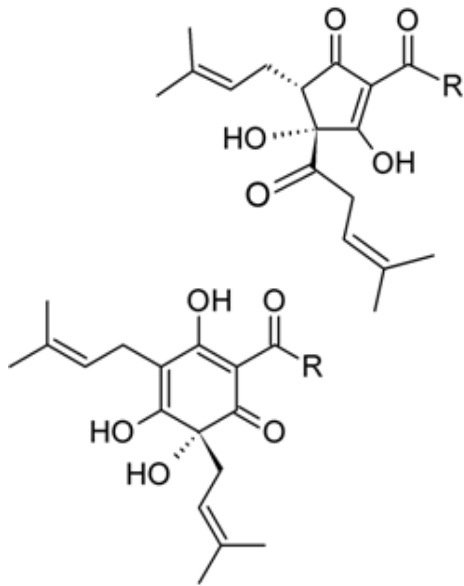
- Willamette
- Mt. Hood
- Fuggle
- Sterling



Extract

- Apollo
- Summit
- Super Galena
- Galena
- **CTZ**
- Nugget
- Warrior
- Brava

Separation of Hop Constituents

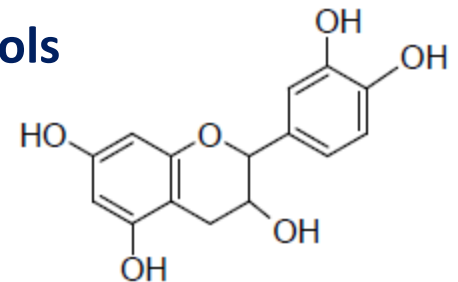


**Organic
Extractable**

Lipids
Waxes
Essential Oils
Soft Resins
Hard Resins
Some polyphenols

**Aqueous
Extractable**

Cellulose
Lignin
Proteins
Polyphenols



Separation of Hop Constituents

Chemical Composition

Total Resins 15-30%

Essential Oils 0.5-3.0%

Cellulose ~43%

Protein 15%

Polyphenols 4%

Waxes/Steroids trace -25%

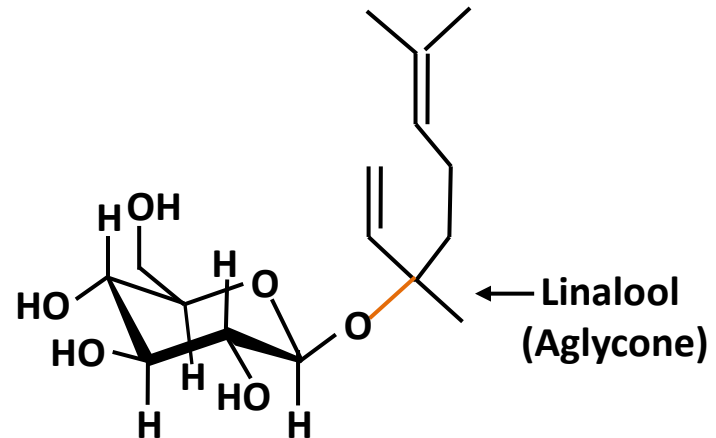
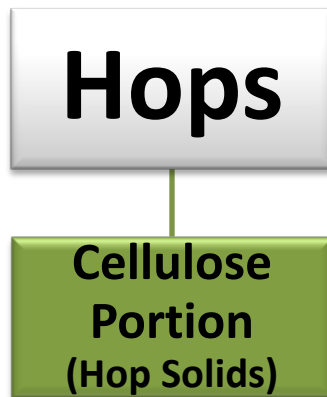
Moisture ~10%

Aqueous Fraction

Glycosides: A Secret of Hop Flavor Revealed

In 1998, Miller Brewing found that the cellulose portion (hop solids) after CO₂ extraction contains a mixture of water soluble substances composed of 92.4 mole% of glucose with a majority of 55% terminal and other linkages.

- A group of β -glycosides survive the kettle boil because they are **water soluble** and **non-volatile**.

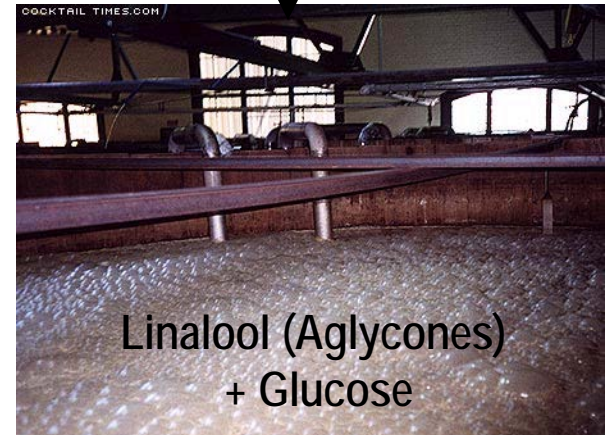
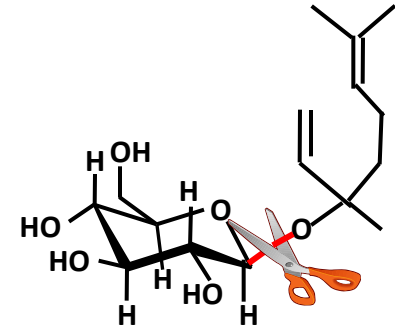


Linalyl β -Glycoside

Glycosides: A Secret of Hop Flavor Revealed

- Yeast can hydrolyze β -glycosides and further convert aglycones into hop flavor.
- The **β -glycosides** present in the hop cellulose portion contribute the true kettle hop flavor in beer.
- Further supported by
 - H. Kollmannsberger and S. Nitz, 2002
 - M. Biendl, H. Kollmannsberger and S. Nitz, 2003
 - L. Daenen, D. Saison, L. De Cooman, G. Derdelinckx, H., Verachtert, F. R. Delvaux, 2006

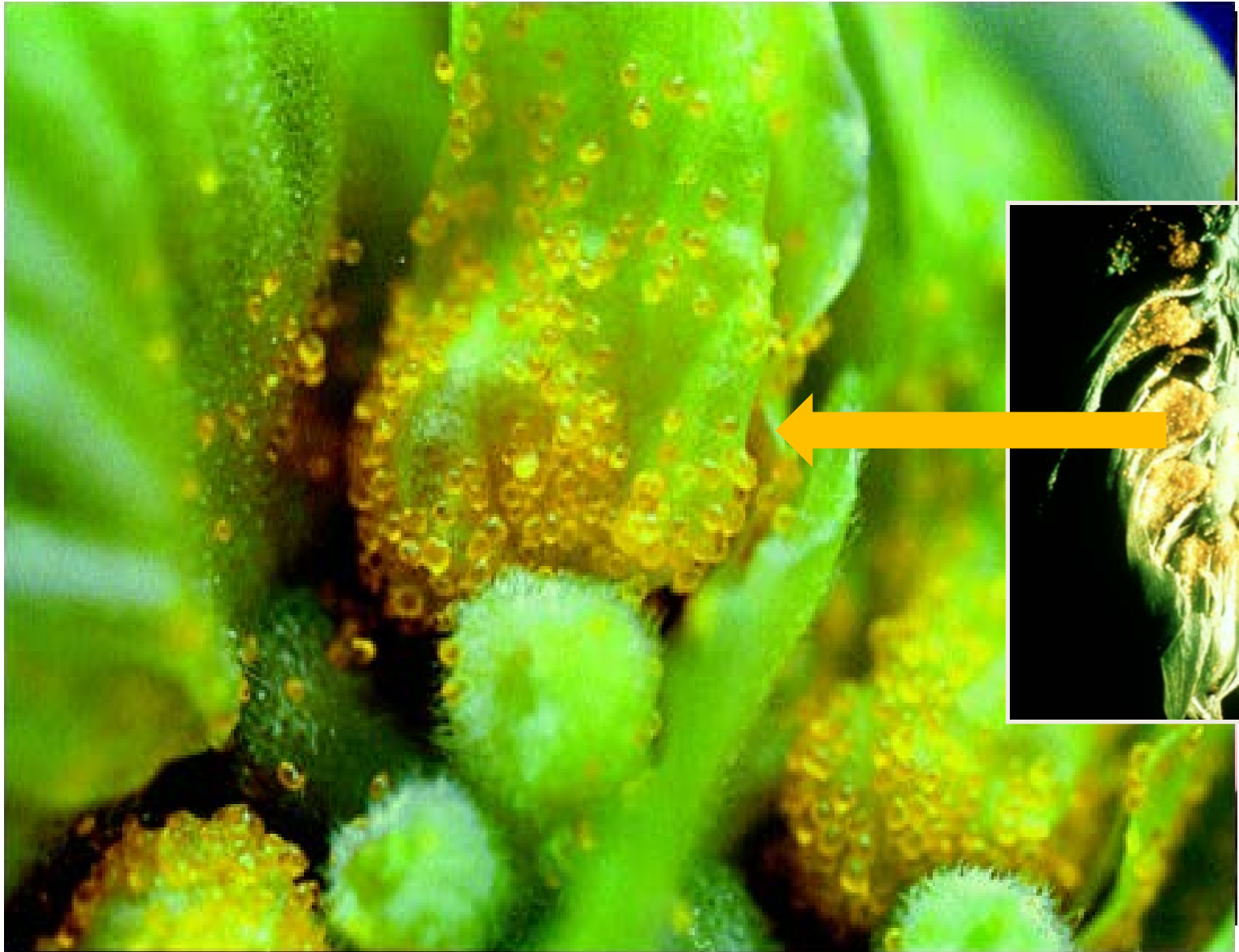
Aglycones are representative of the oxidative and sulfur containing compounds of the Hop Oil Fraction: alcohols, carbonyls and others



HOP FLAVOR
COMPOUNDS

Organic Fraction

Lupulin



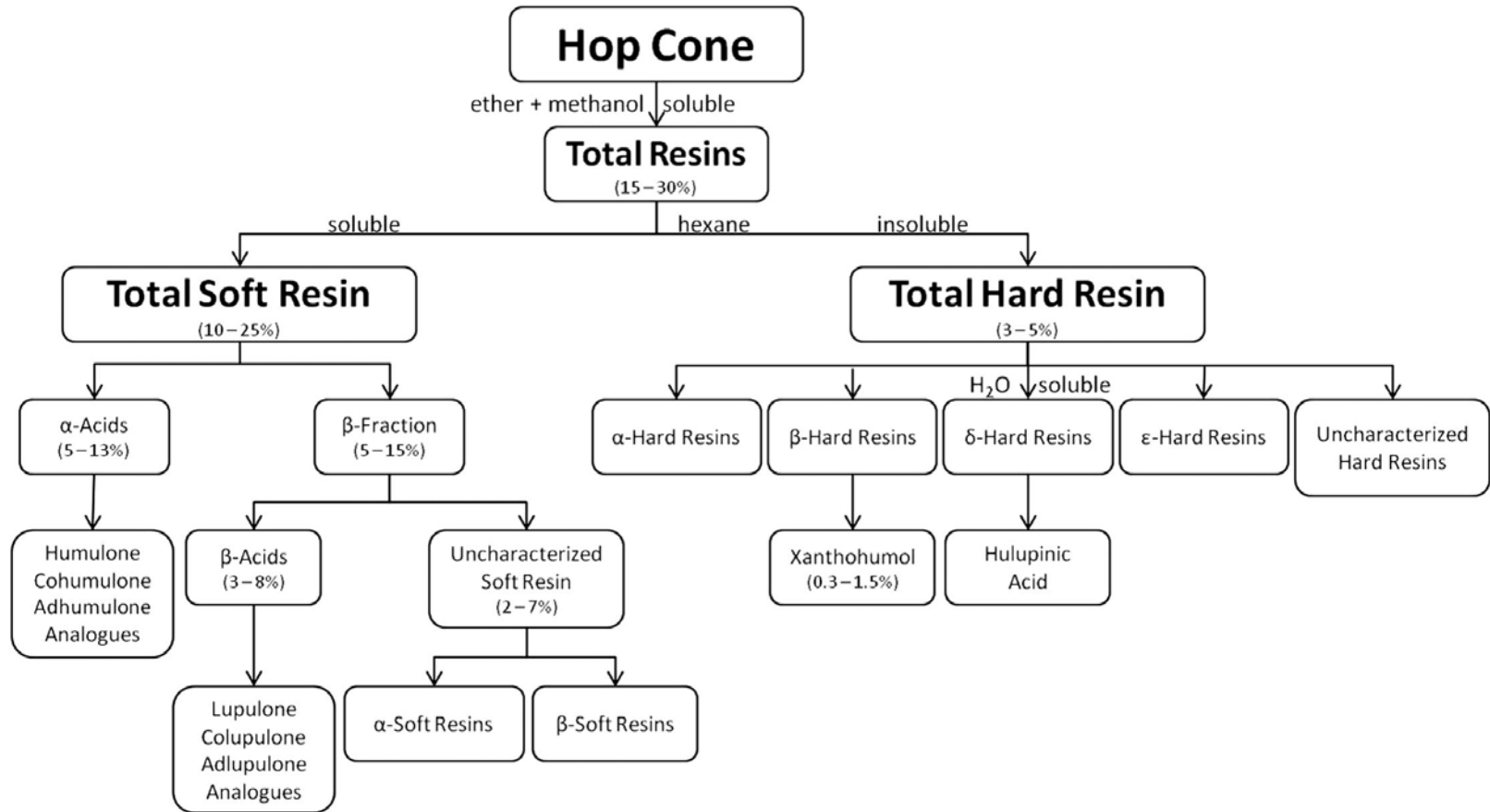
LUPULIN

RESINS

HOP OILS

RESINS

Resins



Soft Resins

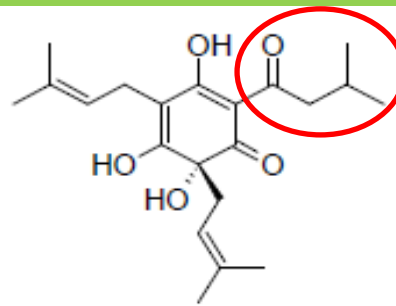
- Alpha Acids – Bitterness and degradation lead to flavor.
- Beta Acids – Degradation may lead to flavor and oxidation leads to bitterness
- Soft resins will oxidize into uncharacterizable or 'intermediate fractions'
- Intermediate fraction may have brewing value – but not exactly known.

Hard Resins

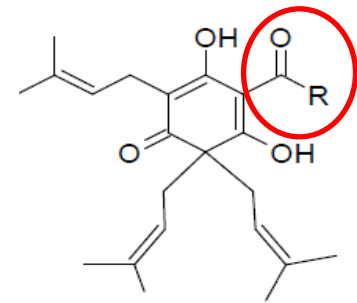
- Hard resins. Generally thought to arise from oxidation of soft resins – however not well defined.
- Believed that majority of hard resins are beta derived.
- Found in cones during the early stages of development... due to auto-oxidation during kilning and storage?
- As hops age soft resins decline and hard resins increase

HOP ACIDS and ESTERS

- Bitterness and Flavor
- Aged hops;
 - Organic acids and esters of hop acid side chains lend aromatic characters, sweaty, citrus, fruity.
 - Sunstruck Aroma



Humulone



Beta Acids

α -Acids	β -Acids	R-group
humulone	lupulone	COCH ₂ CH(CH ₃) ₂ isovaleric
cohumulone	colupulone	COCH(CH ₃) ₂ isobutyric
adhumulone	adlupulone	COCH(CH ₃)CH ₂ CH ₃ 2-methylbutyric
prehumulone	prelupulone	COCH ₂ CH ₂ CH(CH ₃) ₂ Isohexanoic
posthumulone	postlupulone	COCH ₂ CH ₃ Isopropanic

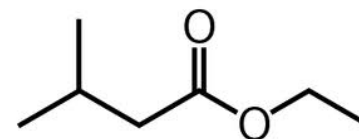


GC-O evaluation of Hop Acid Side Chain Degradation

- Organic acids, aldehydes and esters are degradation products of the hop acid side chain (R-group) from beta and alpha acids.
- Once acid side chains are introduced into ethanol these esterify and become esters:

Ethyl isobutyrate – Fruity/Cherry/Vomit

Ethyl isovalerate – Pungeant Black Cherry.



<u>Elution Time (min)</u>	<u>Pattie's notes</u>	<u>Compound name(s)</u>
4.15	Waxy, Solvent, apple peels	Butanal, 3-methyl, Isovaleraldehyde
5.86	Fruity Cherry, Vomit	*Ethyl Isobutyrate
8.29	Apple Pie, Baked Apple	Ethyl 2-methyl butyrate, Butyric Acid, 2-methyl-ethyl ester
8.54	<u>Pungeant Black Cherry/Tropical Fruit</u>	*Ethyl Isovalerate
11.47-11.70 (11.715 min)	Blueberry/Fruity	Ethyl Isohexanoate
17.6	Apple Skins, Waxy, Pungeant	Isobutyric Acid
20.65	Cheesy, Dirty Socks	**n-Valeric Acid, Isovaleric Acid

HOP OILS

HOP OILS

1. Hydrocarbons:

1. Monoterpenes – Myrcene
2. Sesquiterpenes – β -caryophyllene, farnescene, humulene
3. Aliphatic hydrocarbons – pentane, octane

2. Oxygenated Compounds:

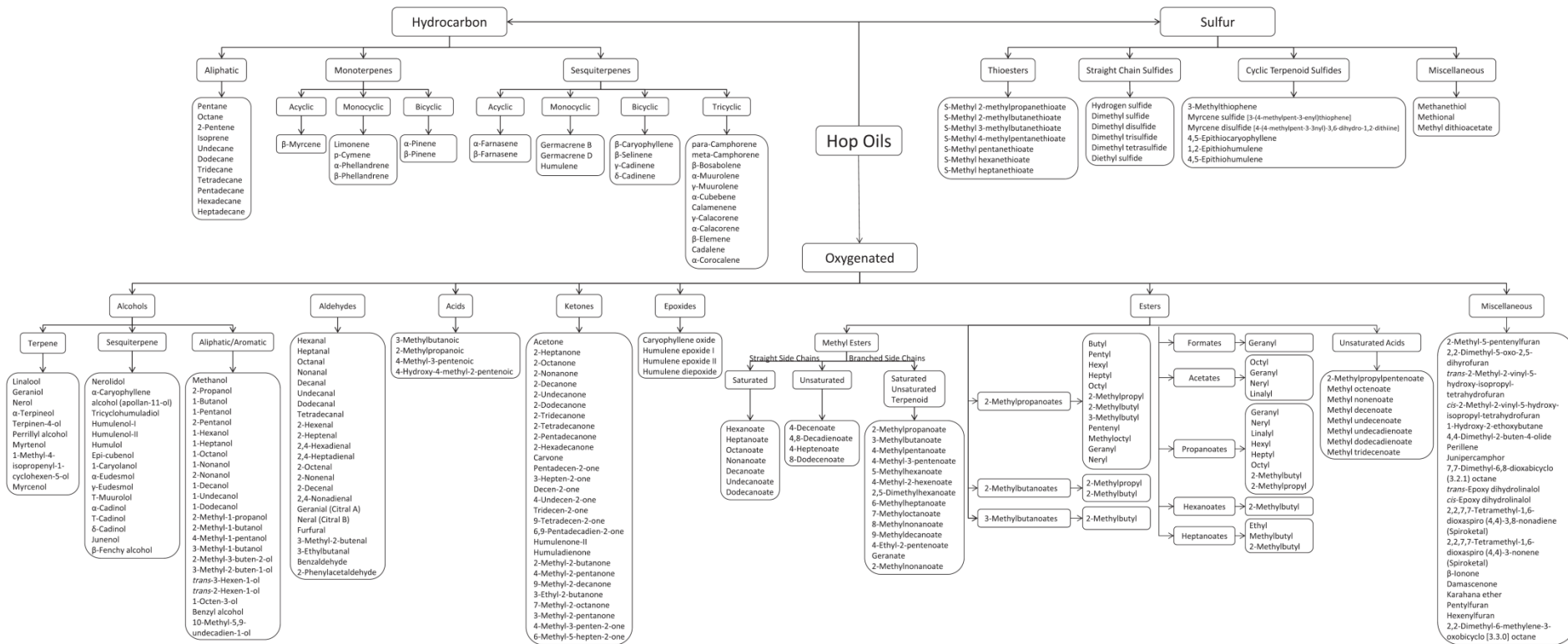
1. Terpene alcohols – linalool, geraniol, nerol, α -terpinol
2. Sesquiterpene alcohols – humulenols,
3. Others – aldehydes, acids, ketones, esters, epoxides:

Examples: hexanal, nonanal, 3-methylbutanoic acid, geranyl acetate, caryophyllene oxide,

3. Sulfur containing compounds:

1. Thioesters – S-Methyl 2-methylpropanethioate
2. Sulfides- H₂S, DMS, DMDS
3. Cyclic terpenoid sulfides and others - methanethiol

TOTAL HOP OILS = 0.5-3.50% w/w
 ~ 1000 Compounds
 70% Hydrocarbons
 30% Oxygenated Compounds



Kettle Hop Aroma

No single hop oil component has been shown unequivocally to be present in kettle-hopped beer.

- Sandra and Verzele
- Peacock and Deinzer
- Rigby
- Miller Brewing

.....and the chemistry of hop flavor is still not properly understood.



Fractionation of hop oils
Haley, Peppard, Westwood
et al. of BRI in 1985

Spicy fraction
Floral fraction
Citrus fraction
Noble Hops
Late Hops
Dry Hops

Commercial post-fermentation products mimic late
and dry hopping.....

However, these fractions may not produce
desired early kettle hop flavor.

Floral/Citrus Aroma

Active Monoterpenes and Terpene Alcohols

Myrcene

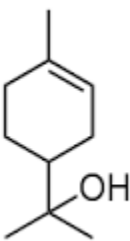
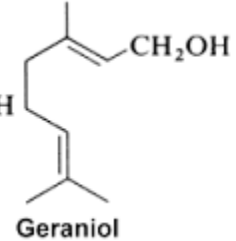
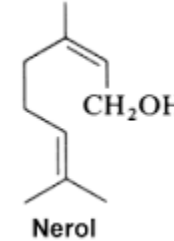
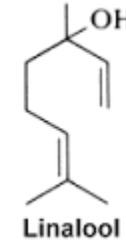
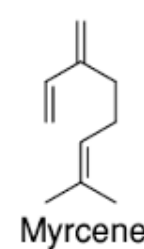
Linalool – R and S

Geraniol - varietal specific

β -Citronellol

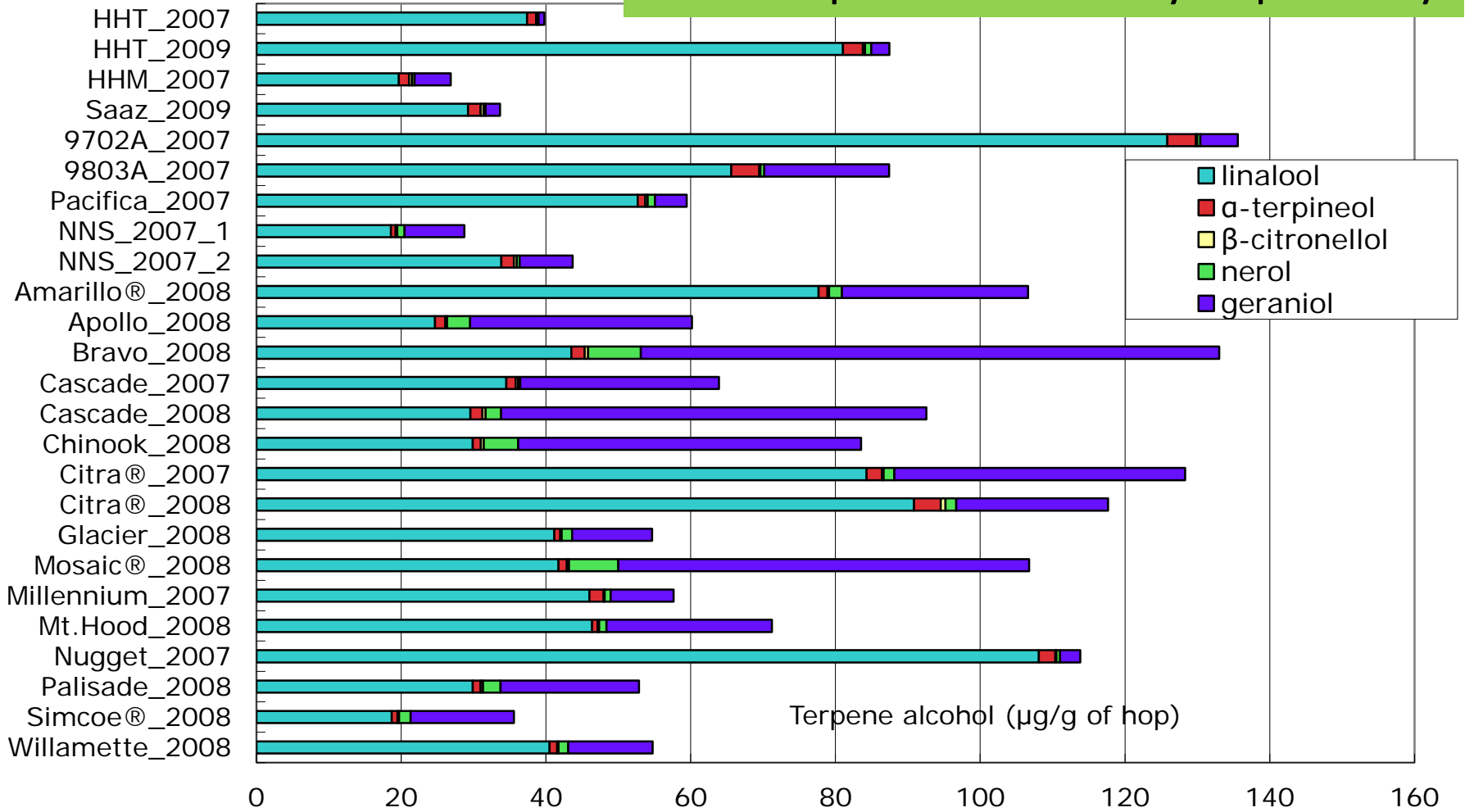
Nerol

α -Terpineol



- Correlated with cedar/orange, piney, lavender, lilac, lemongrass, rose, lime/citrus.
- Threshold at ppb levels
- Varietal impact: Geraniol rich hops could be impactful due to biotransformation and synergies.

Monoterpenol content by hop variety



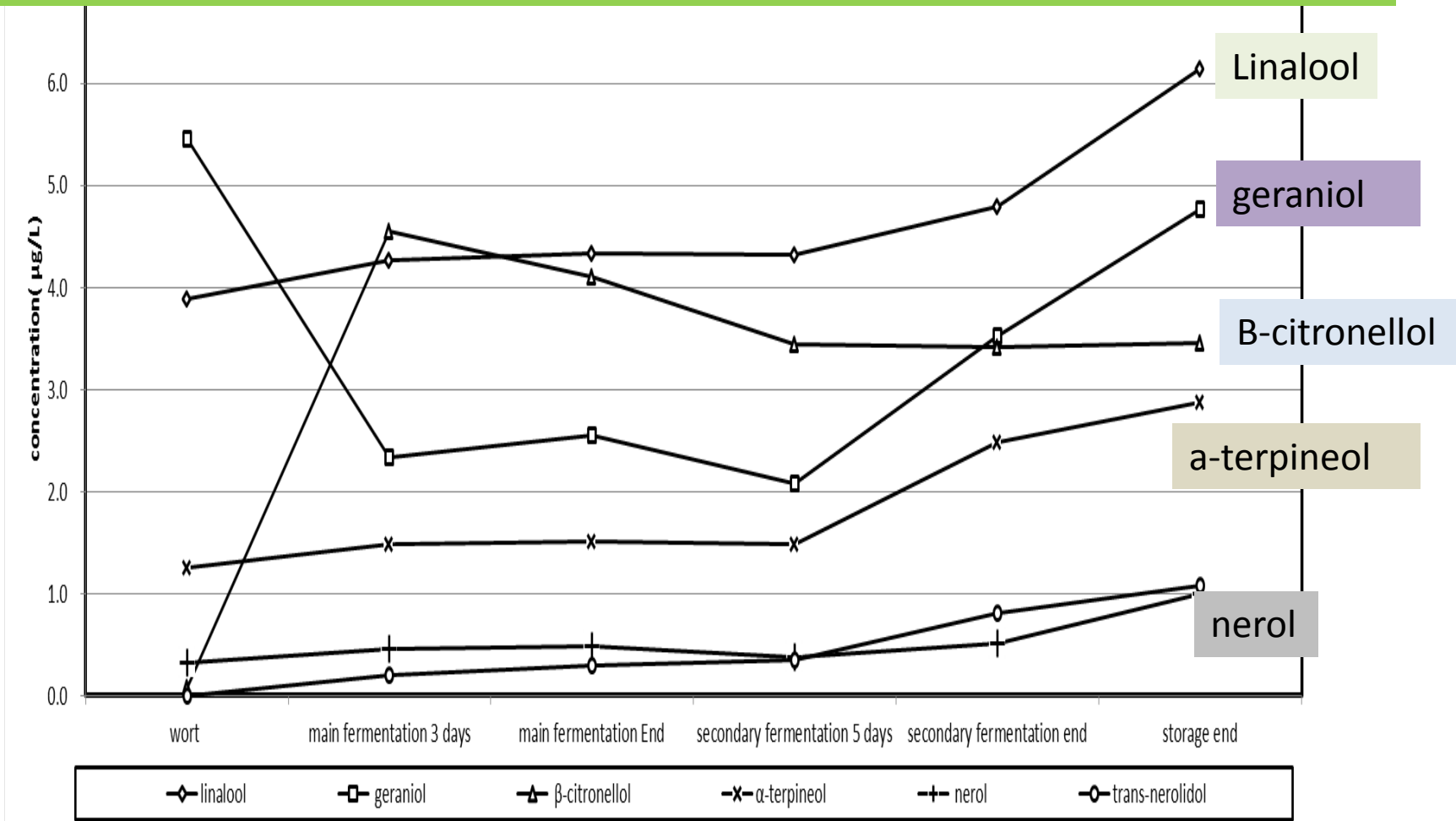
German (HHT, Hallertau tradition, HHM, Hallertau Magnum, 9702A; 9803A)

New Zealand (NNS New Zealand)

Czech (Saaz)

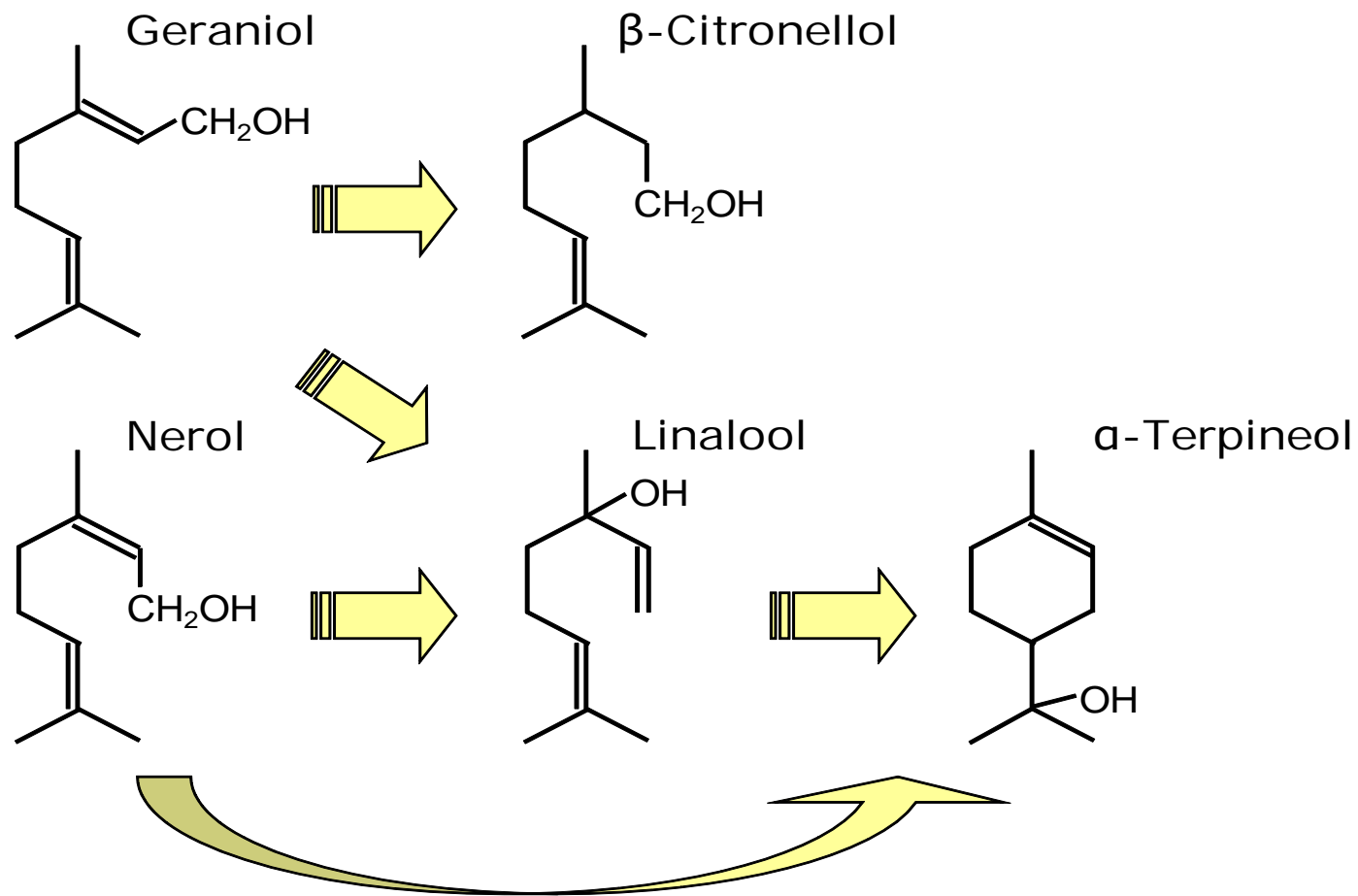
US (Amarillo, Appollo, Bravo, Cascade, Chinook, Citra, Mosaic, Millennium, Mt. hood, Nugget, Palisade, Simcoe, and Willamette)

Fate of Terpenols during fermentation



Evolutions of terpenols ($\mu\text{g/L}$) during fermentation process of the Chinese lager brewing.
 (\diamond) linalool; (\square) geraniol; (Δ) β -citronellol; (x) α -terpineol; (+) nerol; (0) *trans*-nerolidol

Biotransformation of Monoterpene alcohols

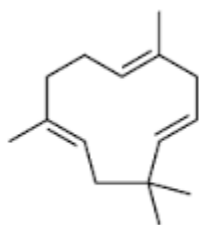


Takoi, et al 2010; Praet et al.; King et al 2003

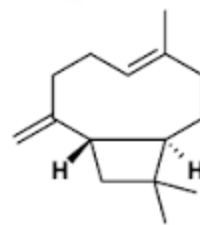
Spicy and Woody – Noble Aroma

Sesquiterpenes and oxygenated Sesquiterpenes

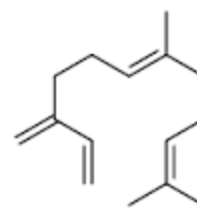
- Humulene/humulene epoxide
- Caryophyllene/Caryophyllene Oxide
- Farnescene
- Humulenol II
- Damascenone -floral



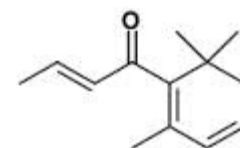
Humulene



Caryophyllene



Farnesene



β -Damascenone

Fate of aroma compounds during boiling:

- Myrcene
- Linalool
- Geraniol
- Humulene
- Caryophyllene
- Humulene epoxide
- Eudesmol
- Farnescene
- Humulenol II
- Damascenone

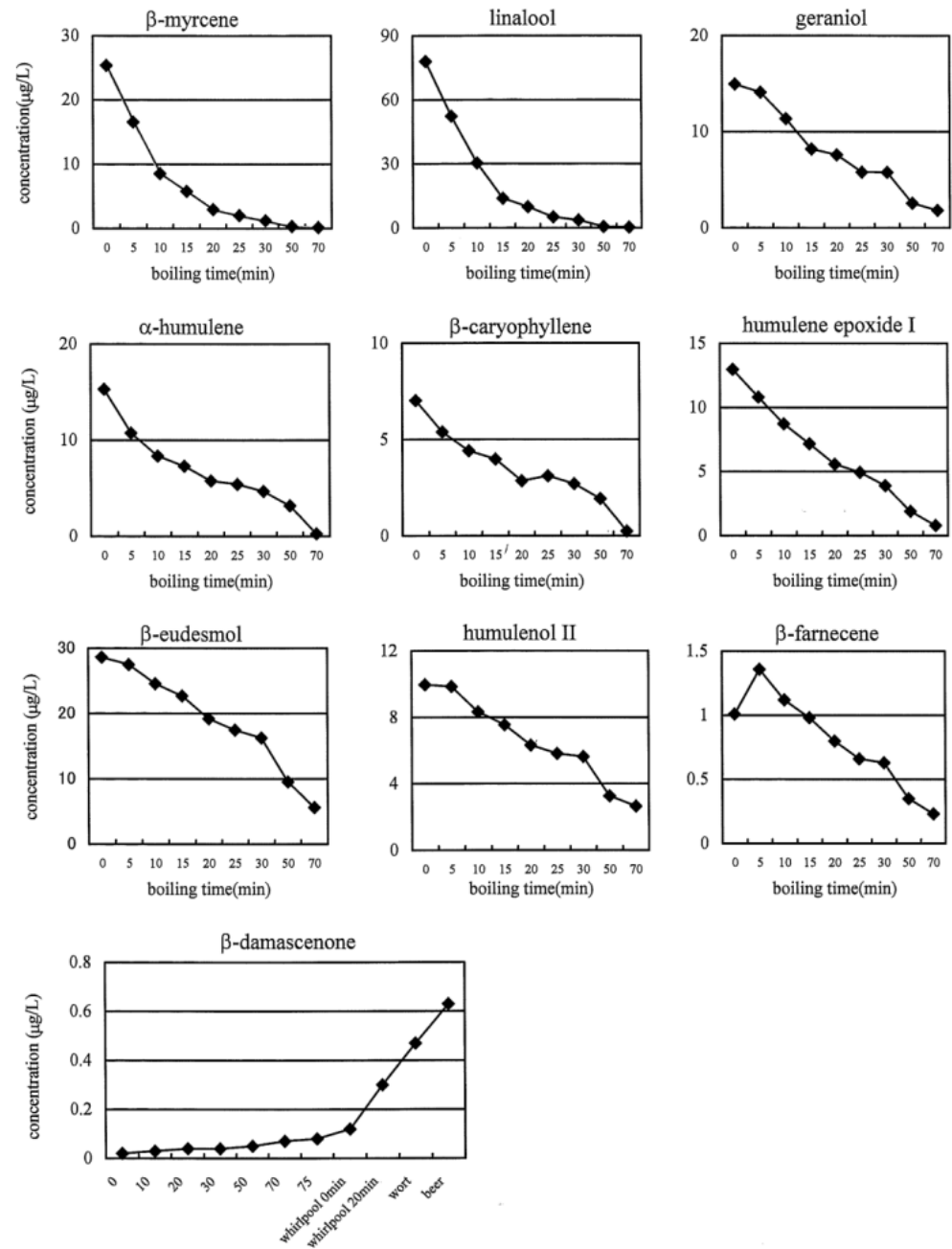


Figure 1-4. Behavior of hop-derived terpenoids during wort boiling.

SULFUR AROMA

Sulfur Derived Aromas

- ❖ Free thiol or sulfanyl compounds
- ❖ Hydrolysis/reduction/esterification of cysteine and thiol conjugates
- ❖ Citrus/lemon (grapefruit, orange, lemon, lychee, mango, Sauvignon....)
- ❖ **Thresholds extremely low: ng/L or ppt**



Introducing
CITRA™
brand HBC 394



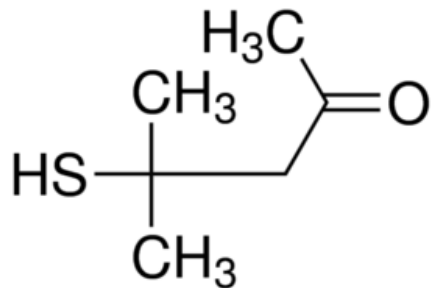
Nizet, Gros, et al.
Kishimoto, et al.
Lermusieau, et al.

Sulfur Compounds and Citrus Flavor

Kishmoto detected 7 hop-derived odorant thiols:

- **4-MMP**, 4-methyl-4-mercapto-pentan-2-one
- **3-MH**; 3-mercaptohexan-1-ol
- 3-MHA; 3-mercaptohexyl acetate (**malt and hops**)

4-MMP not detected in European hops due to either genetic or environmental effect.





4-MMP in US hops:

- SIMCOE
- SUMMIT
- APOLLO
- CASCADE

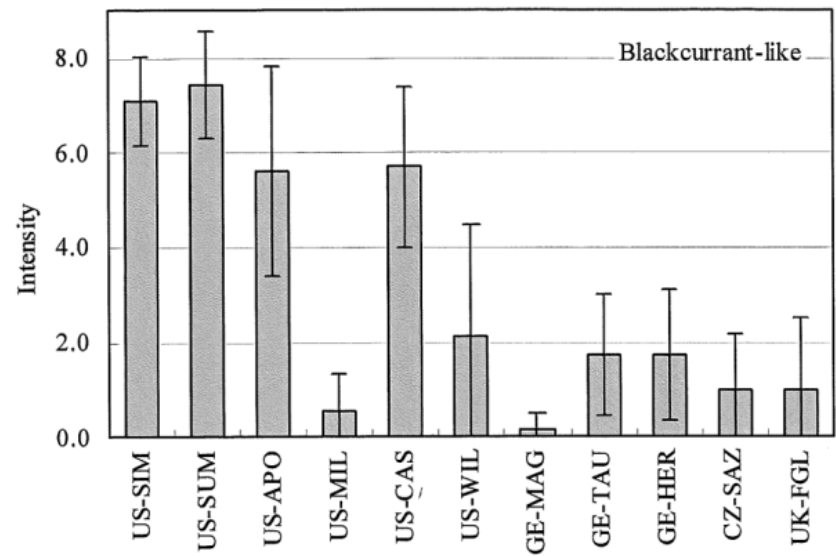


Figure 3-4a. Intensities of the blackcurrant-like aroma evaluated in sensory analysis.

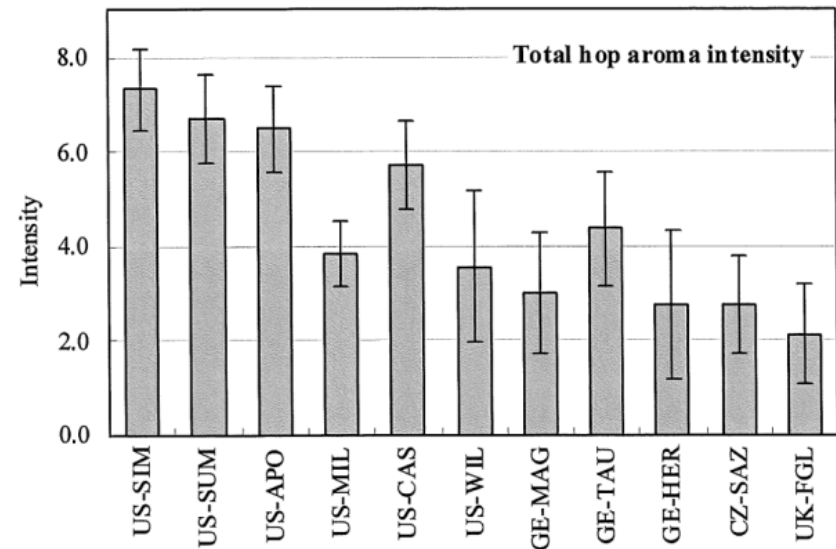


Figure 3-4b. Intensities of the total hop aroma evaluated in sensory analysis.

SUMMARY - HOP AROMA

- Chemical background of hoppy aroma still not well understood.
- Impact of hop glycosides not fully elucidated
- Soft Resins: Cheesy, Butyric, Caproic, Sweat Socks, Skunk
- Hop Essential Oils: Kettle Hop, Late Hop
Spicy, Floral, Citrus, Woody, Herbal, Dank
- Sulfur chemistry most recent - but still many questions and analytical measurement challenges.

Thank YOU!



THE
SCIENCE
OF BEER

