

Bitterness and the IBU: What's it all about?

Homebrew CON

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Minneapolis, MN

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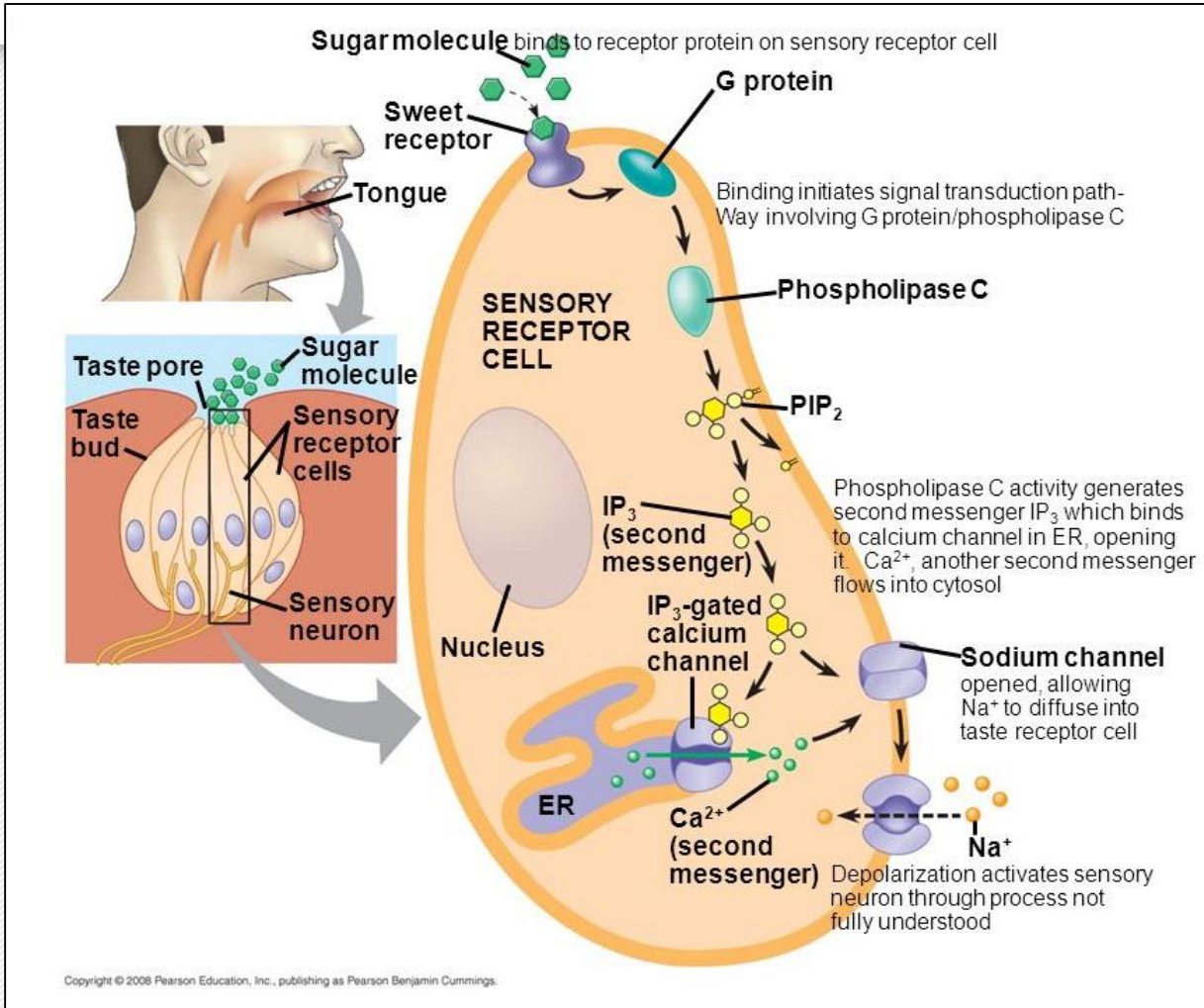
Bitterness

- Bitterness Perception
- Factors that affect perception
- Hop Products and Reduced Hop Products
- Chemistry and Utilization
- Analytical Measurement
- Sensory and the IBU

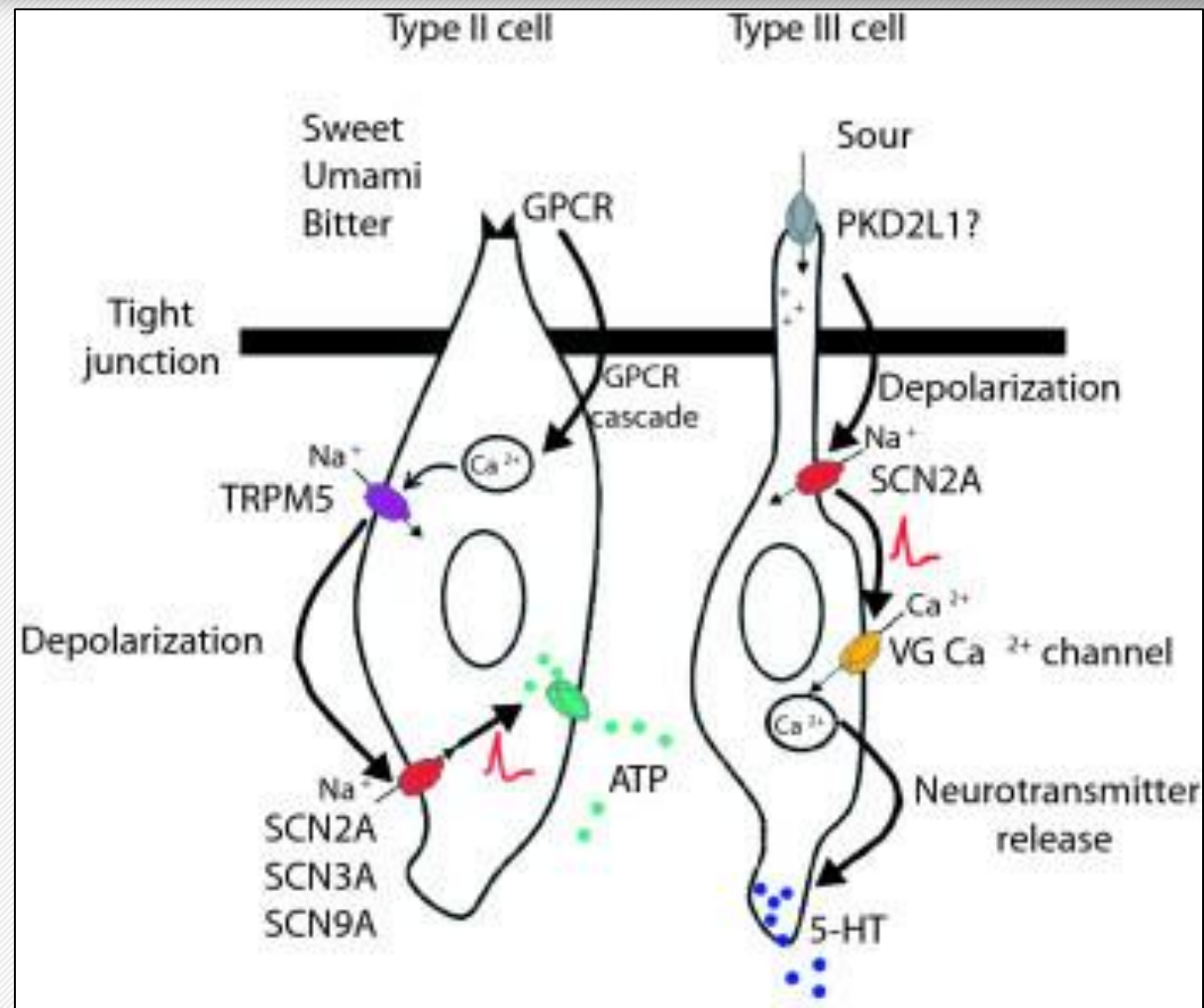
Bitterness Perception

- Molecules bind to receptors on the tongue
 - Type II receptor cells (sweet, umami, bitter)
- Ligand binding site changes shape
- Interacts with a G-protein coupled receptor (GPCRs)
- G- protein activates messenger cell...cascade effect.....
- Ion channels activate and cell gradient changes
- Nerve cell stimulated
- Signals the Brain
- **BITTER!**

G - Protein Response



Type II Receptor



Bitterness - Perception Factors

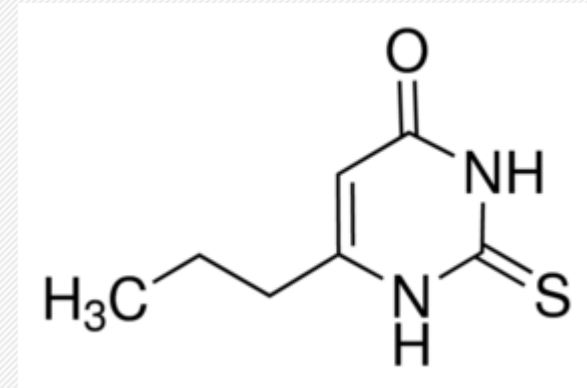
- **Genetics** -
 - Heritage - 25 Taste Type II Receptors
 - Cluster of genes located on c 5p, 7q, 12 p
 - # of fungiform papillae vary by individual
 - Sex
- **Age** - response declines with age
- **Diet** - brain response change due to 'training'
- Presence of **suppressants and enhancers**
 - Sugar
 - Salt
 - Acids
 - Metals

[Nutrients](#). 2014 Sep; 6(9): 3363-3381.



Bitterness Genetics and PROP

- PROP (6-propyl-2-thiouracil)
 - Bitter receptor - TAS2R38
 - Linked to chromosome locus at 5p15
 - Dominant trait
 - 70% of Caucasians are sensitive
 - 90% of Asians and African Americans
 - Subgroup - supertasters
 - More women than men



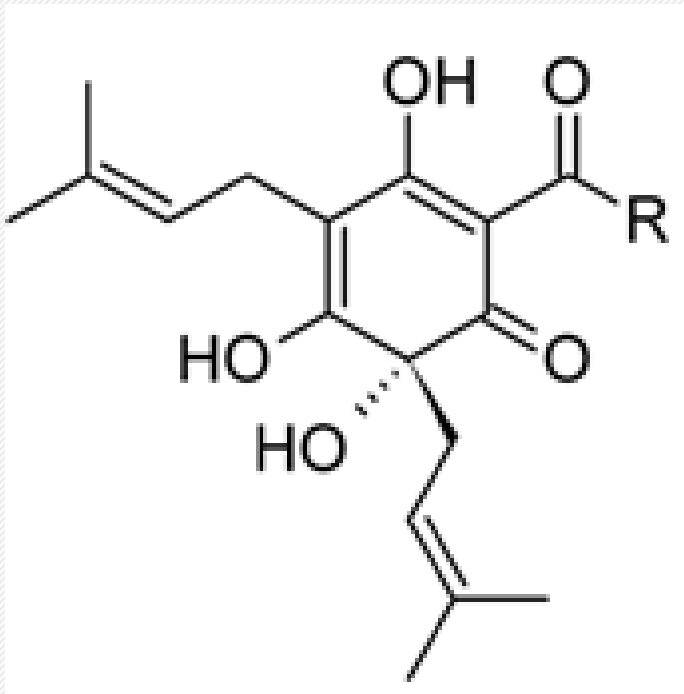
Bitterness - Beer Contributors

- **Color** (malt roast) - bitter compounds
- **Alcohol** may enhance or reduce
- **Higher pH** - enhances bitterness
- **Mineral Content**
 - Burtonization - sulfate = crisp
 - Carbonate - broader, harsher bitter
- **Carbonation bite** can enhance bitterness
- **Aging** decreases bitterness
- **Hop Oils** - Oil 'burn' may enhance bitterness
- **Polyphenols** - bitter
- **Hop Acids and their products...**

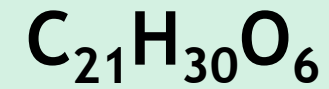
Bitterness - Hop Acids

- Alpha Acids: humulones
- Beta Acids: lupulones
- Isomerized alpha acids: Isohumulones
- Advanced Hop Products: Extracts, Reduced Hop Acids, etc

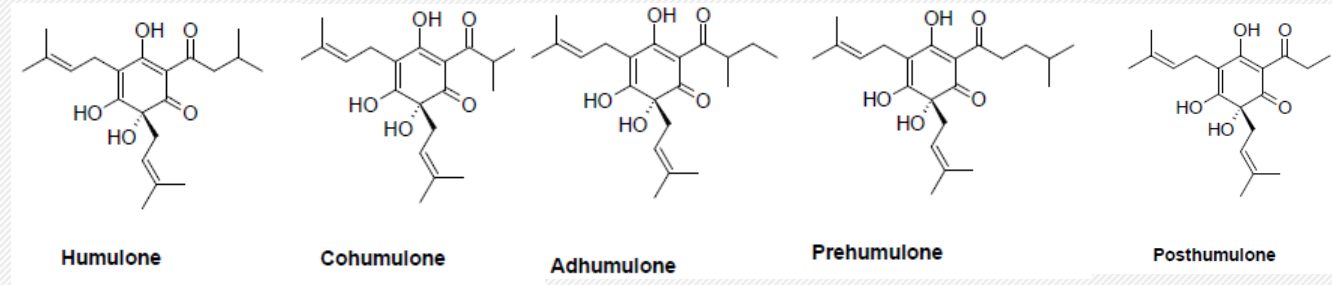
The Alpha Acids: Humulones



Empirical Formula:



The Humulones: Alpha Acid Analogues



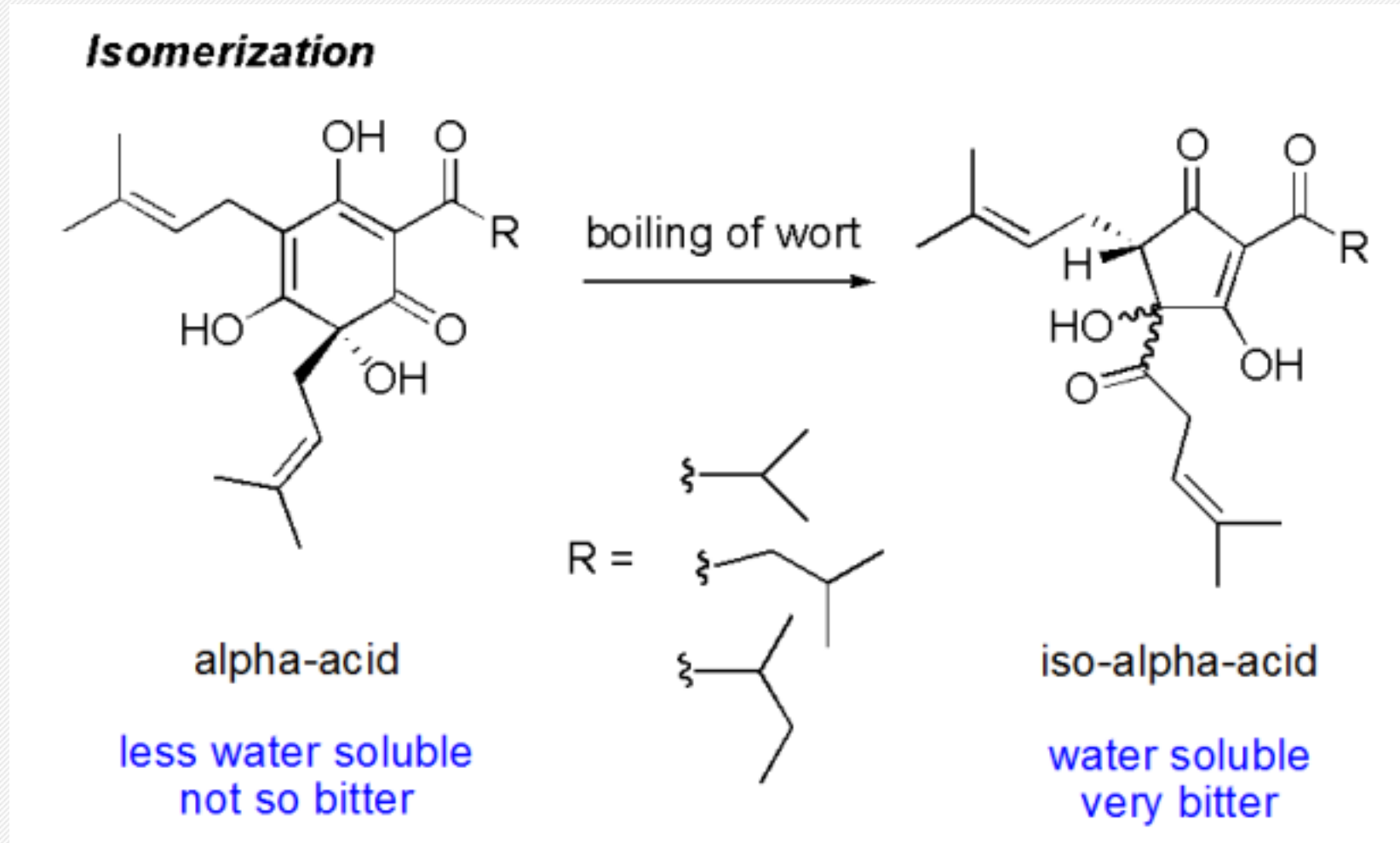
Alpha Acid	Acyl R	MW	%
Humulone*	$\text{CH}_2\text{CH}(\text{CH}_3)_2$	362	35-70
Cohumulone*	$\text{CH}(\text{CH}_3)_2$	348	20-65
Adhumulone**	$\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$	362	10-15
Prehumulone***	$\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$	376	1-10
Posthumulone***	CH_2CH_3	334	1-3

(Rigby, Bethune, *1952, **1953 and ***Verzele 1955)

Bitterness - Alpha Acids

- Not bitter - per se
- Unstable - oxidize readily in presence of oxygen, heat and light.
- Oxidized alpha acids form hard resins that do not contribute to beer bitterness.
- *Oxidized alpha acids* do contribute to bitterness:
 - humulinones and humulinic acids.
- At 25°C humulone aqueous solubility is low ~6mg/L
- Alpha acids are relatively insoluble in wort at pH 5, reaching a maximum of about 84 ppm when heated at pH 5.2, and even higher at pH ~6.5.

Isomerized alpha acids: Iso humulones



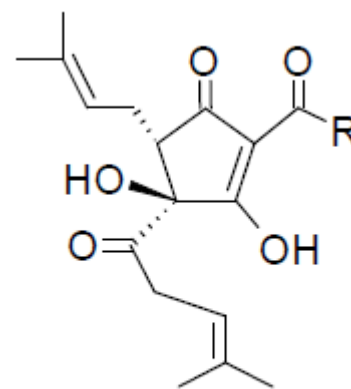
Isomerized alpha acids: cis and trans

1952, 1957 - Rigby and Bethune/Howard et. Al:
Bitter substances give 6 peaks, representing epimeric isomers of each of the three major analogues of alpha acids

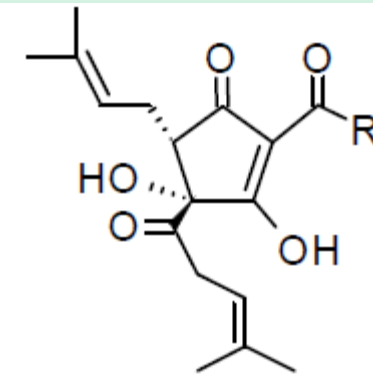
*The higher the pH = more trans

*Trans is less stable

Iso humulone A and B, Spetsig (1964)



trans-isohumulone



cis-isohumulone

Isomerization

Isomerization from a 6 membered ring to a 5 membered ring:

Heat $>100^{\circ}\text{C}$, readily above 180°C (Lance et al. 1975)

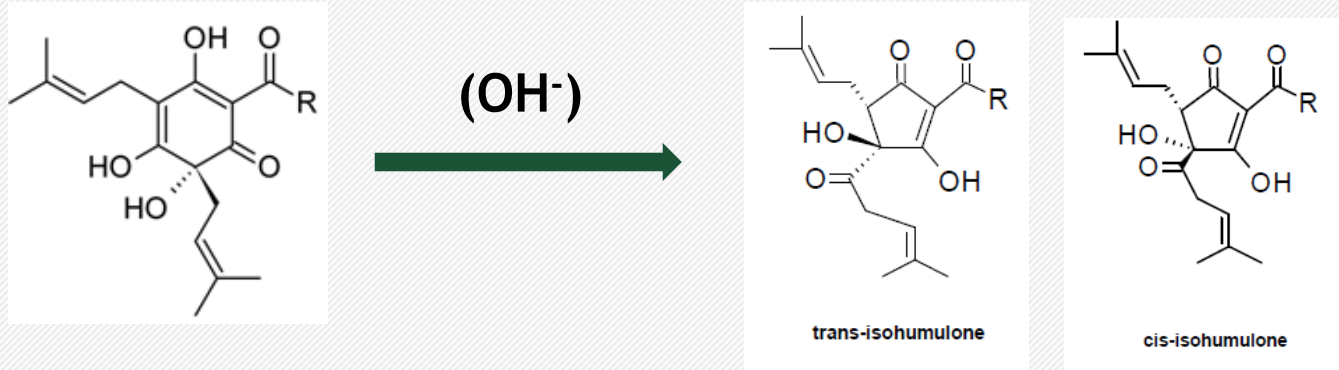
Higher pH yields higher conversion (Anteunius and Verzele 1959)

Divalent Cations such as Mg^{2+} increase rate (Koller 1968)

Normal Brewing Conditions yield (pH 5-5.5) = 32:68 Trans:Cis ratio

Cis is thermally more stable, higher pH more trans.

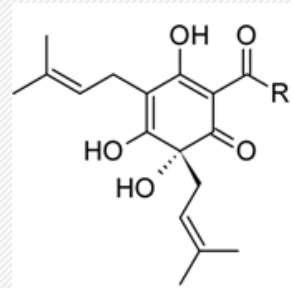
Photoisomerization can also occur under prolonged exposure to irradiation at 254 or 350 nm, 10-12 hours (mostly trans) -1961, 1979.



Maximize Utilization

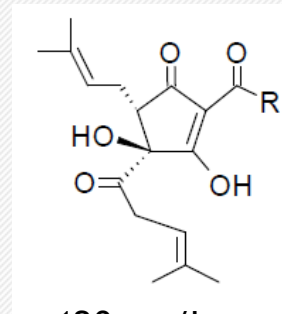
- Isomerized-alpha acids are relatively soluble in water and wort.
- Boiling in wort utilization ~25-35%
- Maximum conversion ~60% from alpha to iso-alpha
- Losses due to insufficient boiling time, dispersion, oxidation, adsorption foaming.....
And more in fermentation and filtration.

Alpha Acids



3 mg/L

Iso-Alpha Acids



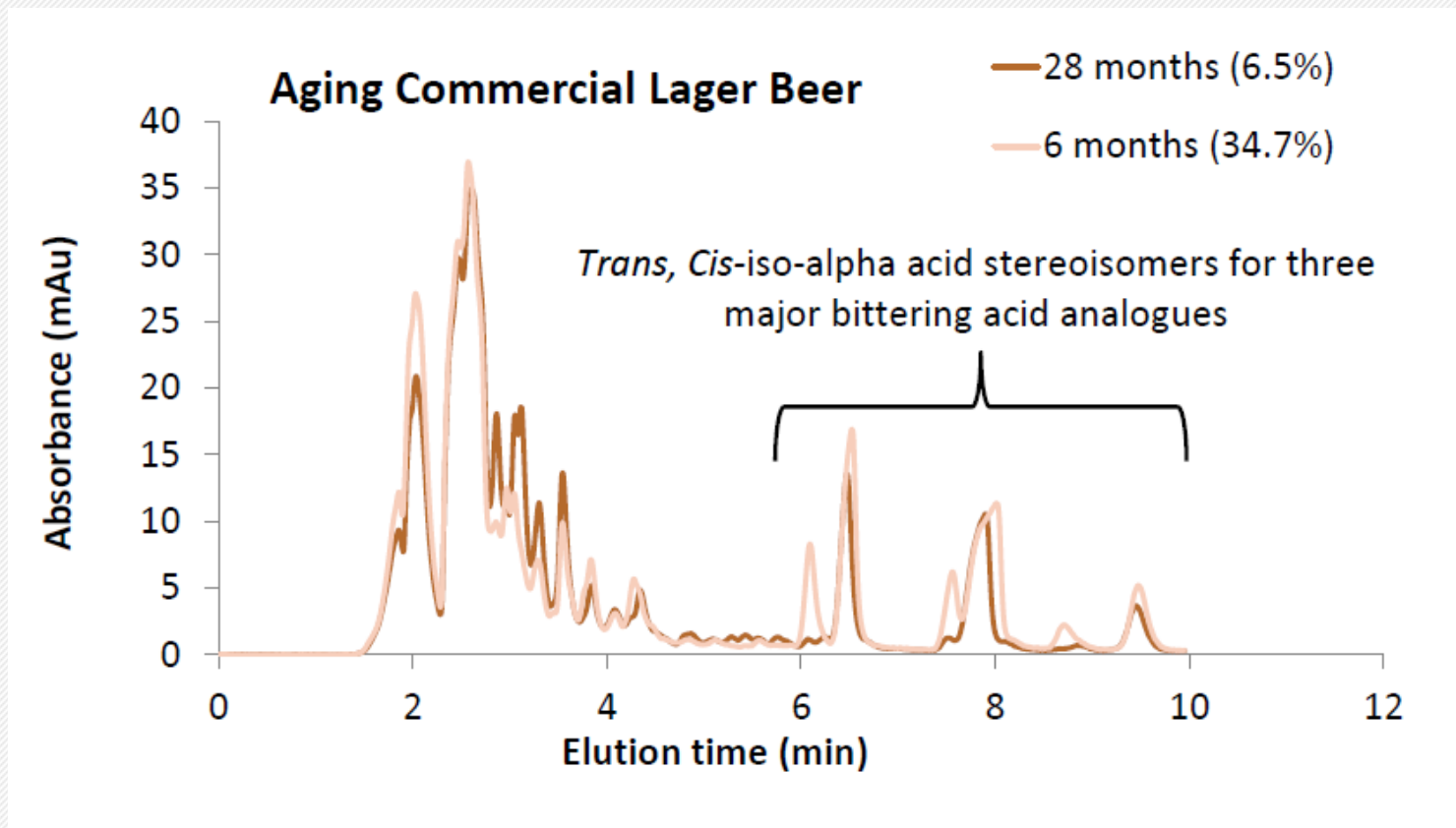
120 mg/L

Heat/(OH⁻)

*Peacock 1998

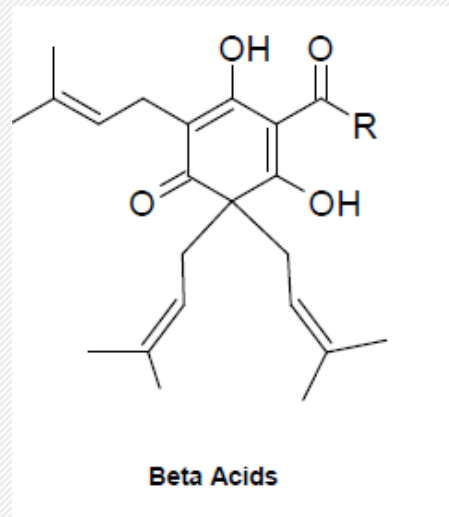
Iso-alpha acid stability

Thermal instability - Cis is thermally more stable, losses of trans occur over time



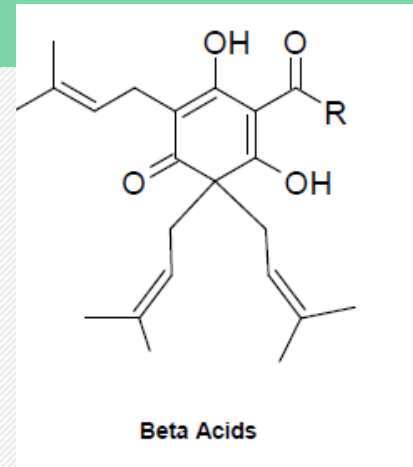
The Lupulones: Beta Acid Analogues

Beta Acid	Acyl R	%
Lupulone*	$\text{CH}_2\text{CH}(\text{CH}_3)_2$	30-55
Colupulone*	$\text{CH}(\text{CH}_3)_2$	20-55
Adlupulone**	$\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$	10-15
Prelupulone***	$\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$	1-3
Postlupulone***	CH_2CH_3	?



Bitterness - The Beta Acids

- Not bitter unless oxidized.
- Poorly soluble in water and wort.
- Poor solubility as pure compounds (1 g/100mL), but more soluble as a mixture
- Susceptible to oxidation comparable to alpha acids
- Oxidation results in hulupones - products have ‘undesirable?’ bitterness and can make up for loss of alpha in old hops.



Advanced Hop Products: Increased Utilization

- Pellets
- Organic and Aqueous fractions
- Extracts
- Pre-isomerized Pellets and Extracts
- Reduced Hop Products

Pelletization



Type 90 - 100 kg of raw hops = 90 kg of pelletized hops

Type 45 - 100 kg of raw hops = 45 kg of pelletized hops

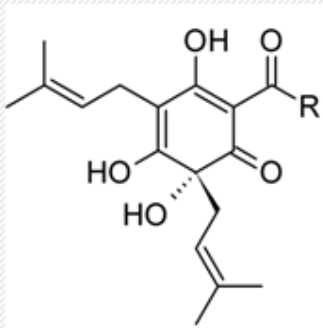
- Retains most of the hop character
- More compressed than whole cones
- Packed under inert gas or vacuum extends life
- Blending can produce pellets of consist alpha acid content

Whole leaf hops: 20-20% utilization
T90 Pellets: 30-40% utilization



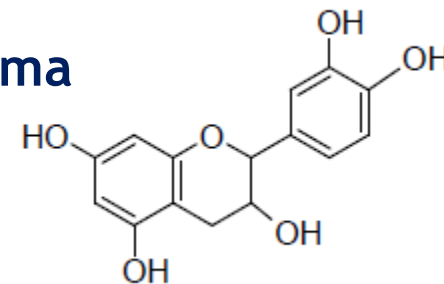
Organic Extractable

Lipids
Waxes
Essential Oils
Soft Resins
Hard Resins
Some polyphenols



Aqueous Extractable

Cellulose
Lignin
Proteins
Polyphenols
Glycosidic Aroma
Precursors



Liquid or Supercritical CO₂ Extraction

1975 - Laws et al. of BRF introduced **liquid CO₂ hop extracts** (rich in α -acids, β -acids, and essential oils) under 1000 psi (69 bar) and 50°F(10°C), which was then commercialized by Carlton & United Breweries.

1978, Muller, Vitathum and Huber developed **supercritical CO₂ hop extraction** under 3000 psi (207 bar) and 110°F(43°C).



CO₂ Extracts

- Golden/Amber/Green Semi-fluid Resin or Paste
- Alpha Acid is Variety dependent
 - ~ 30% aroma hops
 - ~ 50% high alpha variety hops
- Contains hop oil fraction
 - Late addition maintains more volatiles
- Up to 40% utilization in the kettle
 - Late addition = lower utilization

- Ensures more standardized product
- Extremely Stable – up to four years from production date.
- Easy to transport
- Easy to store
- Available in bulk (tote), buckets or cans
- Pre-isomerized CO₂ extracts are available

Separation of CO₂ Extract into components.....



1982- Miller Brewing Patent:
Process of directly separating α -acids, β -acids, and hop oils from CO₂ extract using pH partitioning.

Isomerized Pellets and Extracts

Chemothermic process converts alpha acids to iso alpha acids.

Pellet Products

- Stabilized by the addition of magnesium salt
- up to 20% iso-alpha ~90% of alpha in original pellet is converted
- Utilization 45-55%

Pre-isomerized hop extracts

- Magnesium or potassium salts

Can be added late in the kettle or even after fermentation, better exploitation of bittering content

*German beer purity laws prohibit usage.



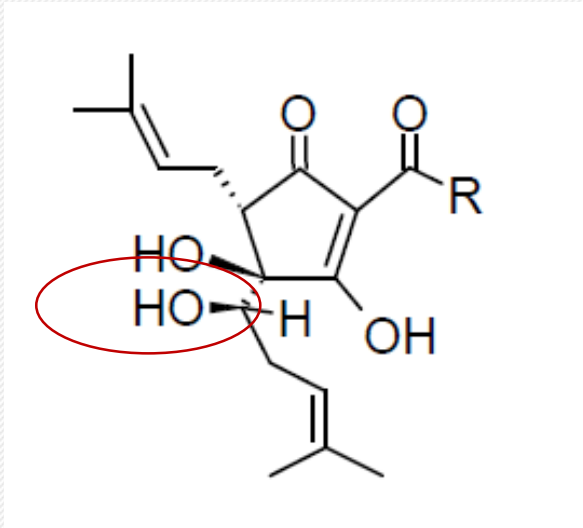
Overall Advancements in Utility through product innovation

Hop Form	Utilization BU from Alpha	Shipping and Storage Volume (100K Hectoliters of beer	%alpha loss during Cold Storage for one year
Baled Hops	15-30%	80m ³	14%
Pellets	25-40%	24m ³	5%
T45 Pellets	25-40%	14m ³	5%
Extract	25-40%	8m ³	5%
Pre-Isomerized Extract	60-85%	3m ³	3%

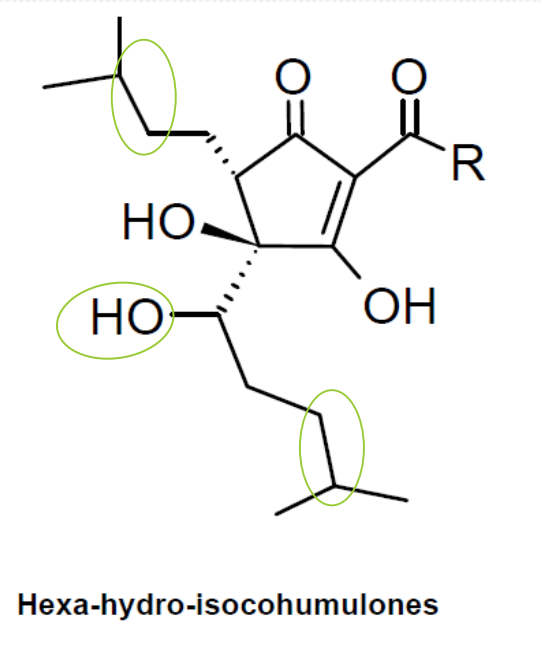
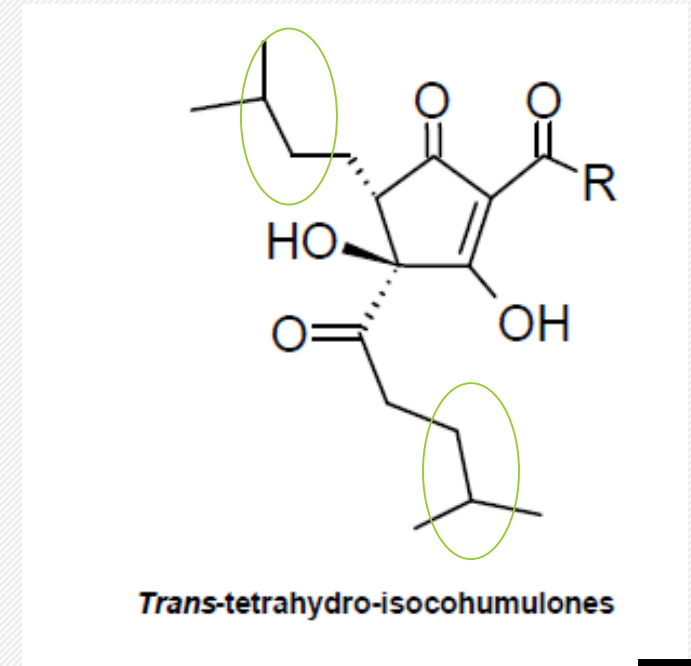
Reduced Iso-alpha Acids

Reduced Iso-alpha acids (Rho)

Trans-DIHYDRO-ISOHUMULONES or *Trans*-RHO-ISOHUMULONES



Tetrahydro-Iso-alpha acids



Hexahydro-Iso-alpha acids

Understanding the IBU

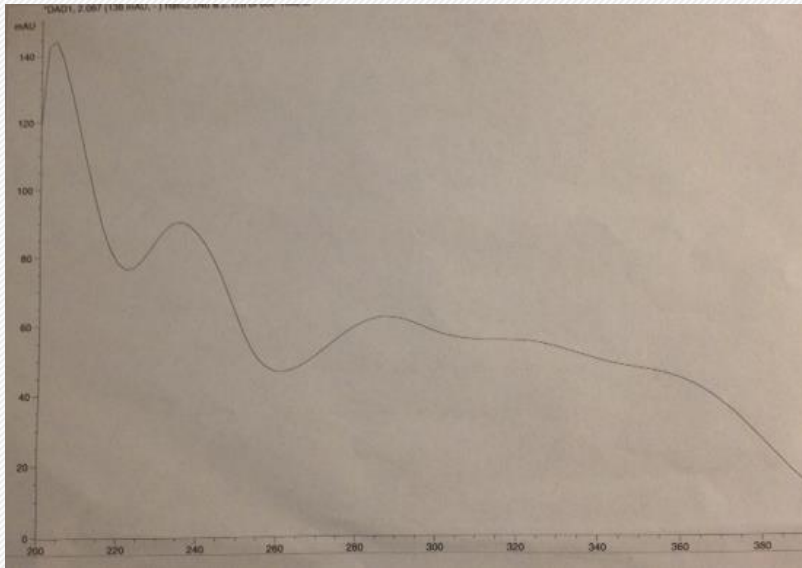
- History of the IBU
- Definition of IBU
- Contributors to IBU
- IBU and Dry Hopping
- IBU vs Bitterness
- Sensory

IBU method History

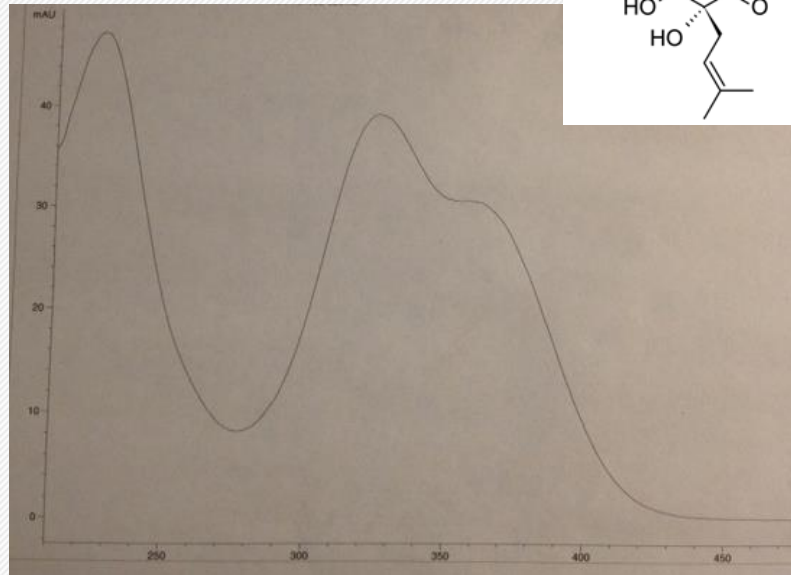
- **1955 - Lloyd Rigby**
 - @255 nm basic conditions
 - Iso-alpha acids
- **1955 - Morten Meilgaard**
 - @275nm in neutral conditions
 - All derived bittering compounds

Notes: pre-dates pellets (@1972), whole hops used, aged, and oxidized, dry hopping not as prevalent, lager beer.

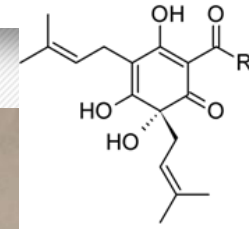
IBU: pH and analysis



Alpha acids - Acidic Conditions
 λ max = 240, 285



Alpha acids - Neutral Conditions
 λ max = 245, 325, 370



IBU method History

- ASBC adopts a method based on Meilgard's method (1967 - acidic)
- ASBC Beer-23 A: Beer Bitterness
 - Modification: Manual Isooctane extraction: reduced solvent technique (2011)

Beer	+ Acid	+ Non - Polar Sovent
ISO- Alpha Acids (IAA) and others. Bitter and Non Bitter Compounds	3 N HCL Protonates all carboxylic acid groups	2,2,4 trimethylpentane (Isooctane) With lower pH, compounds of interest are more non-polar.

Definition of IBU

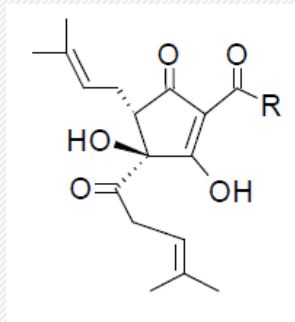
Calculation: $\text{ABS @275 nm} \times 50 = \text{BU}$

International Bitterness Unit (IBU) \neq ppm iso-alpha acid (IAA)

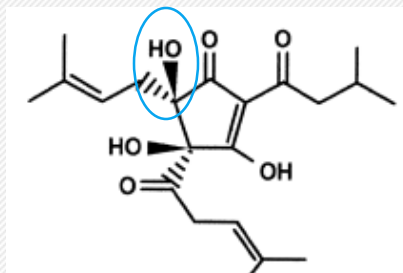
IBU = PPM IAA 'if' @70% of bitter substances are IAA.

Contributions to the IBU

- The IBU measurement includes:
 - Iso-alpha acids, α , β , and oxidized products:
 - Humulinones - more soluble than IAA
 - Beta acid derivatives
 - Other hard resin derivatives
 - Anything soluble in isooctane that also absorbs near 275 nm under acidified conditions:
 - Phenolics: xanthohumol, flavonoids, etc.



Iso- alpha acid



OXI- Iso- alpha acid
(humulinone)

Contributions to the IBU

- Method is a compromise overall.....
 - many components contribute to the IBU
 - hop variety, age and form, addition rate and time will alter the chemical components but maybe not the IBU value.....but sensory?

Contributions to the IBU: Aged hops

Age Fresh hops for 18 months and brew with same weight of hops

Storage Temp.	Alpha Acids In Hops	Iso-Alpha Acids In Beer	Beer IBU's
-15° F	3.22%	19.8 ppm	13.5
25° F	2.91%	18.1 ppm	12.0
45° F	1.71%	14.4 ppm	13.5
70° F	0.41%	2.9 ppm	11.0

***The Peacock Rule: IBU's = 5/7(ppm iso + ppm non-iso)**

*Source: WBC 2014, V. Peacock The IBU method, its creation and what it measures.



Contributions to the IBU: Dry Hopping

Humulinone and Iso-Alpha Acids Concentration In Dry-Hopped Beers

Sample	lbs Hop Pellets per Barrel of Beer	ppm of Humulinone in Beer	% Utilization Humulinone	ppm of Iso-alpha acids in Beer	*Calculated Bitterness Intensity
Low IBU Beer	0.0	0.8	–	8.6	9.1
	0.5	8.0	98	8.1	13.0
	1.0	14.0	91	7.9	17.0
	2.0	28.0	88	7.5	26.0
High IBU Beer	0.0	1.0	–	48.0	49.0
	0.5	8.0	98	39.0	44.0
	1.0	14.0	91	35.0	44.0
	2.0	27.0	87	30.0	47.0

*Calculated Bitterness = ppm iso-alpha acids + (ppm humulinone x 0.65)

****Sensory Bitterness Humulinones = 66% of IAA**

*Source: Simon H. Steiner Newsletter June 2015

* *Source: EBC 2015, T. H. Shellhammer, Beyond iso-alpha acids - Hops contributions to beer bitterness



Contributions to the IBU: Dry Hopping

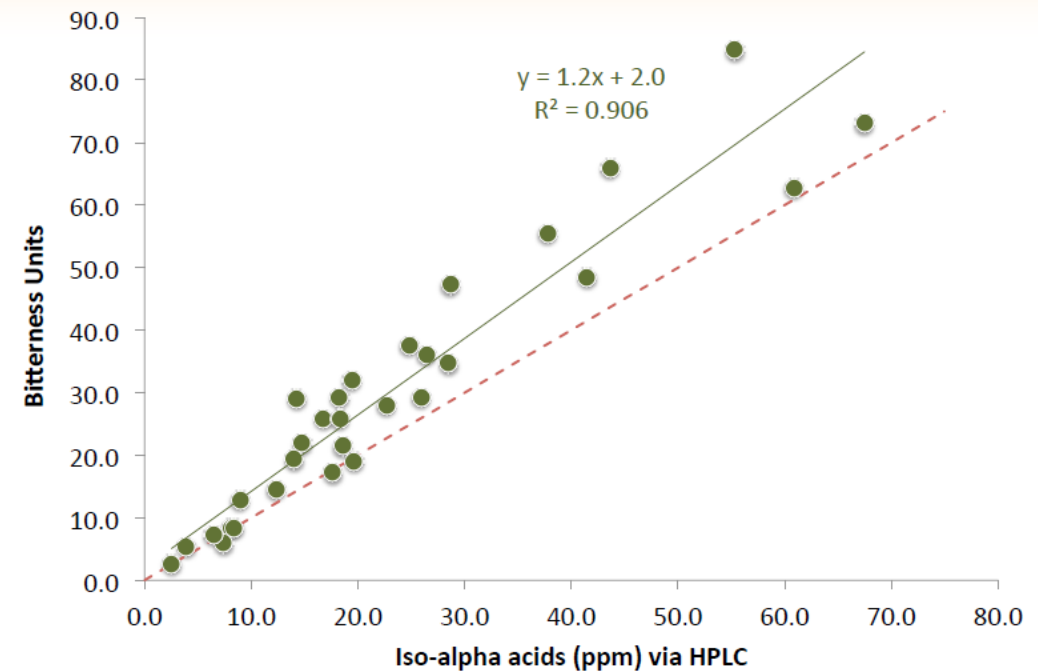
BU deviation with increased hopping rate:

Shellhammer et al: $BU = 1.2(IAA) + 2.0$

BU of 62 = 50 ppm

* *Source: WBC 2014, T. H. Shellhammer,
Dry hopping contributions to bitterness

Correlation between total IAA & IBU




Contributions to the IBU: Dry Hopping

The current IBU method overestimates the bitterness in dry hopped beers. To account for this a calculator has been employed to estimate the IAA portion of the IBU result when analyzing dry-hopped beers. *(Published 2015)*

$$\text{IAA} = (\text{IBU}) \times 0.85$$

<http://methods.asbcnet.org/extras/IAAcalculator.pdf>

 **Methods of Analysis**

Iso Alpha Acid (IAA) Estimated Calculation from BU Value

Estimated IAA = (BU result) X 0.85

Calculation:

- 1.) Measure the BU of your dry Hopped beer (i.e. 41.5 BU spectro).
([ASBC Methods Beer 23](#) A or D)
- 2.) 85% of the BU is the estimate of the IAA (Multiply the BU X 0.85)

Example Calculation:

Dry Hopped Product measured BU = **45**
BU - Bitterness unit from spectrophotometer or SFA

Estimated IAA = (45) X 0.85 = **38.25**

Reset

BU= Enter BU Value

Calculate

IAA= Calculated Estimate of IAA

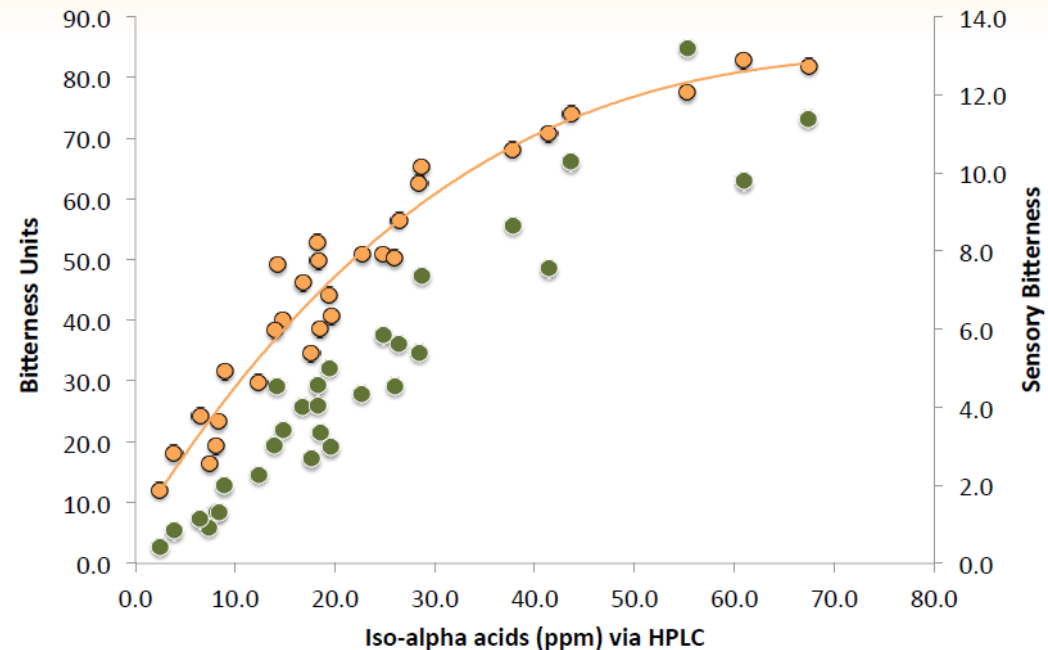
2015

Contributions to the IBU: Sensory

Sensory bitterness will vary based on hopping rates, hopping technology, age of hops, variety of hops.

Qualitative differences may not correlate to IBU!

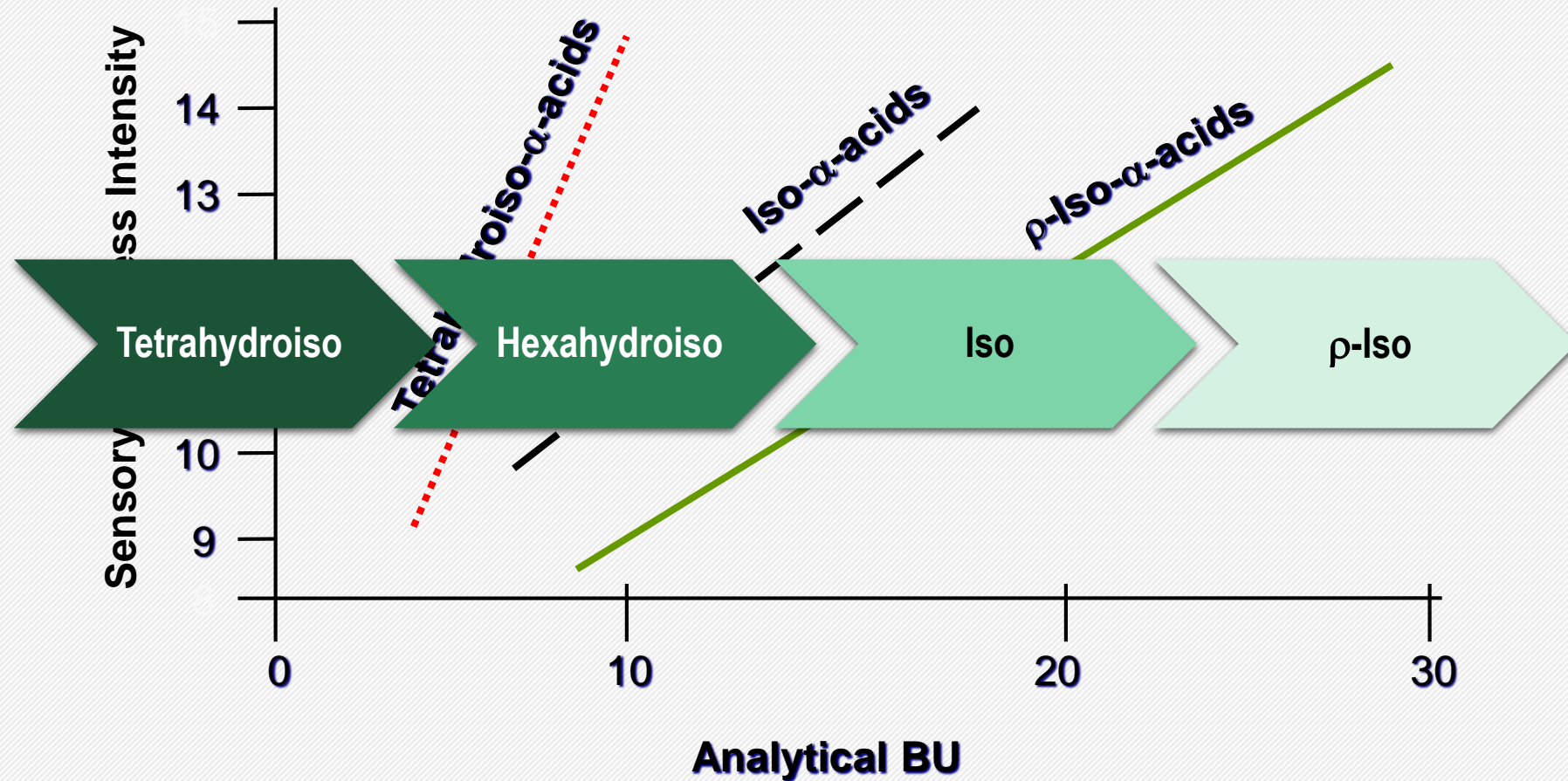
Sensory bitterness does not track BU/IAA



Source: WBC 2014, T. H. Shellhammer, Dry hopping contributions to bitterness

Reduced Hops

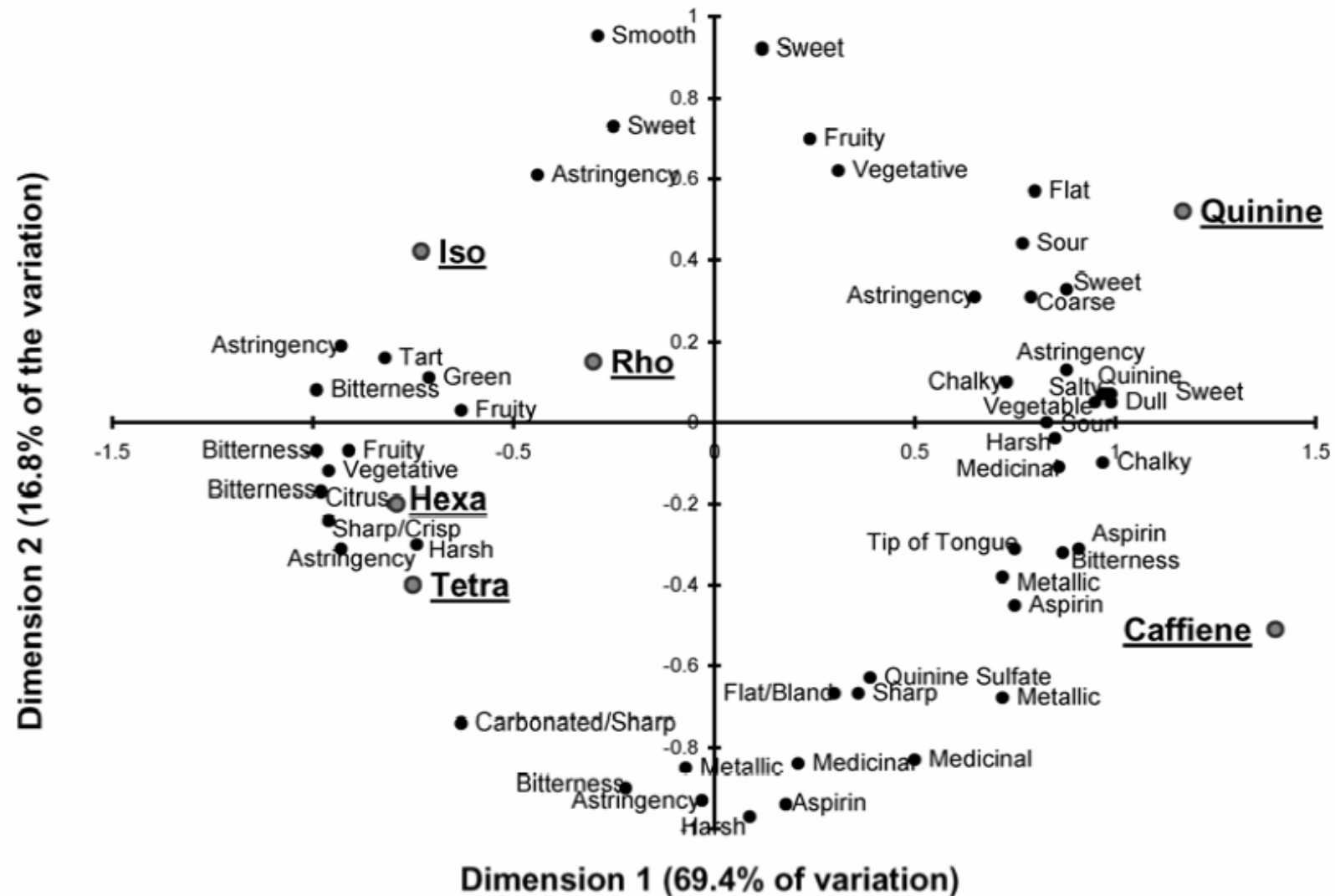
Comparison of Sensory vs. Analytical Bitterness



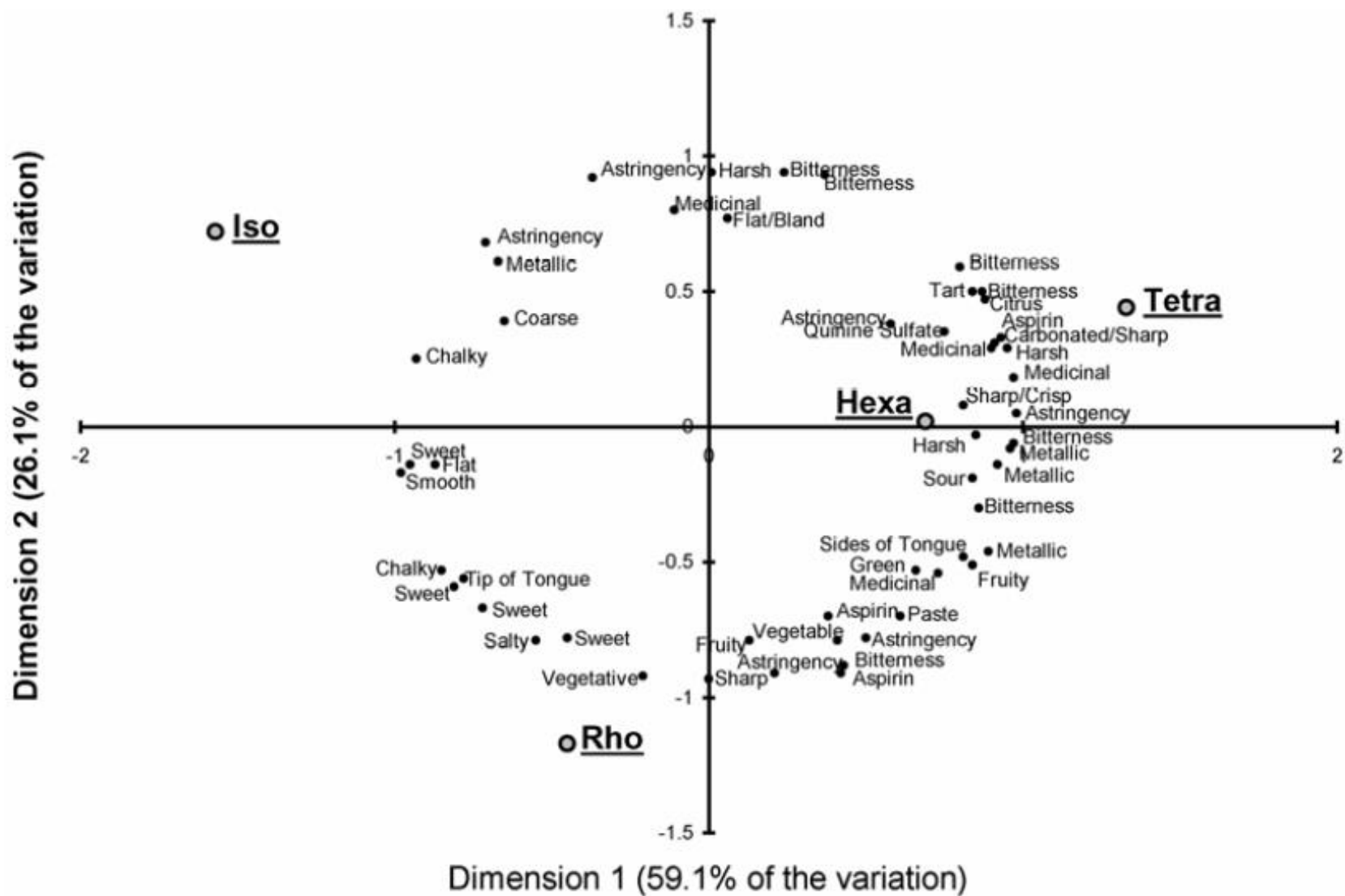
Bitterness Perception - Quality

- Harmonious
- Harsh
- Vegetative
- Medicinal
- Short
- Lingering

Bitterness Quality



Bitterness Quality



Bitterness Intensity and Time Intensity



Food Research International

Volume 86, August 2016, Pages 104–111



Modification of perceived beer bitterness intensity, character and temporal profile by hop aroma extract

Olayide Oladokun^a, Amparo Tarrega^a, Sue James^b, Trevor Cowley^b, Frieda Dehrmann^b, Katherine Smart^b, David Cook^a, Joanne Hort^a  

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Highlights

- Aroma modified intensity, character and temporal profile of bitterness in beer

Bitterness Perception

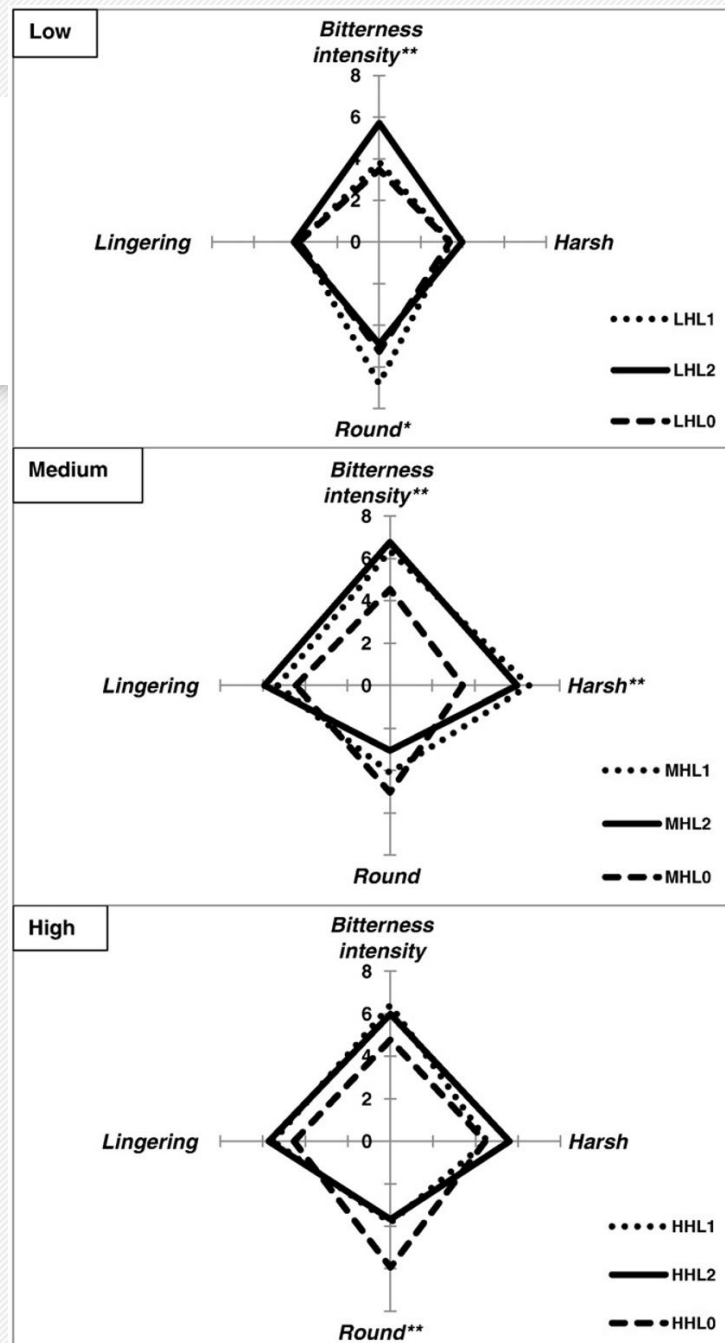


Fig. 1. Spider plots of mean bitterness intensity and bitter character based on intensity ratings. Low: (13 BU) beer, Medium: (25 BU) beer and High: (42 BU) beer. L0, L1 and L2 at each BU level corresponds to hop aroma extract addition levels of 0, 245 and 490 mg/L. Significance denoted at *5% and **1% level.

Time Intensity

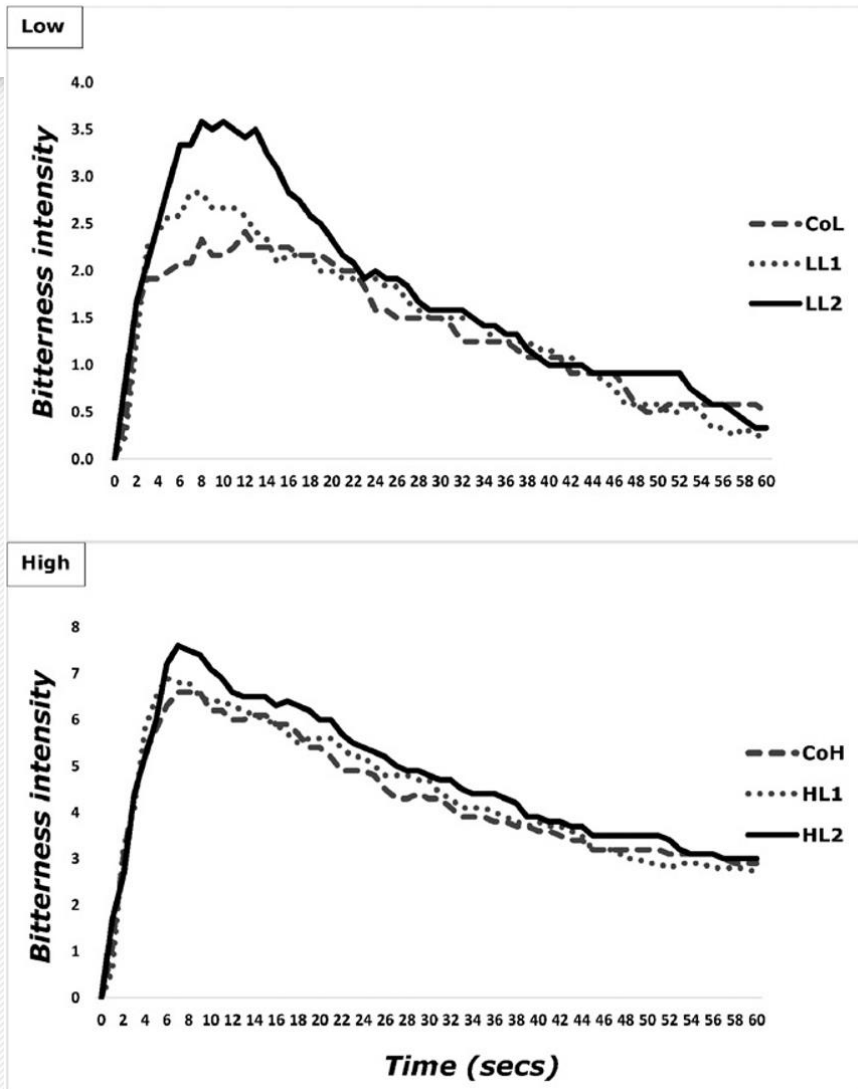


Fig. 4. Average time-intensity curves. Low: (13 BU) beer and High: (42 BU) beer. CoL and CoH, LL1 and HL1, LL2 and HL2 correspond to hop aroma extract addition levels of 0, 245 and 490 mg/L respectively. Significance at 5% level.

Summary

- Many contributors to the IBU
- Hopping Product and Technique affects IBU
- The IBU \neq PPM IAA
- IBU method does not work as well with highly hopped beers
- Sensory Bitterness not linear correlation to IBU
- Other beer attributes confound bitterness

Questions?

Thank you for your time and attention!

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