Hops and Beer Flavor

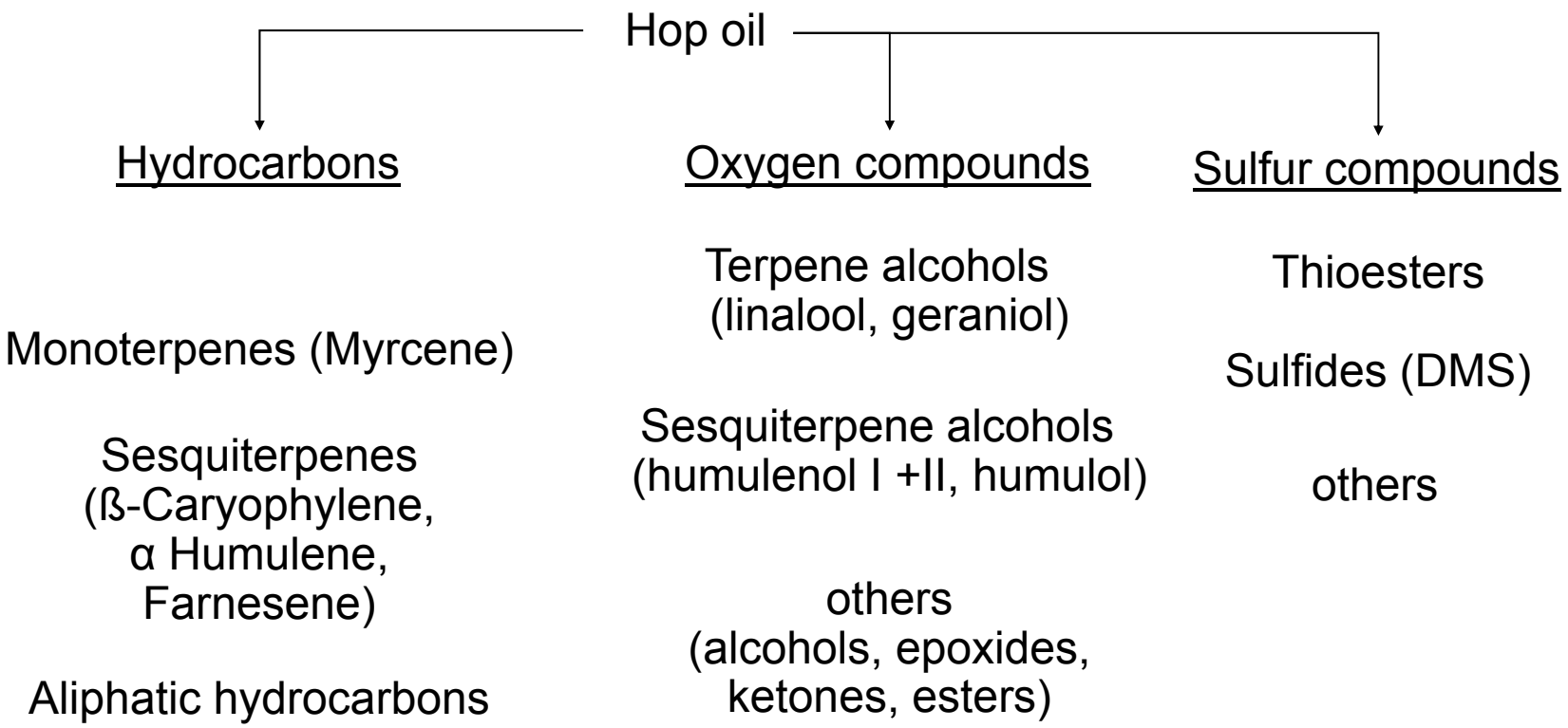
MBAA Brewing Fundamentals
Hops II

June 6, 2014

Tim Kostelecky
John I. Haas, Inc.
Yakima Washington

- Hop oil composition
- Hop aroma in beer
- Bitterness in beer

Hop Essential Oils Classification



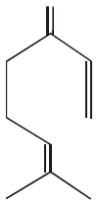
Sharpe and Laws

Substance Groupings in Hop Essential Oil

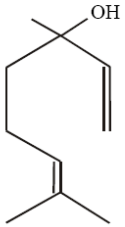
Monoterpenes	~ 40 %
Sesquiterpenes	~ 40 %
Carboxylic acid esters	~ 15 %
Carboxylic acids	~ 1 %
Monoterpenoxides	~ 1 %
Sesquiterpenoxides	~ 1 %
Aldehydes, Ketones	~ 1 %
Aliphatic hydrocarbons	< 1 %
Sulfur containing compounds	< 0,1 %
Glycosidically bound aroma compounds	?

Examples for Monoterpenes and Sesquiterpines

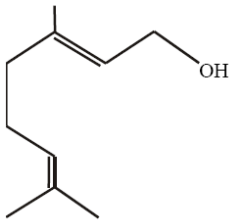
Monoterpenes



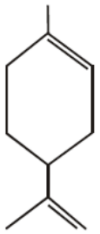
Myrcene



Linalool



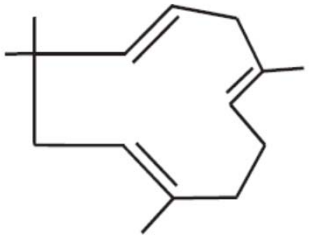
Geraniol



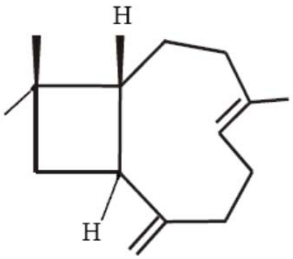
Limonene

beta-Pinene

Sesquiterpenes



Humulene



beta-caryophyllene

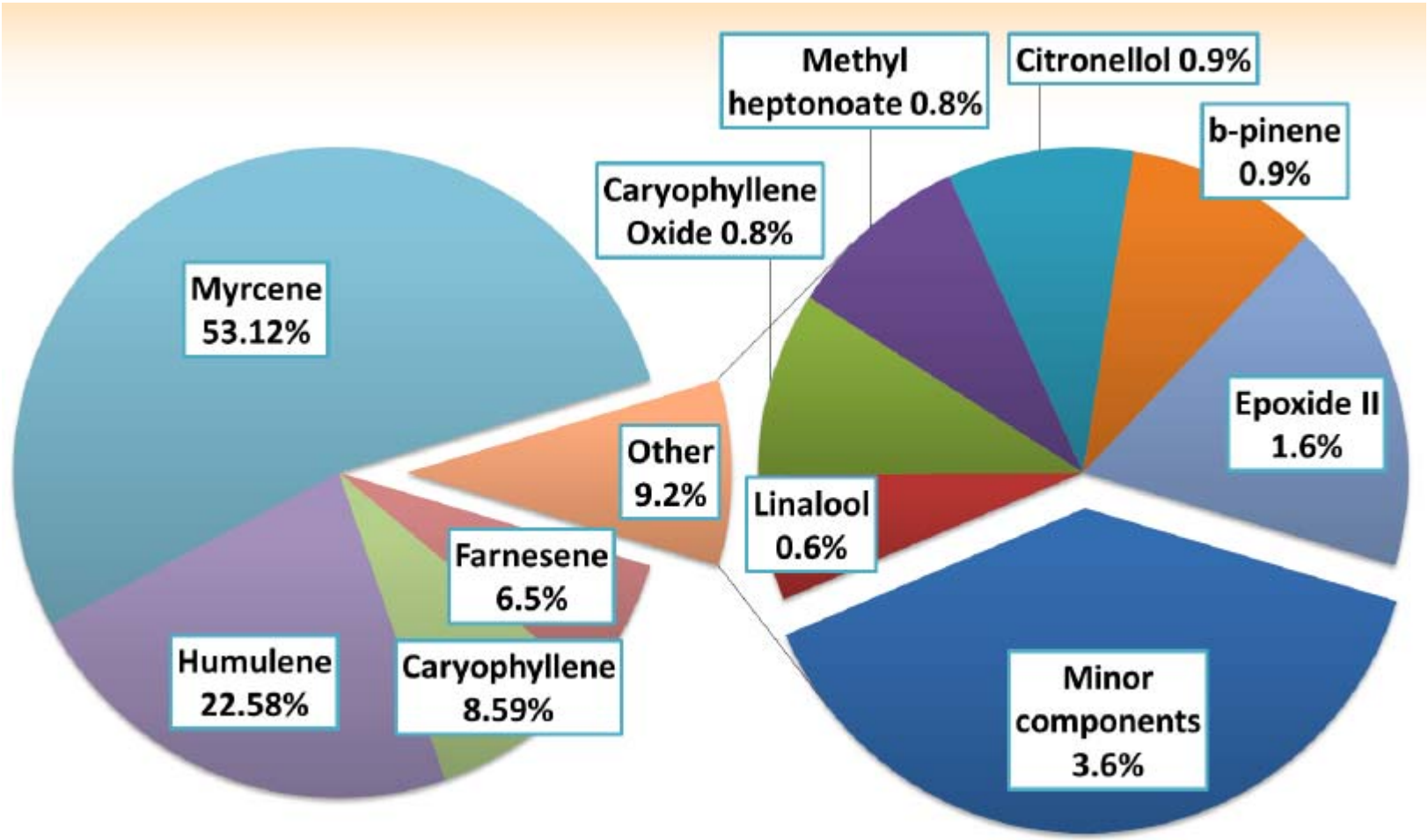
Humulene and beta-Caryophyllene
together can represent more the 50% of the hop oil

Hop Aroma Research

BARTH-HAAS GROUP

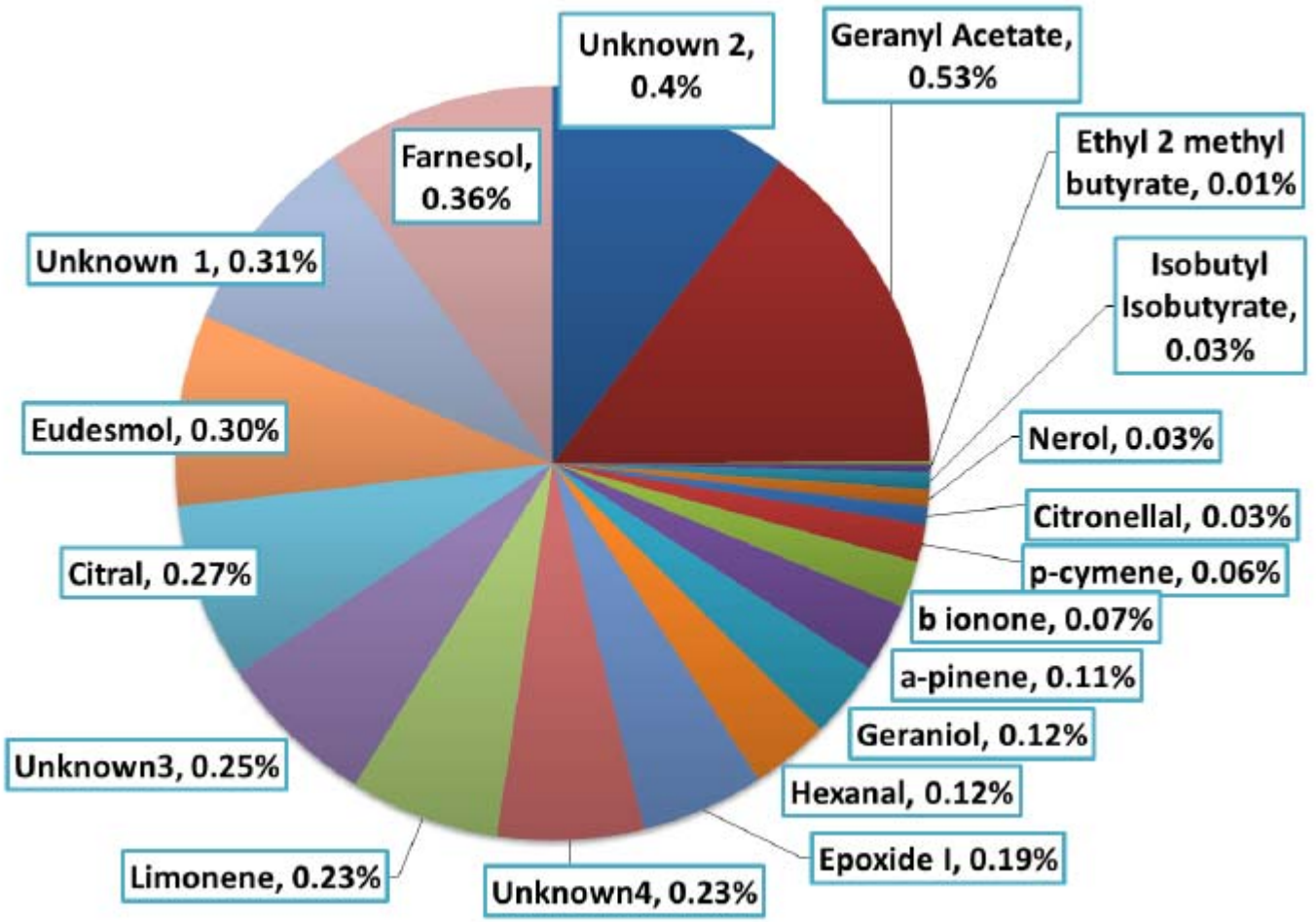
- For 150 years, researchers have tried to characterize hop aroma in beer and determine the responsible compounds.
- So far over 400 hop essential oil components have been identified and can be quantified and their sensory attributes can be defined
- Unlike hop bitterness and iso-alpha acids, no single aroma compound can serve as a marker to quantitate hop aroma, e.g. linalool.
- The complex interaction of hop and beer aroma compounds determines the aroma and flavor and is typically unique for every beer.

Example of Hop Aroma Compounds in Hops



Shellhammer MBAA 2011

Minor Hop Components



Traditional Hop Profiles and Aroma

Table 1. Comparison of analytical properties of hop varieties Citra, Hallertauer Tradition, and Nelson Sauvin

Variable (unit)	Citra	Hallertauer Tradition[a]	Nelson Sauvin[b]
α-Acids (% of cone wt)	11–13	4.0–7.0	12–13
β-Acids (% of cone wt)	3.5–4.5	3.0–6.0	6–8
Cohumulone (% of α-acids)	22–24	24–30	24
Total oil (mL/100 g cones)	2.2–2.8	0.5–1.0	1.0–1.2
Myrcene (% of total oil)	60–65	17–32	21–23
Humulene (% of total oil)	11–13	35–50	35–37
Caryophyllene (% of total oil)	6–8	10–15	10–12
Linalool (% of total oil)	1–2	0.7–1.2	0.8
Farnesene (% of total oil)	<1	<1	0.4
Storage stability (relative retention of α-acids)	Fair	Good	Good

[a] Source: Deutscher-Hopfen (4).
[b] Source: New Zealand Hops Limited (18).

The normal hop characterization does not tell you much about the aroma characteristics!

Traditional Hop Variety Descriptions

Citra™

U.S.
Aroma Hop

Citra™ is a new special aroma hop variety released by the Hop Breeding Company, (a joint venture between John I. Haas, Inc. and Select Botanicals Group, LLC in the Yakima Valley) having unique and highly favored flavor characteristics. As the name suggests, its flavor descriptors include citrus including lime and grapefruit as well as various tropical fruity characters.

Pedigree	50% Hallertau; 25% U.S. Tettnanger
Aroma	Strong citrus, fruity
Alpha Acids*	11.0 - 13.0 %
Beta Acids	3.5 - 4.5 %
Cohumulone	22 - 24 % of alpha acids
Total Oil	2.2 - 2.8 ml/100g
Myrcene	60 - 65 % of total oil
Humulene	11 - 13 % of total oil
Caryophyllene	6 - 8 % of total oil
Farnesene	< 1 % of total oil
Storage Stability	Fair

Cascade

U.S.
Aroma Hop

Cascade was developed in the U.S.D.A. breeding program in Oregon and released as a U.S. aroma variety in 1972. It is characterized by a dark green elongated cone with an aroma that is of medium strength with very distinct floral notes and is often described as having grapefruit-like character. Cascade is the definitive hop for American craft brews.

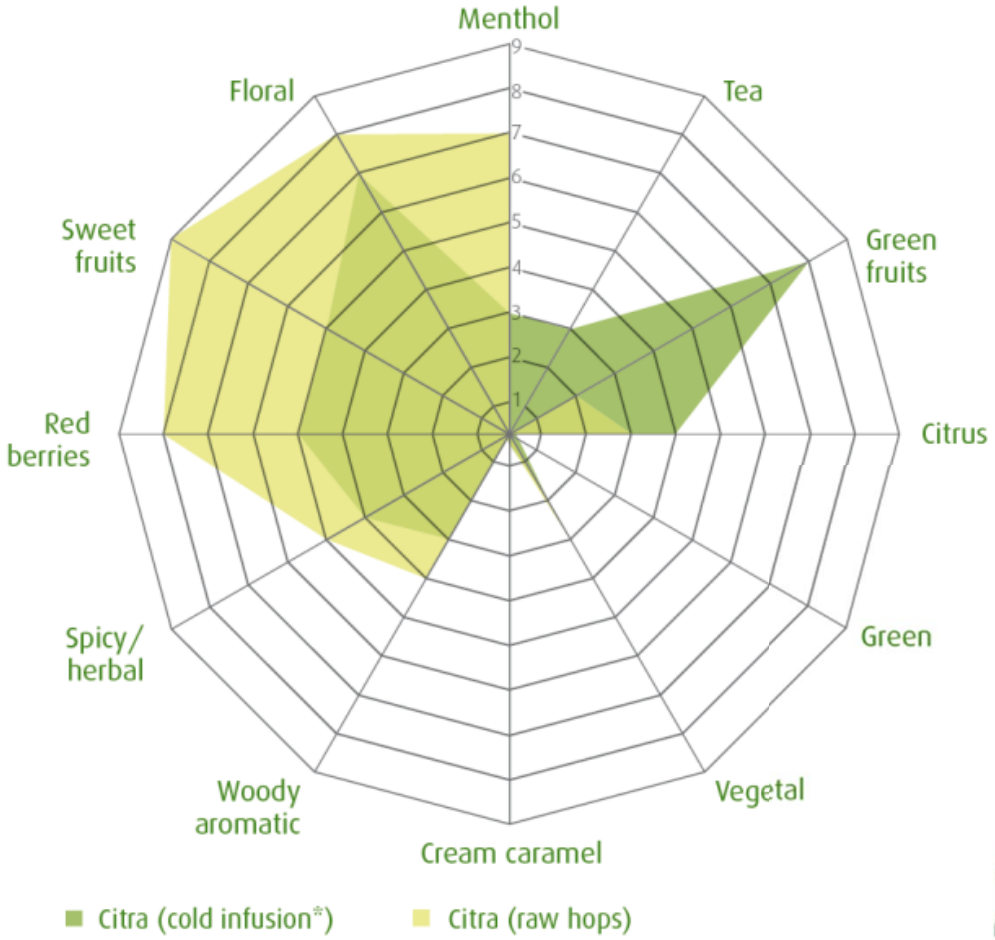
Pedigree	Cross of English Fuggle with male originating from Russian variety Serebrianka
Aroma	Unique floral, citrus
Alpha Acids*	4.5 - 7.0 %
Beta Acids	4.8 - 7.0 %
Cohumulone	33 - 40 % of alpha acids
Total Oil	0.7 - 1.4 ml/100g
Myrcene	45 - 60 % of total oil
Humulene	8 - 13 % of total oil
Caryophyllene	3 - 6 % of total oil
Farnesene	3 - 7 % of total oil
Storage Stability	Very poor

Expanded Categorization of Hop Aroma

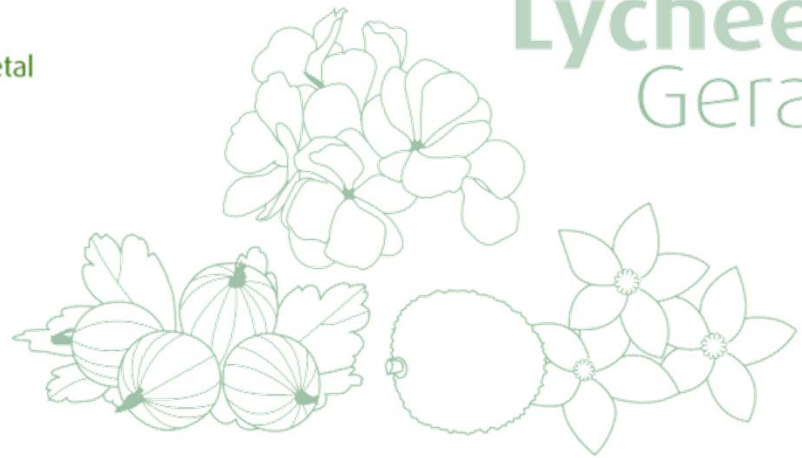
- As described in Barth Hop Aroma Compendium:

Descriptor	This includes the following aromas:
Menthol	Mint, melissa, sage, metallic, camphor
Tea	Green tea, camomile tea, black tea
Green fruits	Pear, quince, apple, gooseberry, wine yeast, ethereal
Citrus	Grapefruit, orange, lime, lemon, bergamot, lemon grass, ginger
Green	Green-grassy, tomato leaves, green peppers
Vegetal	Celeriac, leek, onion, artichoke, garlic, wild garlic
Cream caramel	Butter, chocolate, yoghurt, gingerbread, honey, cream, caramel, toffee, coffee
Woody aromatic	Tobacco, cognac, barrique, hay, leather, tonka, woodruff, incense, myrrh, resin
Spicy/herbal	Lovage, pepper, chilli, curry, juniper, marjoram, tarragon, dill, lavender, aniseed, liquorice, fennel
Red berries	Cassis, blueberries, raspberries, blackberries, strawberries
Sweet fruits	Banana, watermelon, honeydew melon, peach, apricot, passion fruit, lychee, dried fruit, plum, pineapple, white jelly bears
Floral	Elderflower, camomile blossom, lily of the valley, jasmine, apple blossom, rose, geranium

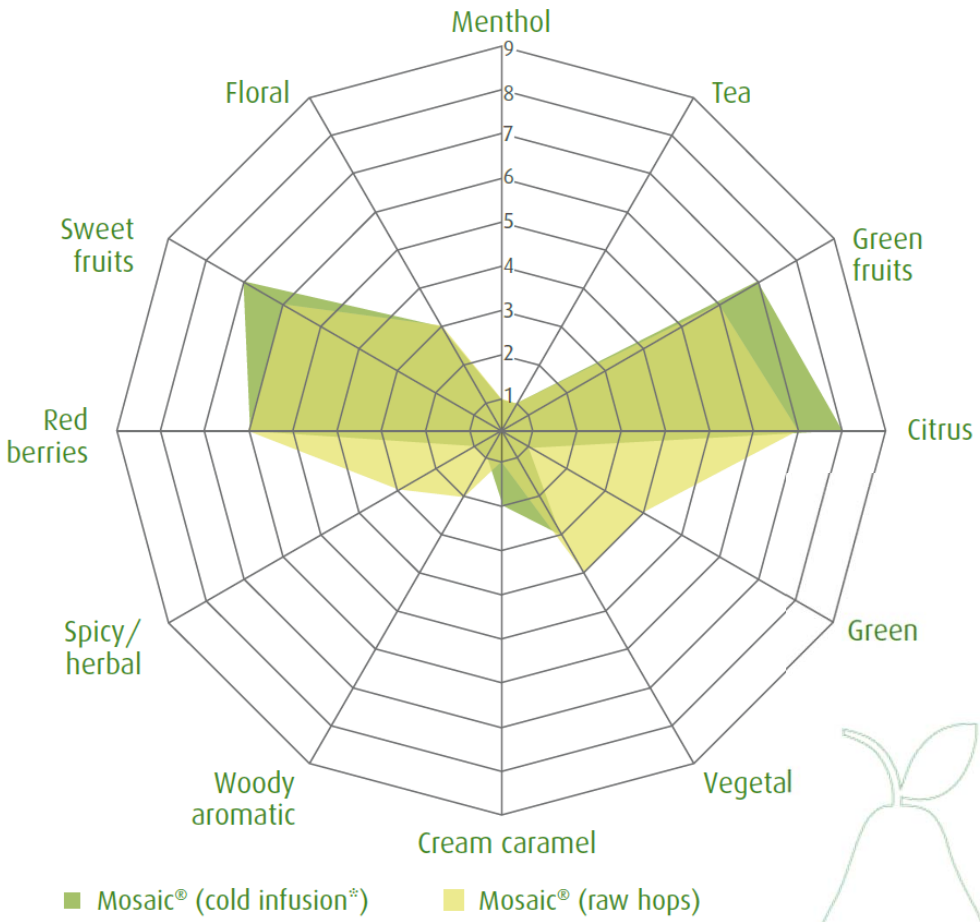
Hop Aroma Compendium Vol. I – CITRA®



Spicy
Jasmine
Gooseberry
Lychee
Geranium



Hop Aroma Compendium Vol. II – Mosaic®



Pear
Gooseberry
Mandarin
Lime
Peach

- Hop oil composition
- Hop aroma in beer
- Bitterness in beer

Factors Influencing Hop Aroma in Beer

variety
time of harvest
crop year, kilning

→

Point of addition
solubility/
evaporation

→

adsorption/
transformation/
interactions

→

dry hopping
(with/out yeast)
duration, temp, agitation etc,

aroma in hops

to hoppy aroma in beer

harvest → brewhouse → fermentation → Lagering

plus…..filtration….bottling…storage

What Happens During Boil?

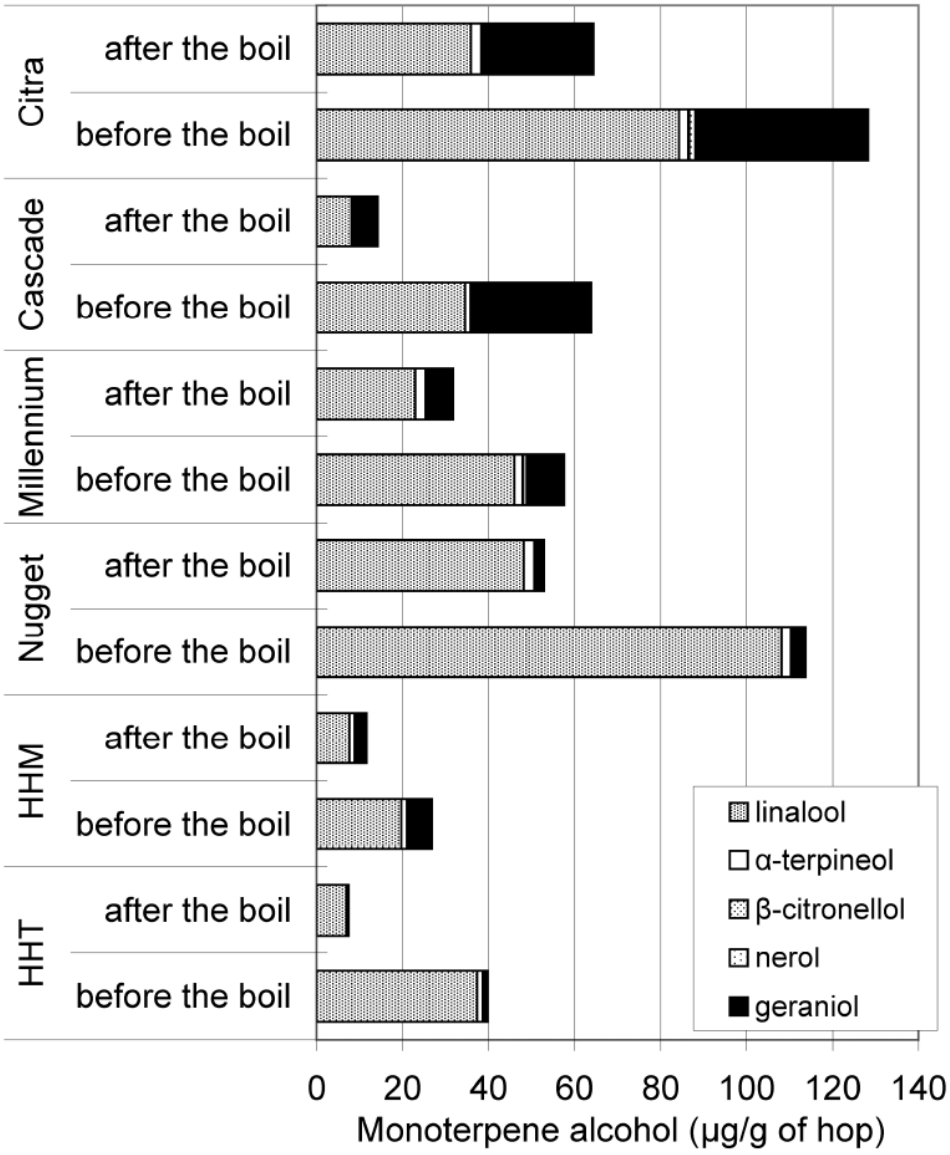


Fig. 2. Composition of monoterpene alcohols (µg/g of hop) before and after the boil (data of the HHT hop was previously reported in reference 27).

Takoi, 2008

When is a Hop Compound of Sensory Importance?

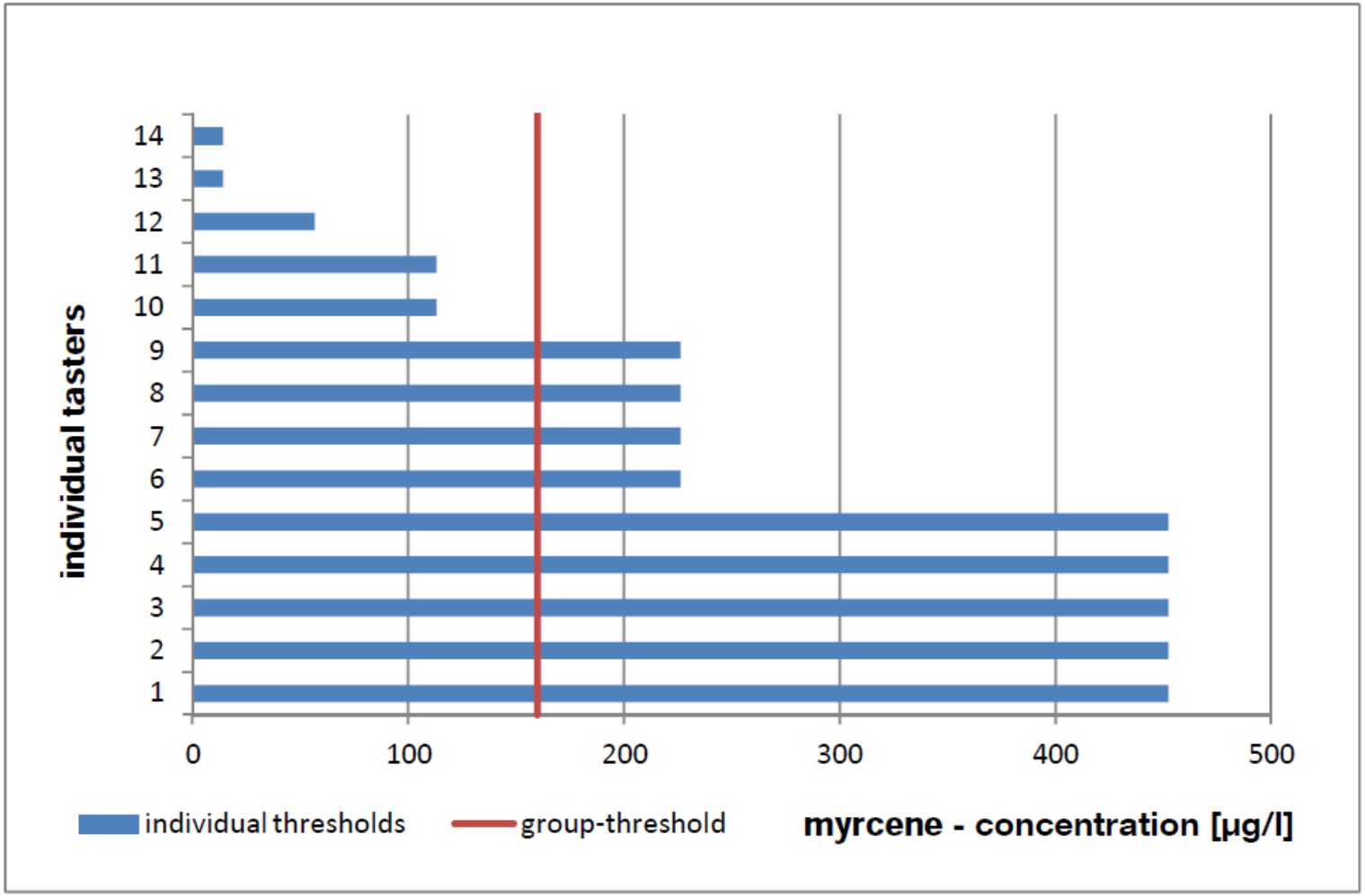
When the threshold is low, but...
Threshold value:

- Depends on the pH value
- Depends on the composition of the beer
- Depends on the tasters

When the concentration in beer is above the threshold, but...
Concentration in beer:

- May act additive/synergistic with others (same aroma or different aroma perception)
- May have a masking influence or none at all

Example for Myrcene Threshold Differences



Teagle, 2011

Hop Aroma in Beer

- Differentiation between “kettle hop“, “late hop“ and “dry hop“ aroma and flavor.
- Kettle hop: subtle, slightly spicy (oxidised sesquiterpenes, aglycones).
- Late Hop Aroma: Citrus aromas can be attributed to carboxylic acid esters, alcohols and ketones.
- Other fruity aromas can be attributed to linalool, geraniol, citronellol, 4-mercapto-4-methylpentan-2-one (4-MMP), 3-mercaptohexan-1-ol (3-MH), 3-mercaptohexyl acetate (3-MHA), ketones, epoxides and esters.
- Dry Hop Aroma: some green and grassy aroma impressions may be due to aldehydes such as hexanal.
- Many unknowns in regard to aroma relevant compounds in dry hopped beers.

Sensory Relevant Hop Aroma Compounds in Beer

Substance	Descriptors	Threshold µg/l
4-mercapto-4-methyl-pentan-2-one (4-MMP)	Muscat, black current	0.002
b-damascenone	Apple, peach, fruity	0.02
3-mercapto-4-methylpentan-2-ol	rhubarb, Grapefruit	0.07
(E,Z)-2,6-nonadienal	Cucumber, green	0.5
b-Ionon	Floral, violet, berries	0.6
ethyl-4-methylpentanoate	Citrus, pineapple	1 – 18
ethyl-2-methylbutanoate	Citrus, apple	1.1 – 45
linalool	Lavendar, floral	2 – 80
ethyl-3-methylbutanoate	Citrus, apple	2
Geraniol	Floral , rose	4 – 300
ethyl-2-methylpropanoate	Citrus, pineapple	6.3 – 164
b-citronellol	Lime, lychee	9 – 40
myrcene	Herbal, piney, resinous	9 – 1000
humulenepoxide I	hay	10
(Z)-3-hexenal	Green, leavy	20
4-(4-hydroxyphenyl)-2-butanone	Citrus, rasperry	21.2

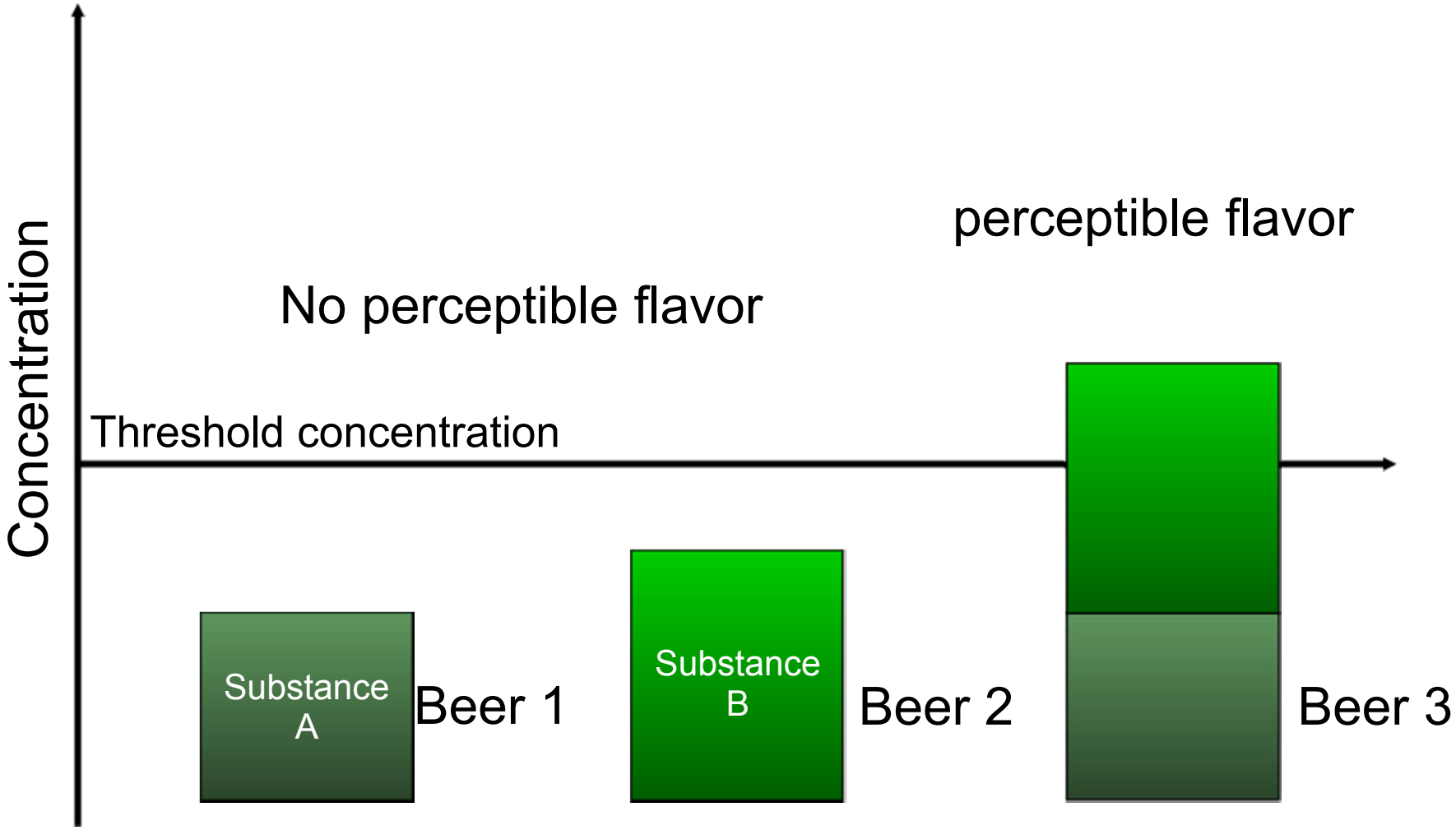
The unique composition of hop aroma compounds in beer together with other beer aroma compounds determines the resulting hop aroma in beer

Interaction of Hop Aroma Compounds

When combining hop aroma compounds

$$1+1 \neq 2$$

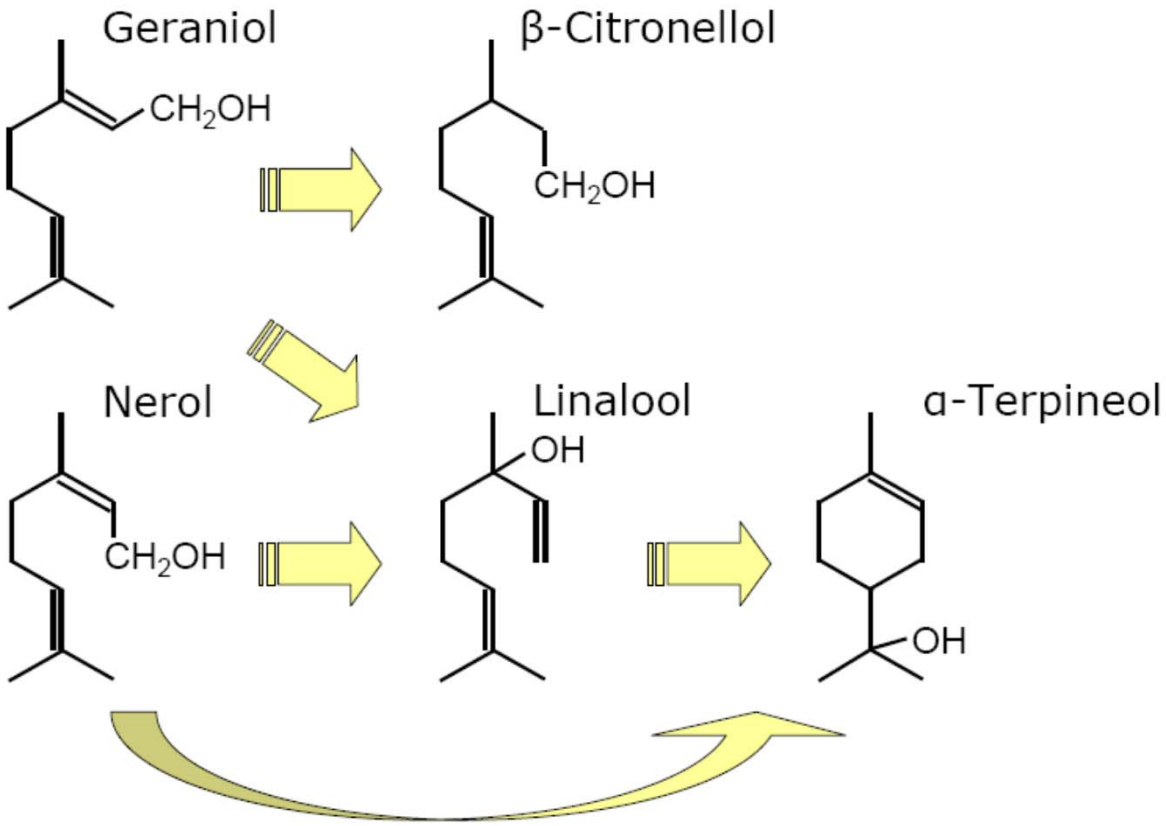
Synergistic Effects of Hop Aroma Compounds



Compound Threshold Interaction - Hanke

µg/l	Linalool	Geran.	Humul.	Caryo.	Nerol	Terp.	Myr.	Far.
Linalool	27	104[a]; 133[b]						493[c]
Geraniol	104[a]; 133[b]	90						2304[d]
Humulene			3483	4346[e]	1843[f]	5668[g]		
Caryophyllene			4346[e]	239	147[h]	1297[i]		
Nerol			1843[f]	147[h]	1206	2699[j]		
Terpineol			5668[g]	1297[i]	2699[j]	1076		
Myrcene							119	
Farnesene	493[c]	2304[d]						2020

Biotransformation During Brewing



King, A. and Dickinson, J. R., Biotransformation of monoterpene alcohols by *Saccharomyces cerevisiae*, *Torulaspora delbrueckii* and *Kluyveromyces lactis*. *Yeast,* 2000, **16(6),** 499-506.

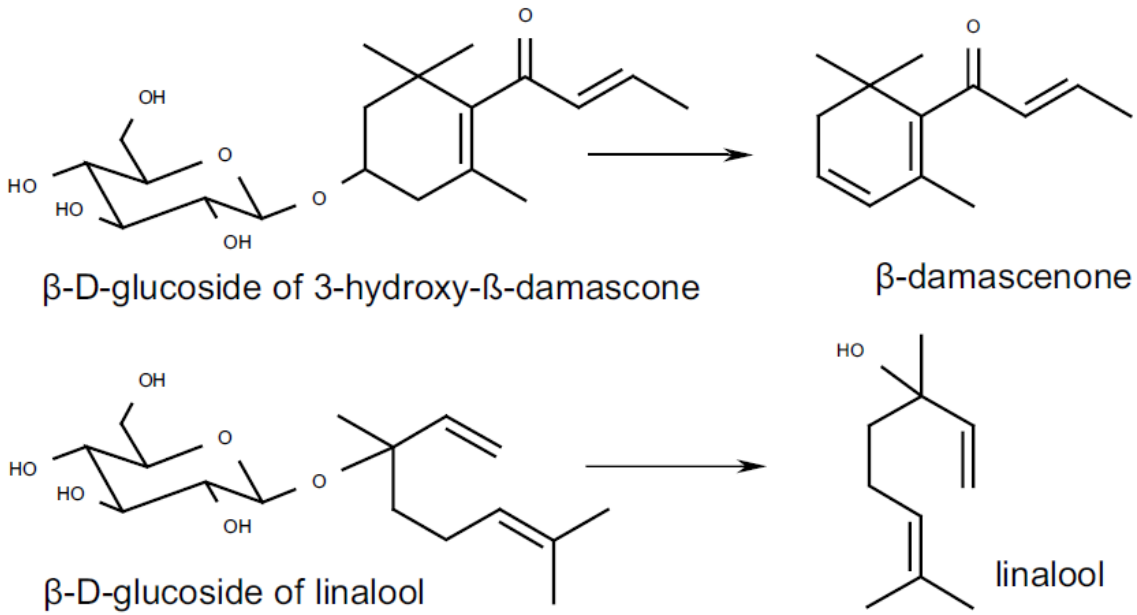
Fruity Thiols

- All thiols show very low sensory thresholds, chemically labile
- **4-MMP,** blackcurrant, muscat
- **4-methoxy-2-methyl-2-mercaptobutane,** grapefruit mercaptan
- **3-mercaptohexan-1-ol** (55 ng/l threshold) can be esterified to **3-mercaptohexyl acetate** (5 ng/l threshold).
- **3-mercapto-4-methylpentan-1-ol (3-M-4-MP) and 3-mercapto-4-methylpentyl acetate (3-M-4-MPA)** grapefruit, rhubarb, Sauvingon Blanc

Onion, burnt, rubber, cat urine ⟺ **grapefruit, rhubarb, black currant, muscat, ribes, grapes**

depending on configuration, concentration, interaction and perception

Glycosidically Bound Aroma Components



Kollmansberger, 2006

- Daenen 2008; pronounced exo-ß-glucanase activity in Saccharomyces brewing yeasts leads to a higher release of certain aglycones. Brettanomyces brewing yeasts hydrolyse glycosidically-bound aroma components of hops.
- Ting (2009) named 28 hydrolysis products by ß-glucosidase from glycosides

Important Points

- Hop Aroma in beer is a very complex issue.
- Many unidentified aroma compounds with unidentified aroma interactions.
- Currently no solid approach for the GC determination of relevant flavor active components.
- Sensory is the most useful instrument in this regard.
- Extent of biotransformation of aroma compounds is not fully understood.
- With more and more hop flavorful beers on the market there is more interest in aroma characterization.
- Existing exciting varieties with very interesting fruity flavors, news are being bred.

- Hop oil composition
- Hop aroma in beer
- Bitterness in beer

Physiology of Bitterness

- Bitter is the most sensitive of the five basic tastes, thought to safeguard animals from consuming toxic substances.
- TASR receptors facilitate taste sensation in the taste buds on the tongue.
- 25 different bitter specific TASRs identified.
- TASR receptors types react to different substances.
- Many receptors react on various substances with different intensity.

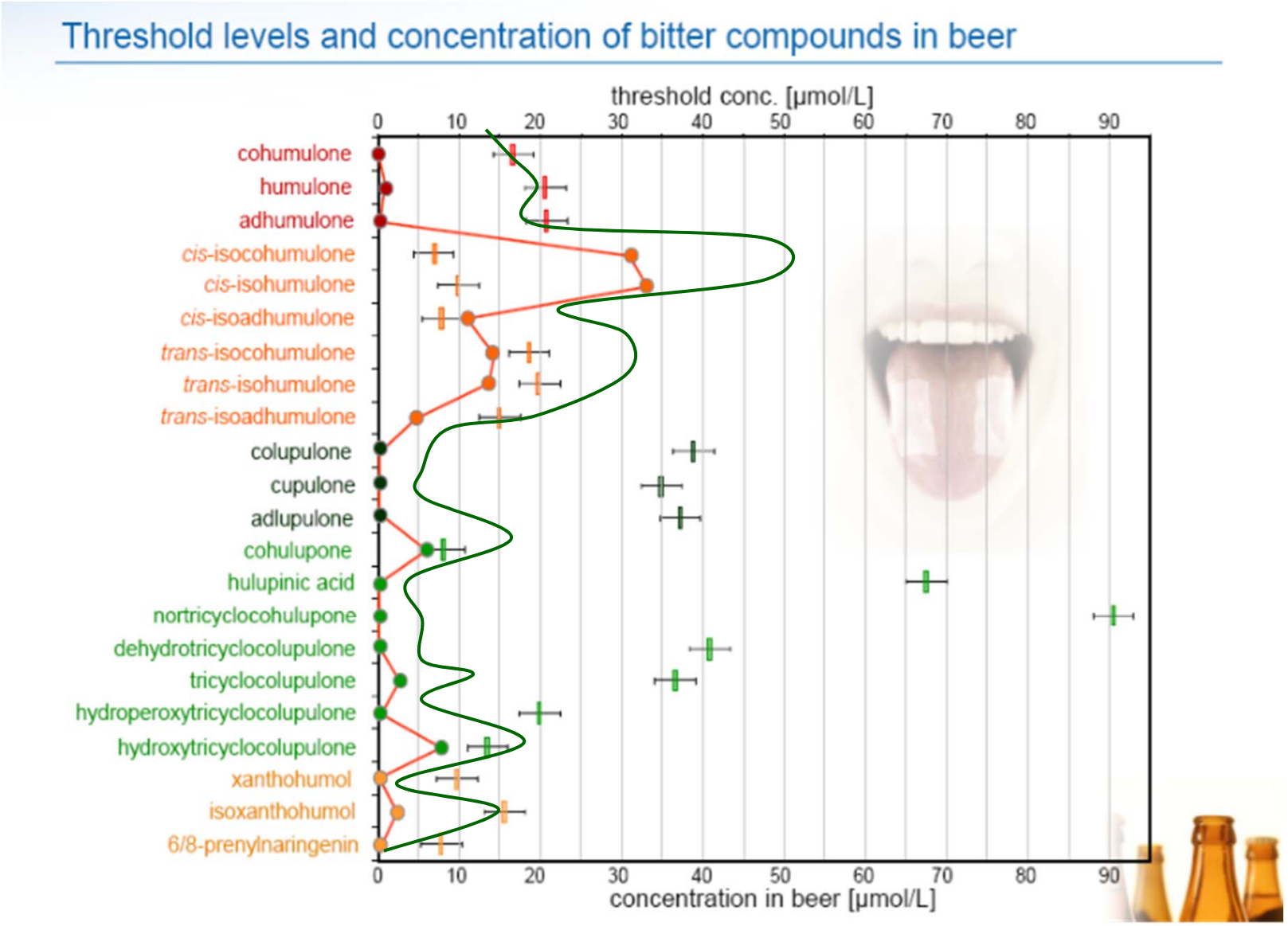
- Threshold values vary and depend greatly on media (water, beer, etc)
  - e.g., in water: Sucrose ~ 10 000 µmol
    Isohumulone ~ 14 µmol
    Quinine ~ 8 µmol

  - The most bitter substance known is denatonium benzoate, detectable at 0.02 µmol, used as an aversive agent. Concentration of 10 ppm is unbearably bitter to most humans.

Contributors to Bitterness in Beer

- Hops
  - Iso alpha acids, reduced IAA
  - beta acid reaction products (oxidised beta acids etc.)
  - xanthohumol / isoxanthohumol
  - degradation products
  - Polyphenols
  - Other phenolic substances: Catechine, Epicatechine, Quercetine
  - Uncharacterised compounds
- Malt : Amino acids, Dipeptide, Di-ketopiperazine, Maillard reaction products
- Water: $MgSO_4$, $CaCO_3$, $CaCl_2$,
- Hop Aroma: Can intensify perceived bitterness (psychological?)

Threshold levels (Hofmann, 2011)



Threshold Ranges of Hop Bitter Acids

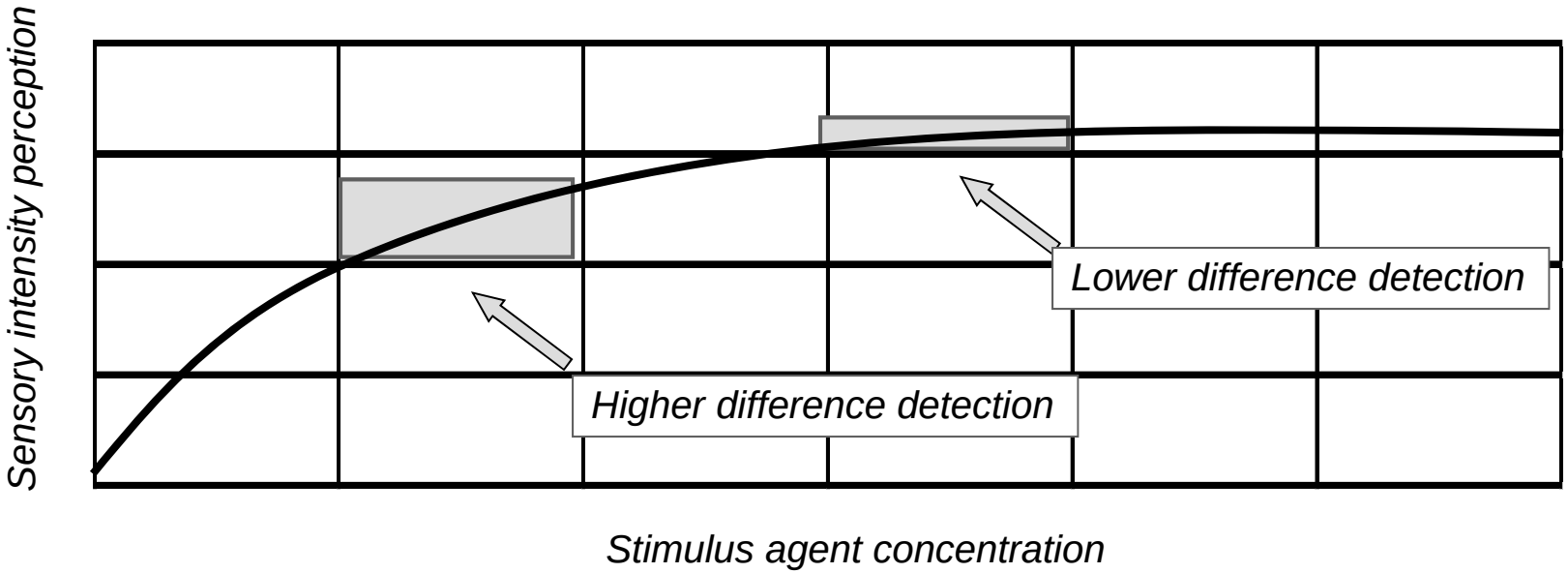
– Bitterness Intensity depends on EtOH content, residual sugars, original gravity, use of adjunct, etc.

Threshold ranges in mg/l	In beer
Iso-alpha acids	3-8 mg/l
Tetrahydro-iso-alpha acids	2-9 mg/l
Rho-iso-alpha acids	6-12 mg/l
Hexahydro-iso-alpha acids	2-10 mg/l

Comparison of Bitter Perception of Various Hop Products

- IAA = 1.0
- Rho IAA = 0.7
- Tetra IAA = 1.0-1.7
- Iso – pleasant, non-lingering
- Tetra - lingering, harsh bitterness
- Rho - less intense, smooth bitterness
- Hexa - smoother bitterness, not as harsh as tetra

Physiology of Detectable Differences



- *Just noticeable difference concept* – Fechner‘s Law.
- With decreasing concentrations of stimulus agent, the ability to distinguish between concentrations increases until the lower detection threshold is reached.
- Therefore, lower bittered beers have more stringent requirements for exact bitterness.

Important Points

- Bitterness perception is fairly well understood, at least compared to aroma.
- Beer is one of the few consumables where bitterness is expected and appreciated.
- Bitterness appreciation often has to be acquired (lupulin drift?)
- Bitterness is dependent on many factors and depending on beer style, iso-humulones may or may not be the primary contributors.
- Unpleasant bitterness is something subjective and can be the result of the interaction of various parameters contributing to lingering and harsh.
- A definition for the quality of bitterness is challenging, e.g. bitterness “harmony”.
- Bitterness interacts with sweetness and other sensations as well as aroma impressions to provide a balance in the taste of beer.

Thank you for your attention!

Tim Kostelecky

John I. Haas, Inc. – Yakima Washington

tim.kostelecky@johnihaas.com