



Bitterness intensity of hop acid oxidation products - humulinones and hulupones

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Humulinones and Hulupones

1. Previous research
2. Origin and chemical structure
3. Sensory Bitterness in comparison to iso- α -acid
4. Impact on beer flavor

Why humulinones & hulupones?

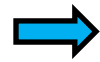
⇒ *humulinones & hulupones are in your beer.*

Commercial Beer Survey

humulinones

hulupones

10 Lagers



5 of 10

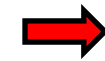


0 of 10

4 Amber-Reds

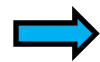


4 of 4



2 of 4

4 Pales



4 of 4



2 of 4

4 IPAs



4 of 4



3 of 4

17

7

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1955

COOK, HOWARD, SLATER

Produces humulinones.
"bitter".

1964

WHITEAR, HUDSON

Humulinones 35% as bitter as iso
 α acids.
"Very little is known of their
importance in beer flavour."

1987

VICTOR ALGAZZALI



2009

HASELEU, INTELMAAN, HOFMANN

Bitterness threshold of 12
oxidized beta compounds
Hulupone most bitter. 7.9 ppm.

1950

1960

1970

1980

1990

2000

2010

1973

PALAMAND, ALDENHOFF

Humulinone are "bitter".
Hulupones are "about 50% as
bitter as iso- α -acids."

2013

KROFTA, VBRACOVA, IKYSKA, JURKOVA

"The bittering potential of
oxidation products of beta acids
reaches 35-40% of iso- α -acids."

1960

SPETSIG, STENINGER

Hulupones discovered. Hop cones
contain up to 3%

1961

STEVENS, F.R.I.C., WRIGHT

Hop cones contain only up to 0.5%

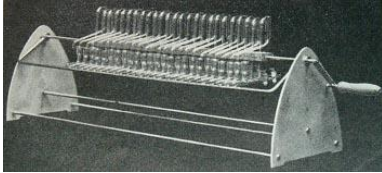
1991

VERZELE, DE KEUKELEIRE

"Hulupone are potentially useful or
not?"
Beer concentration 1 to 2 ppm.

Then and Now

Seperations Chemistry



Sensory Science



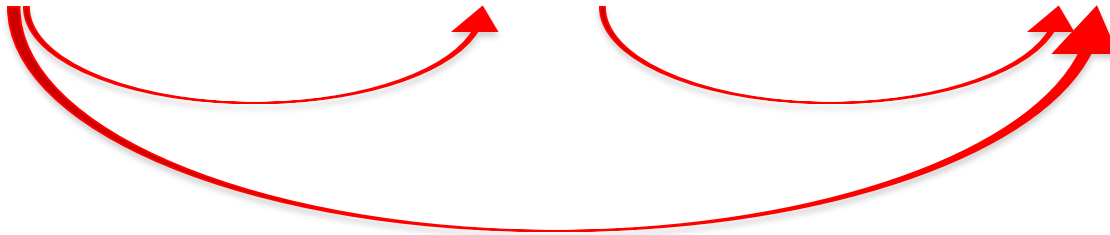
New Brewing Practices



Humulinones and Hulupones

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What is the origin of humulinones and hulupones?



What are Humulinones and Hulupones?

What are

Humulinones and Hulupones?



Humulone



α acid



Hum a song



Lupulone

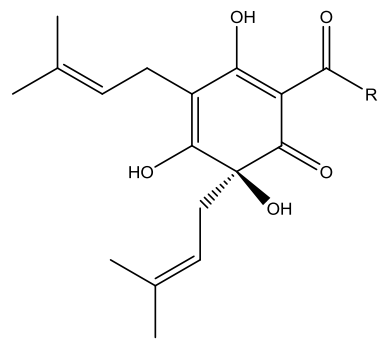


β acid



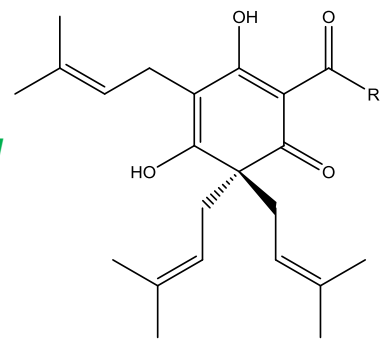
Hulup bastard

humulone



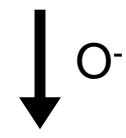
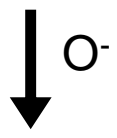
α acid

lupulone



β acid

Heat



oxidized α acid

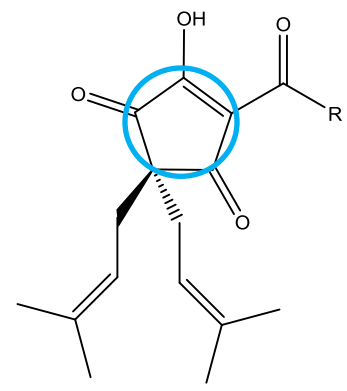
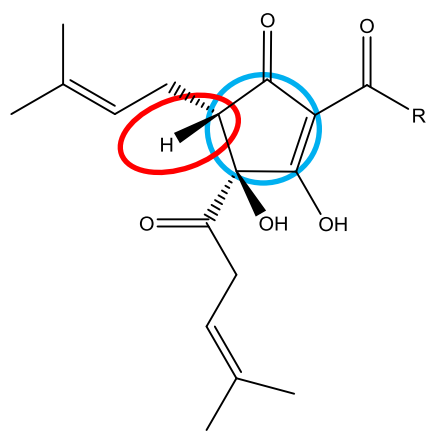
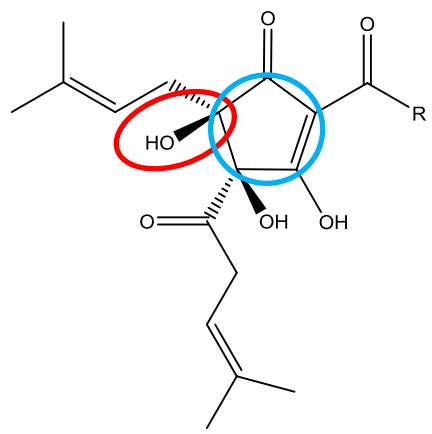
Iso-α-acid

oxidized β acid

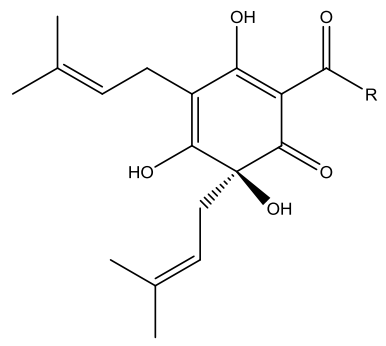
humulinone

isohumulone

hulupone

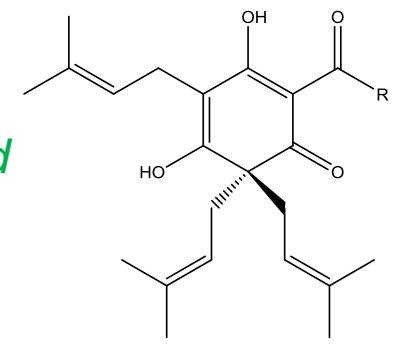


humulone



α acid

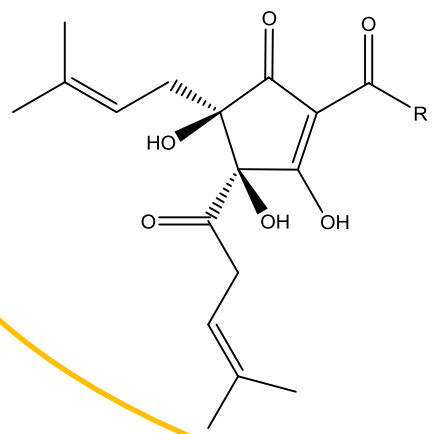
lupulone



β acid

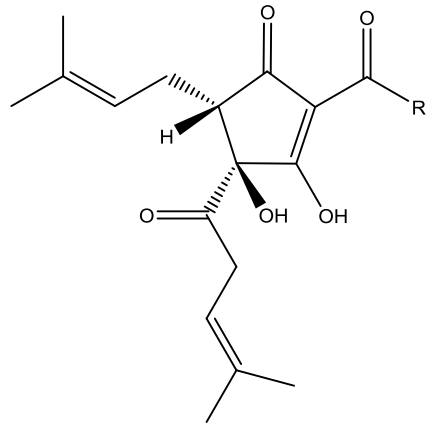
oxidized α acid

humulinone



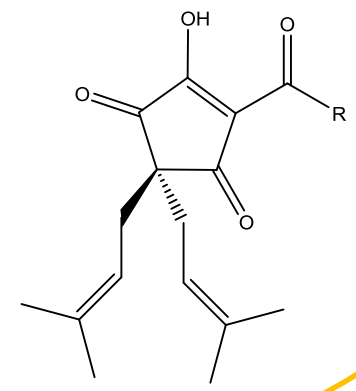
Iso-α-acid

isohumulone



oxidized β acid

hulupone



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The Science of Beer

Methods

humulinone

**Cook, Howard, Slater
1955**



- α -acid, ether, cumene hydroperoxide
- NaHCO_3 bilayer
- Room Temp, 4 days

70% yield

hulupone

**Wright
1963**



- β -acid, ethanol, sodium sulfite
- Continuous oxygen and stirring
- Room Temp. 24 hours

10% yield

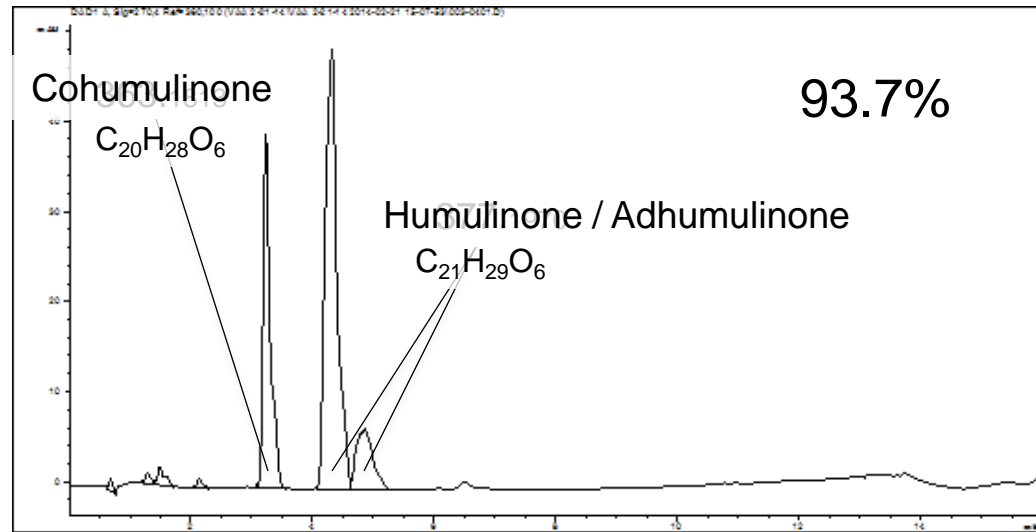
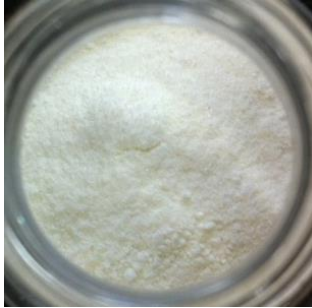
Purification



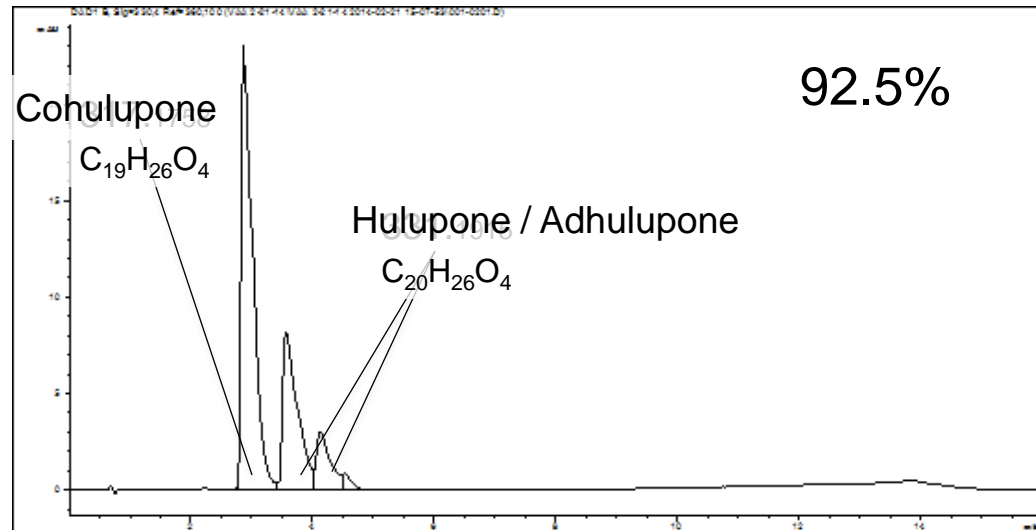
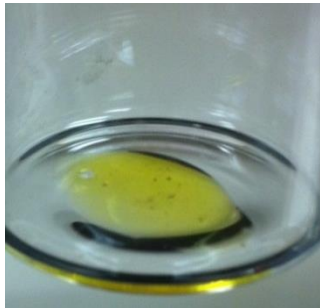
Purification



Humulinone



Hulupone



Safety Testing



Mercury

5

Label

3

10.

2.5

0.2



Unhopped Lager Beer preparation

150 gallons unhopped lager

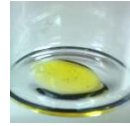
- 2-row pilsner malt and 30% high glucose adjunct
- Wyeast lager strain #2007
- 5% ABV and 2.5% RE



Humulinone



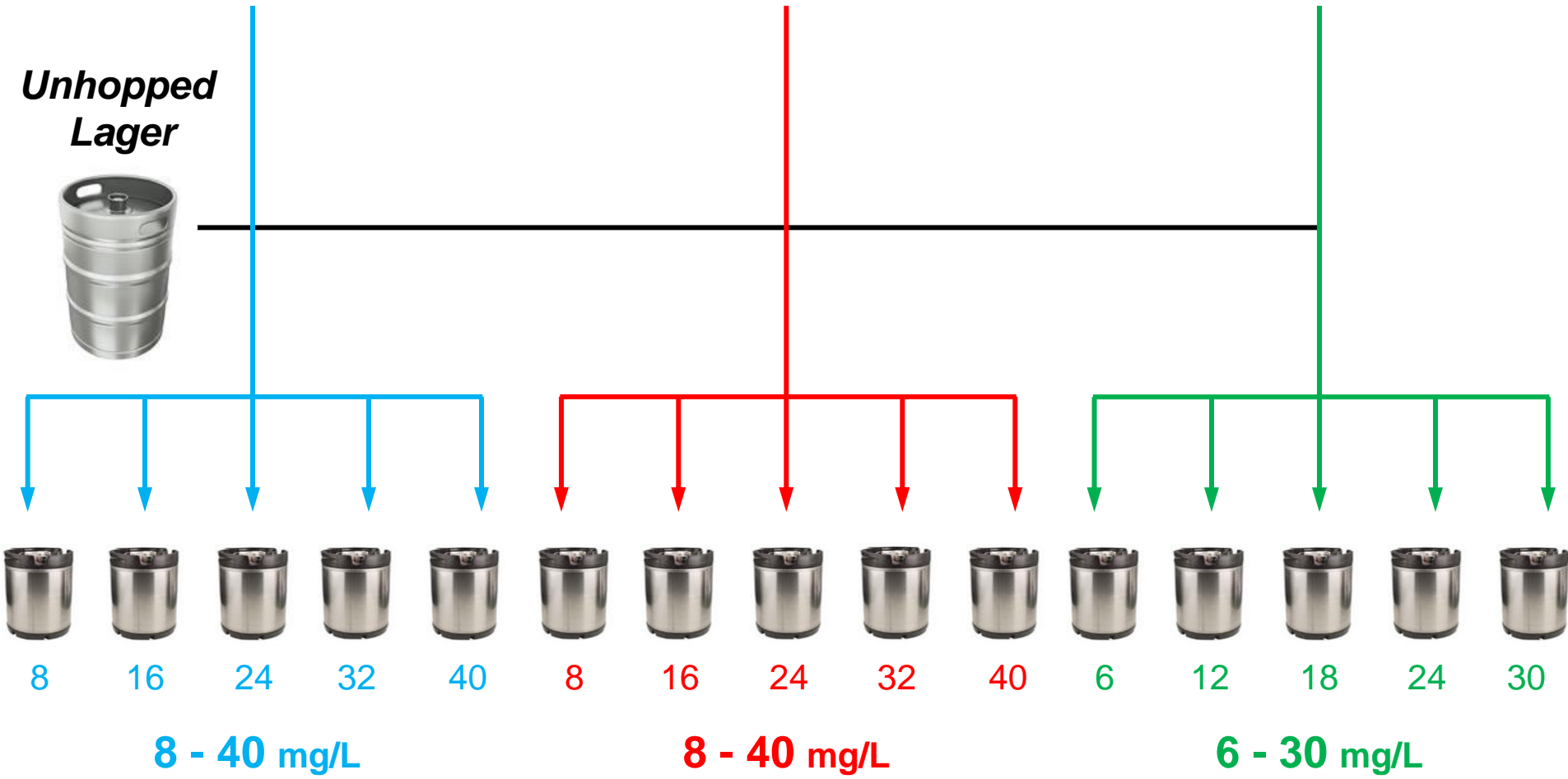
Hulupone



Isohumulone



Unhopped Lager



Sensory Testing

16 samples

- 5 humulinone
- 5 hulupone
- 5 isohumulone
- 1 unhopped lager

Blocked by hop acid

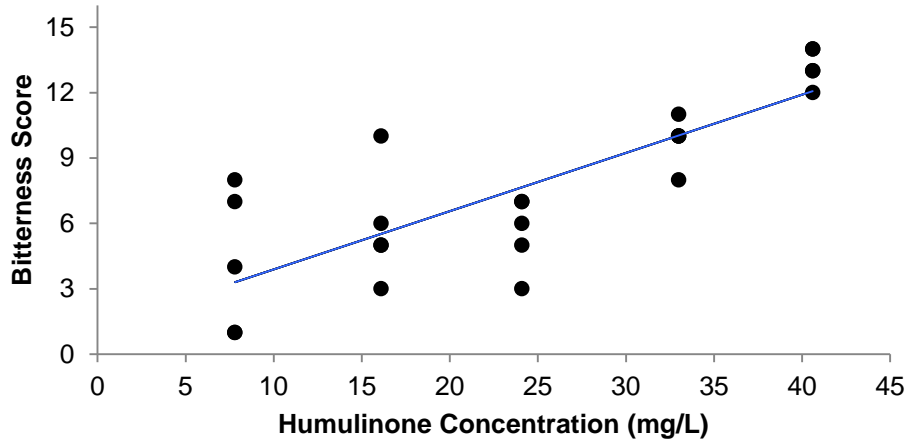


Rate ***Bitterness Intensity*** on a 0-15 scale

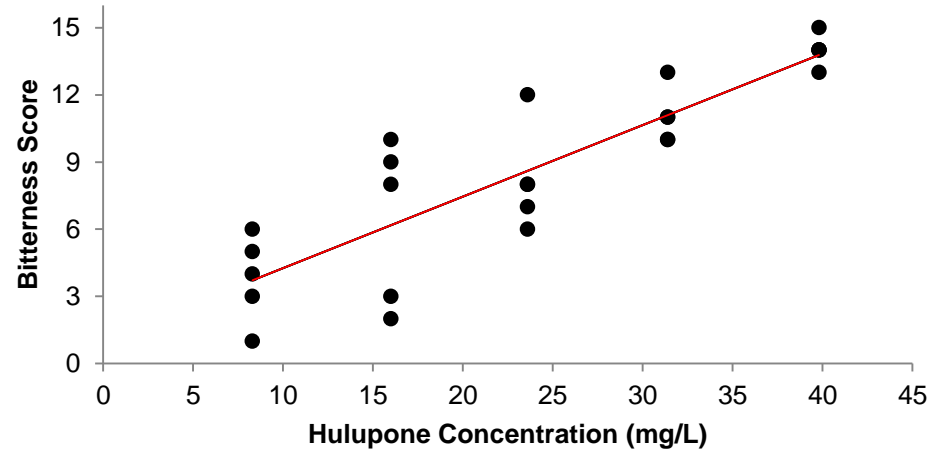
- 9 panelist
- 5 replications

Statistical analysis

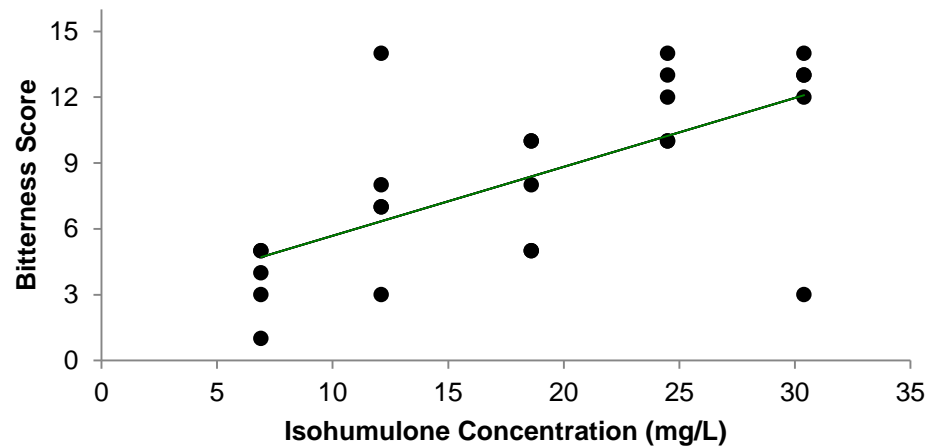
Humulinone



Hulupone

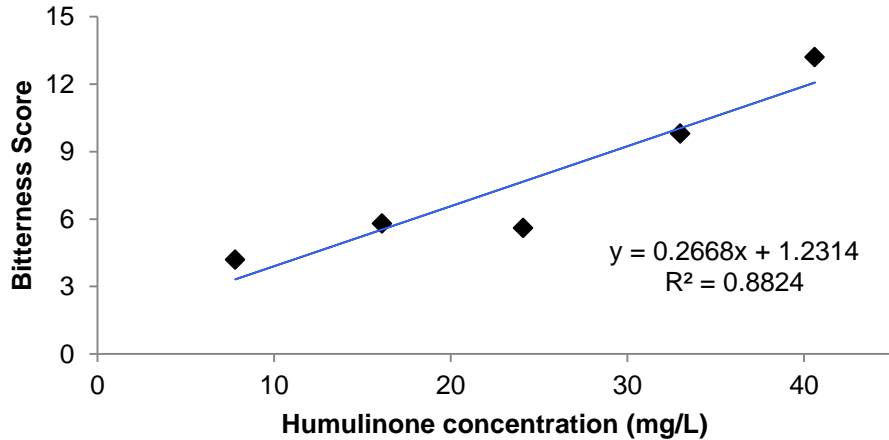


Isohumulone

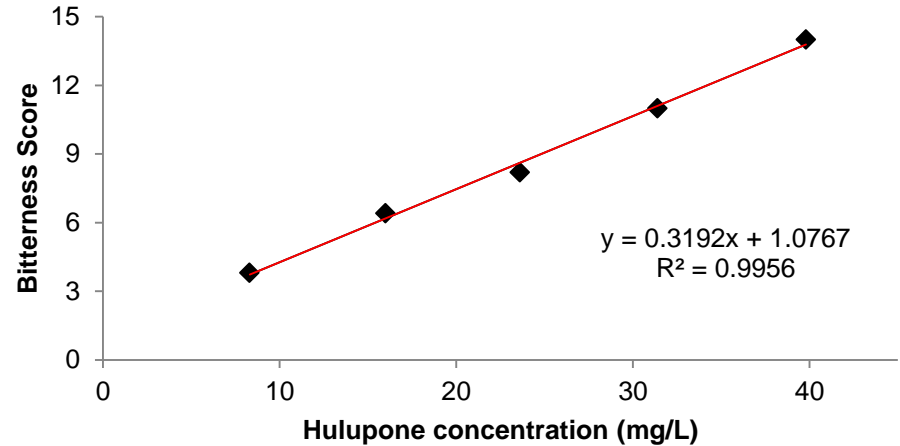


Statistical analysis

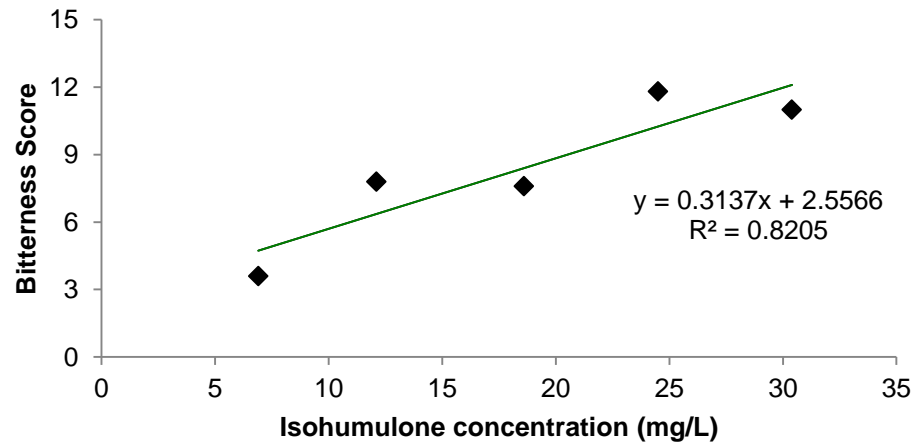
Humulinone



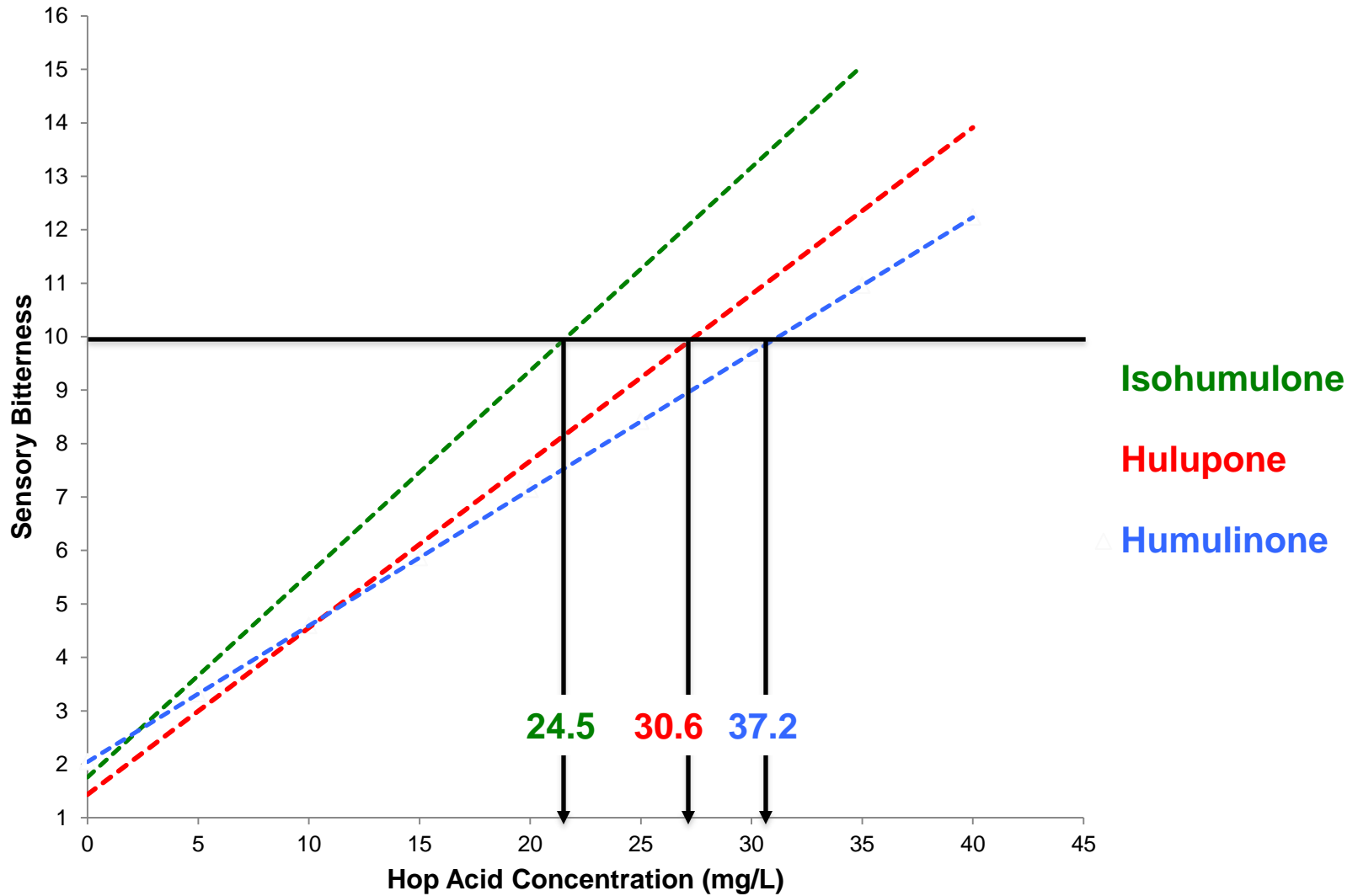
Hulupone



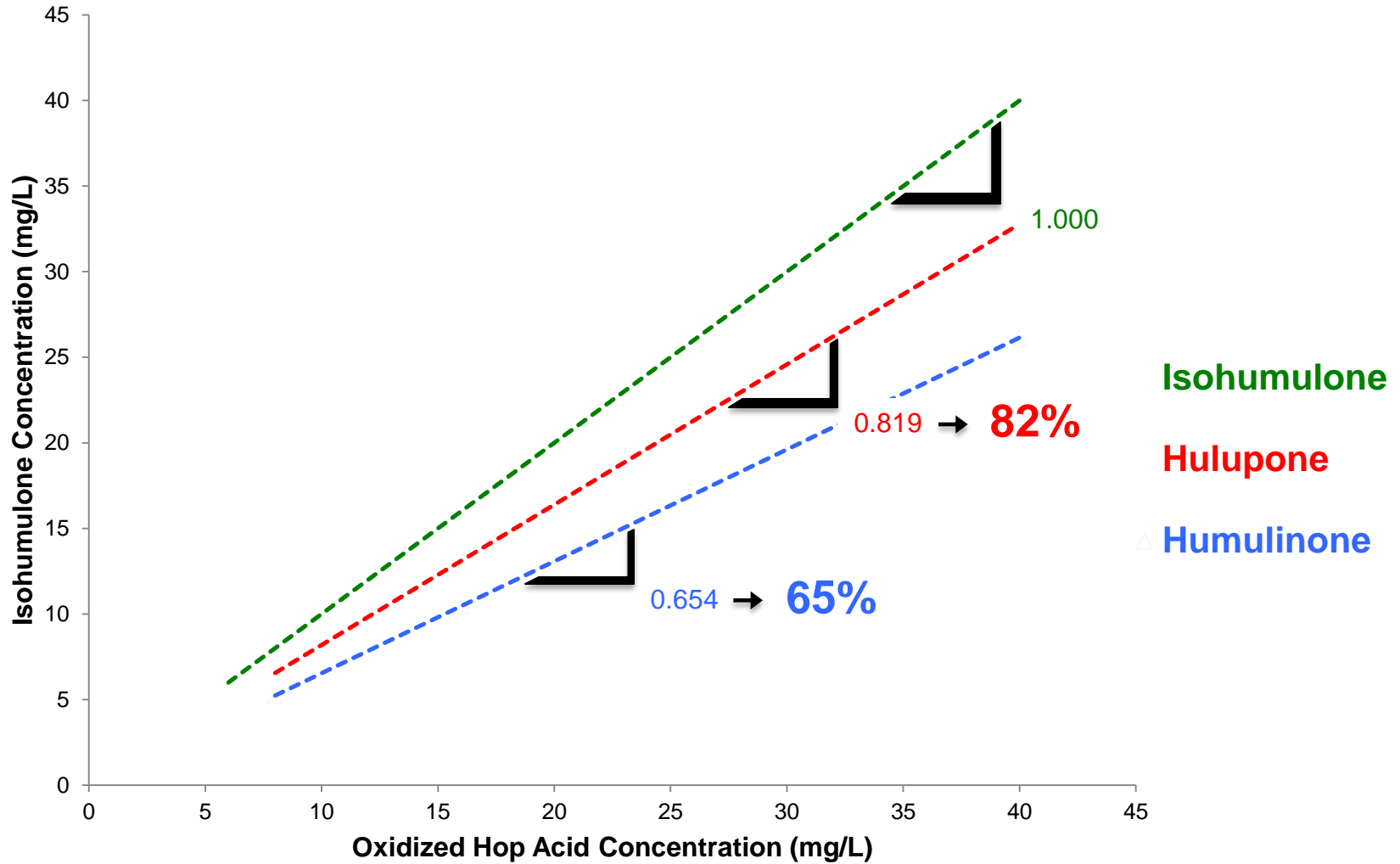
Isohumulone



Comparison of Hop Acids: Sensory Bitterness vs. Concentration



Humulinone and Hulupone Concentrations at Equal Bitterness Intensity to Isohumulone



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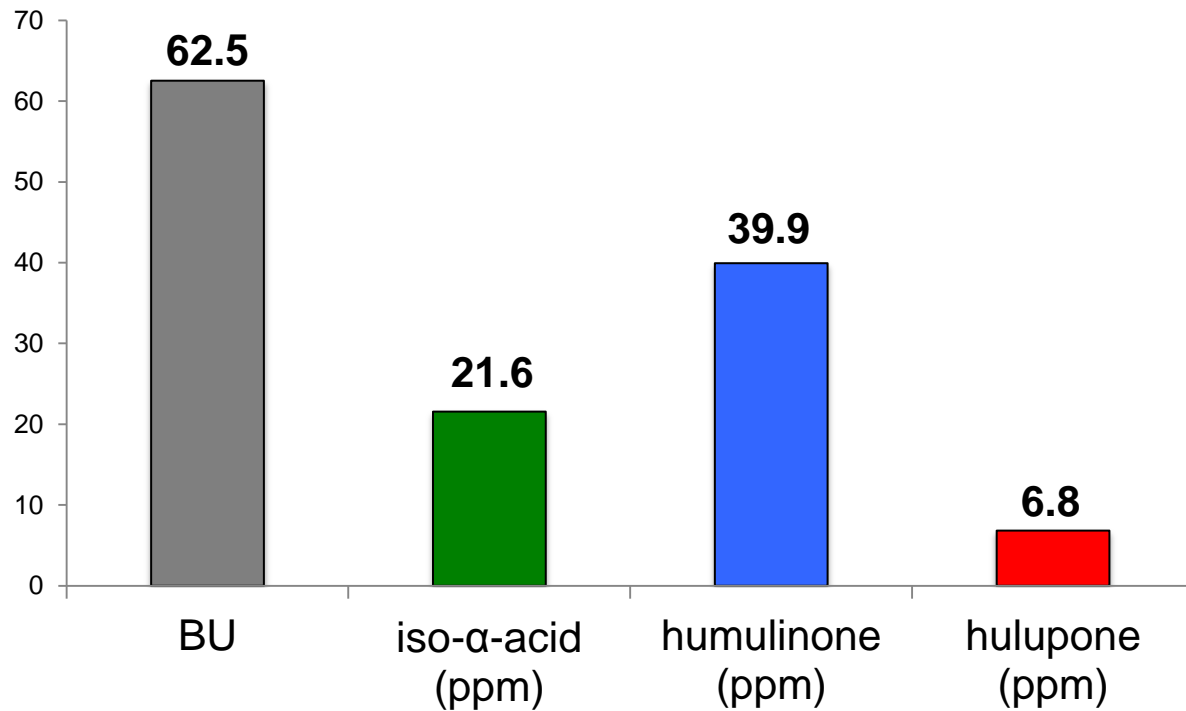
Commercial Beer Survey

humulinones
average (mg/L)

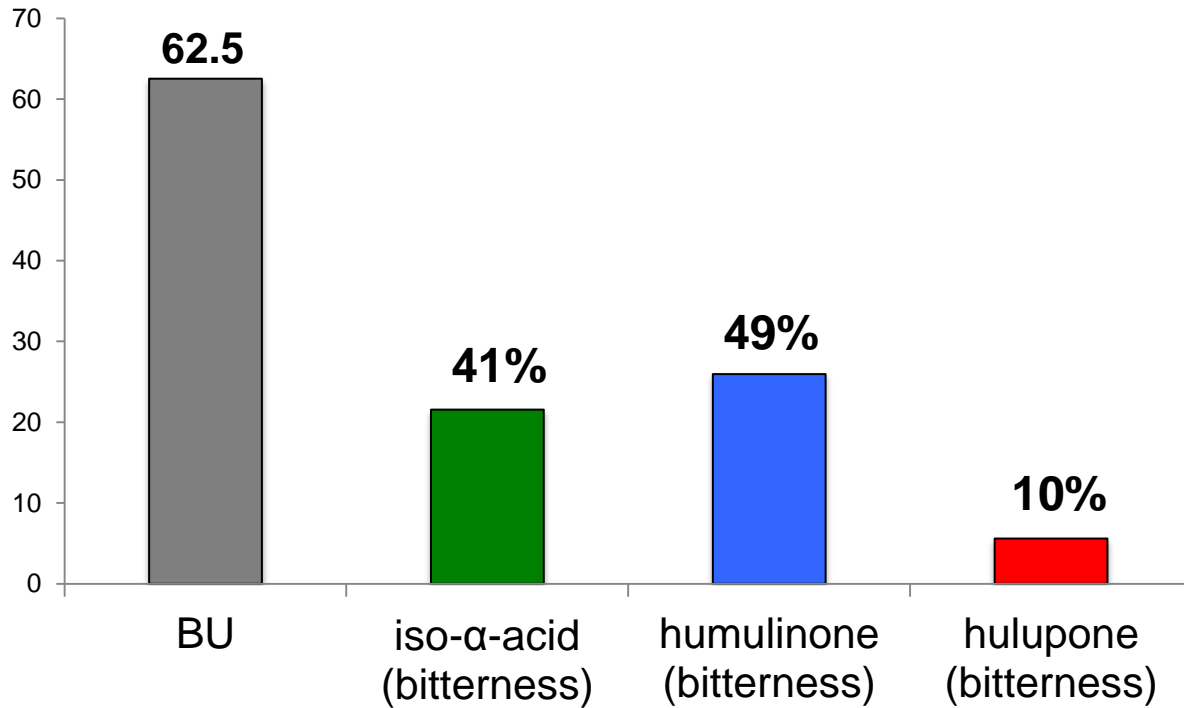
hulupones
average (mg/L)

10 Lagers	1.3 _(0, 4.4)	0.0 _(0, 0)
4 Amber-Reds	14.4 _(1.7, 39.9)	2.0 _(0, 6.8)
4 Pales	8.2 _(3.0, 12.9)	0.8 _(0.0, 1.7)
4 IPAs	20.7 _(11.7, 27.9)	1.8 _(11.7, 27.9)

Example: *Amber-Red 2*



Example: *Amber-Red 2*



Conclusion

- Hulupones are ~ 82% as bitter as iso- α -acids
 - Small impact
 - Not very abundant
- Humulinones are ~ 65% as bitter as iso- α -acids
 - Large impact
 - Abundant
- *alpha* acid oxidation
- other oxidized *beta* acids
- oxidized hop acid formation during the brewing process

Thank you