

Brewing Summit 2014

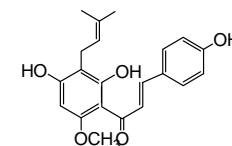
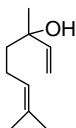
MBAA Fundamentals Track - Hops !

Hop Chemistry 101

Dr. John Paul Maye

Technical Director

Hopsteiner





Hops contribute bitterness, aroma, foam, lacing, antibacterial protection, and antioxidant protection to beer.

Lupulin Glands

Alpha Acids

Beta Acids

Essential Oils

Prenylated Flavanoids

Bract

Glycosides

Polyphenols



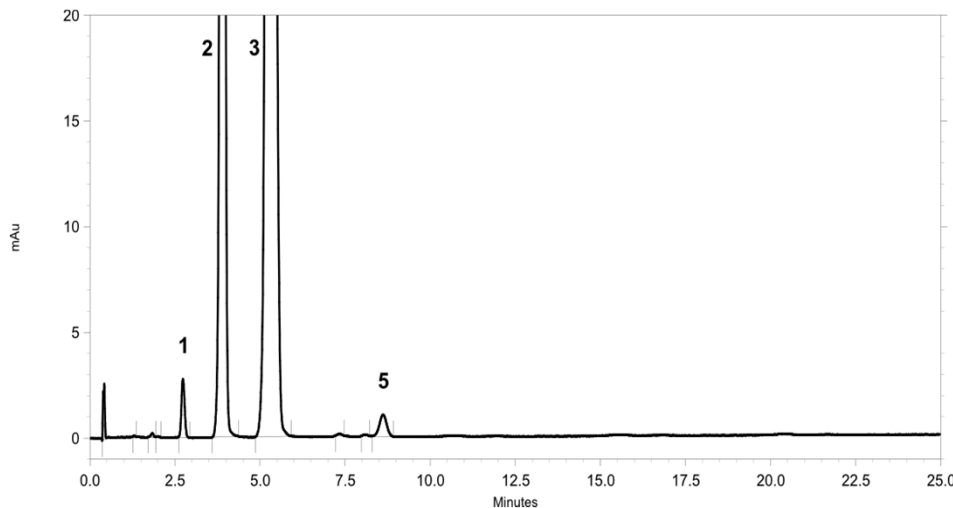
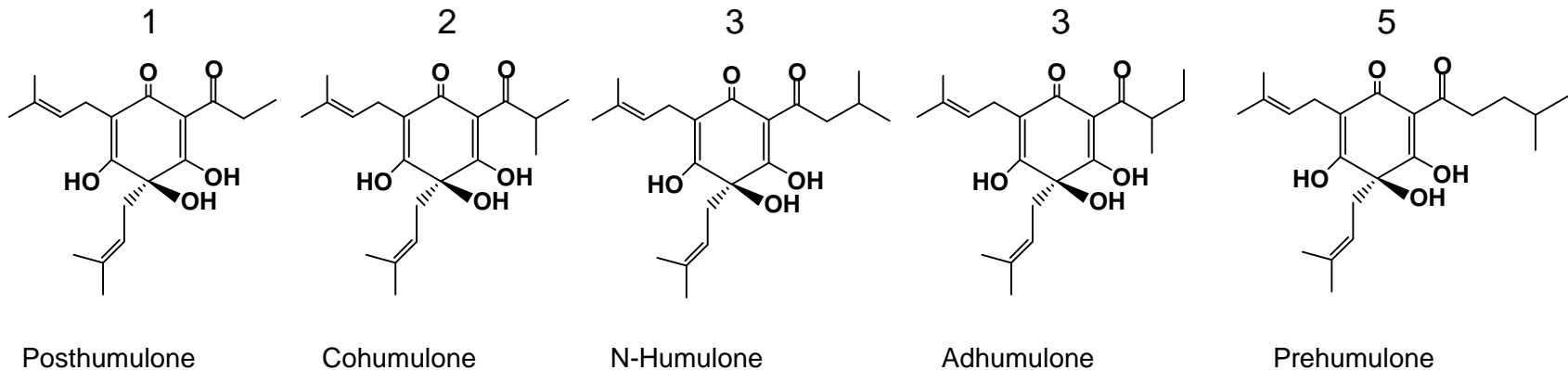


Compounds Found In the Lupulin Gland And Their Chemistry





The Five Alpha Acids

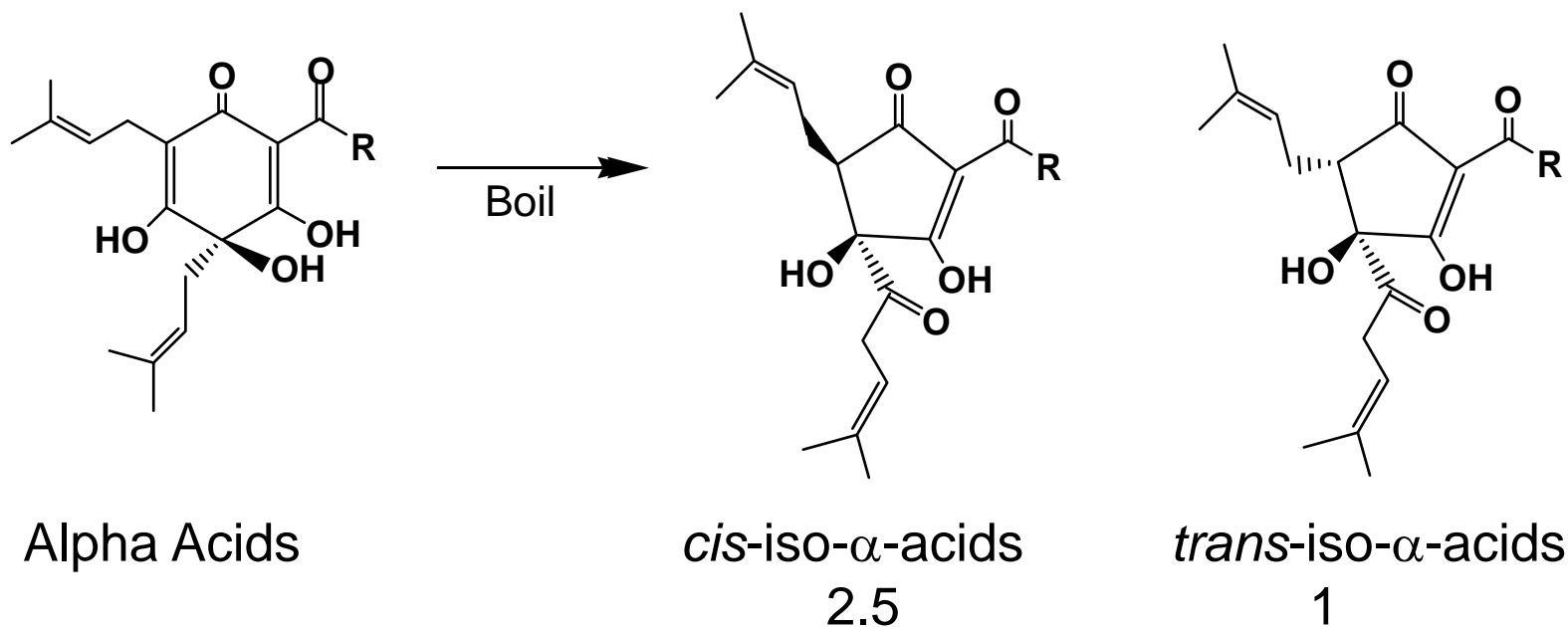


Properties

Found 2% - 20% w/w in hops
Flavor Threshold ~ 16 ppm
Foam Enhancing at 4-5 ppm
Improves Lacing at 4-5 ppm
Antibacterial



The Isomerization of Alpha Acids to Iso-Alpha Acids



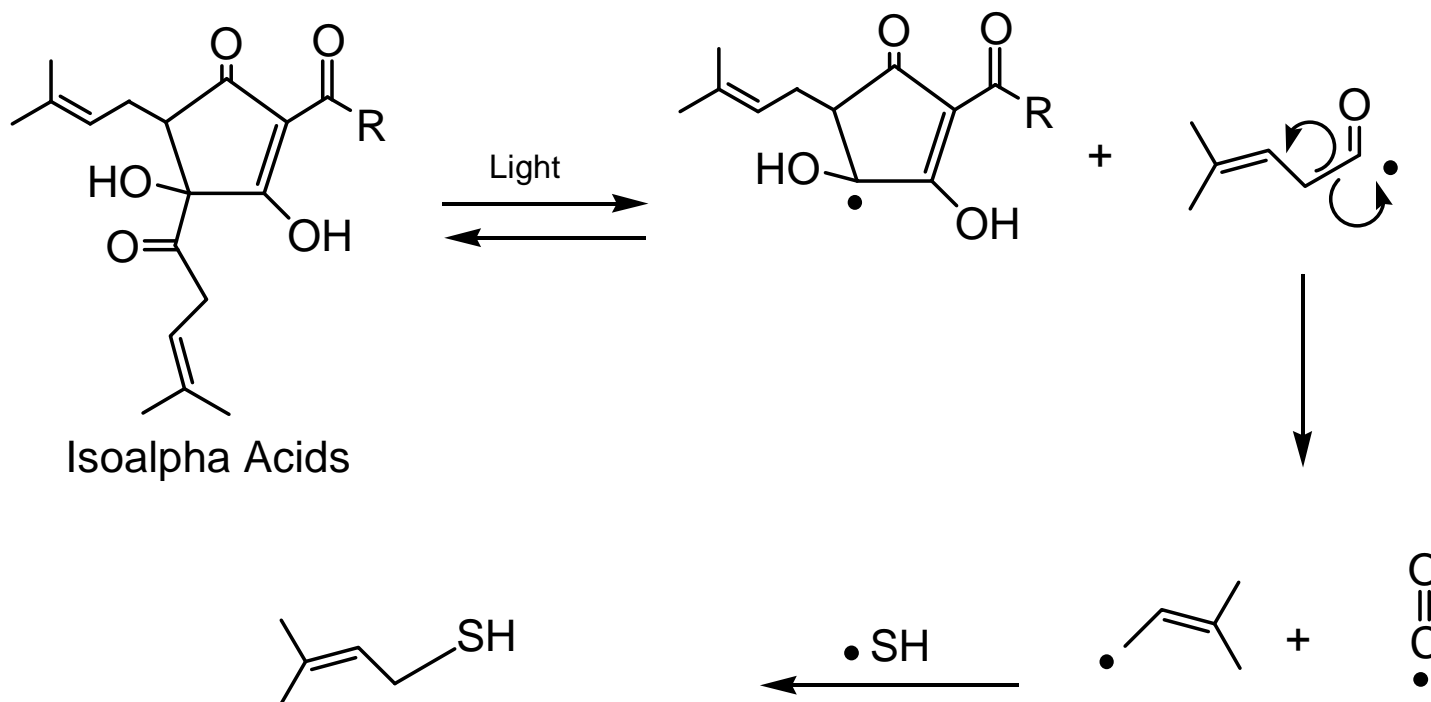
Brew Kettle Efficiency: 25% to 40% isomerized

Flavor Threshold: ~ 4 ppm

Responsible for bitterness, foam, lacing and antibacterial protection during fermentation in beer. Found in beer ~ 4 to ~ 65 ppm.



Iso-alpha Acids Are Not Light Stable



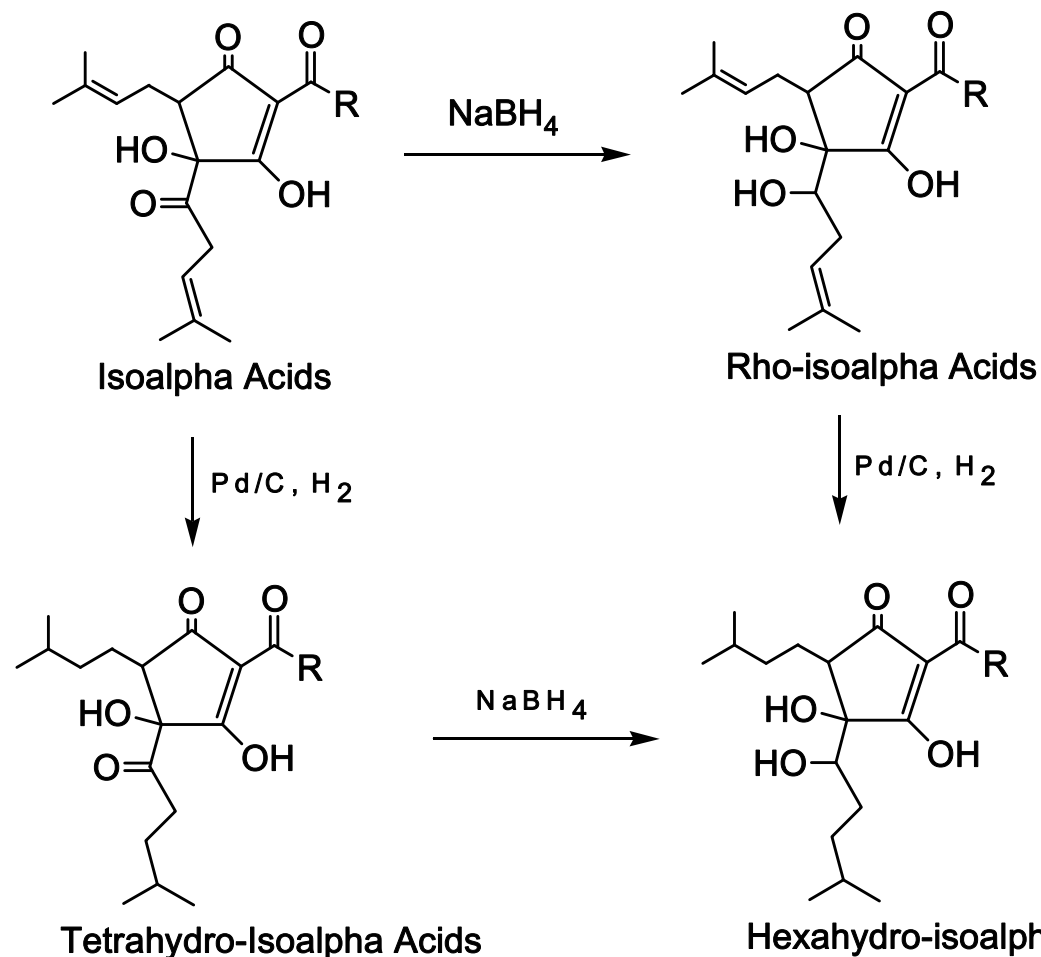
Isoalpha Acids

3-methyl-2-butene-1-thiol

Light-Struck (Skunky, at ppb)



Iso-alpha Acids and Reduced Iso-Alpha Acids



Properties

Light Stable

Different Bitterness

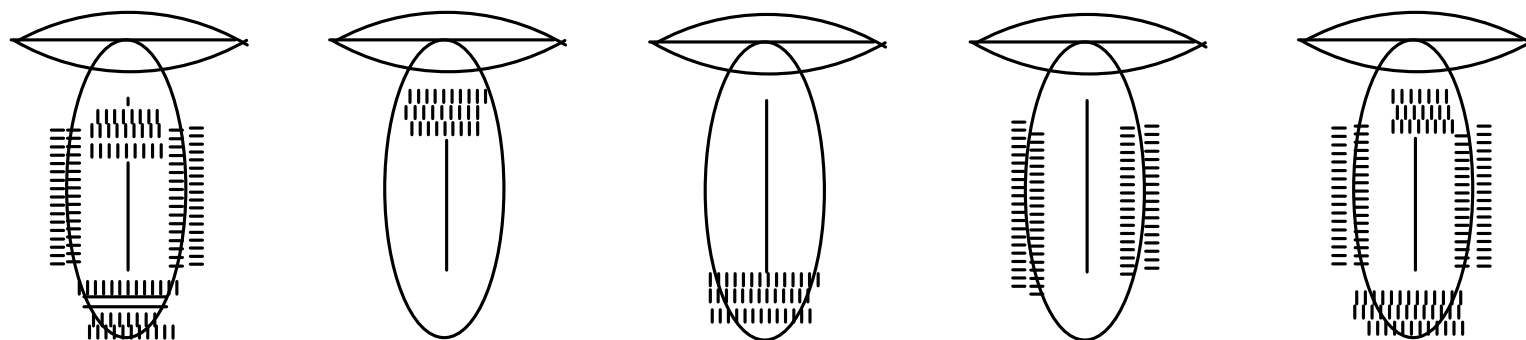
Tetra & Hexa =

Enhance foam &

Lacing & Antibacterial



The Bitterness Profile of Iso-Alpha Acids & Its Derivatives



Isoalpha Acid

1 PPM = 1 IBU

Strong Harsh
All Around the
Tongue Bitterness

Rho-isoalpha

1 PPM = 0.7 IBU

Smooth Back of
the Tongue Bitterness

Tetrahydro-isoalpha

1 PPM = ~ 1 IBU

Sharp upfront
non-lingering

Hexahydro-isoalpha

1 PPM = ~1 IBU

Harsh side of the
Tongue Bitterness

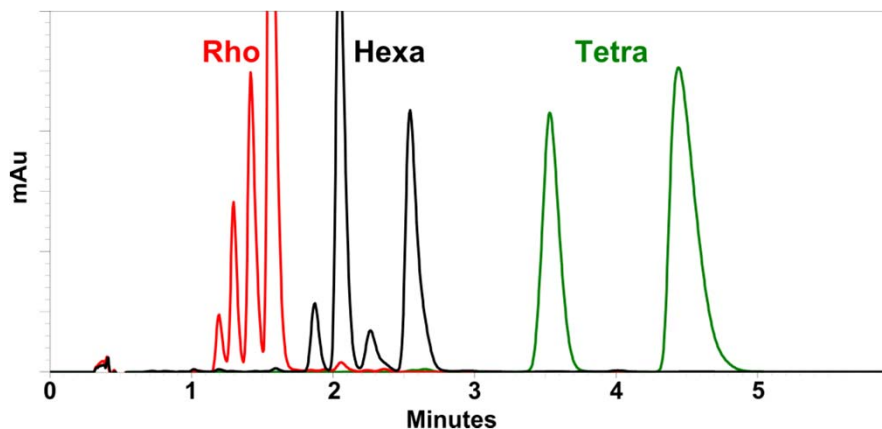
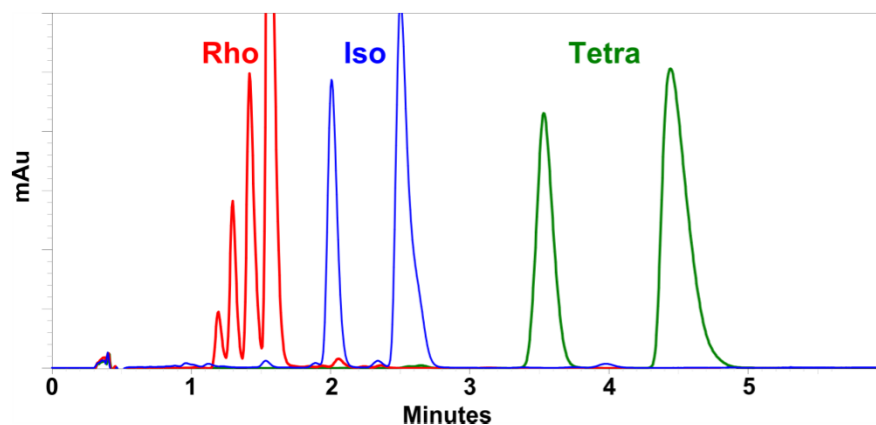
7 RIAA:1THIAA:1HHIAA

1 PPM = 0.9 IBU

Isoalpha Acid like
Bitterness, Light Stable
Improved Foam

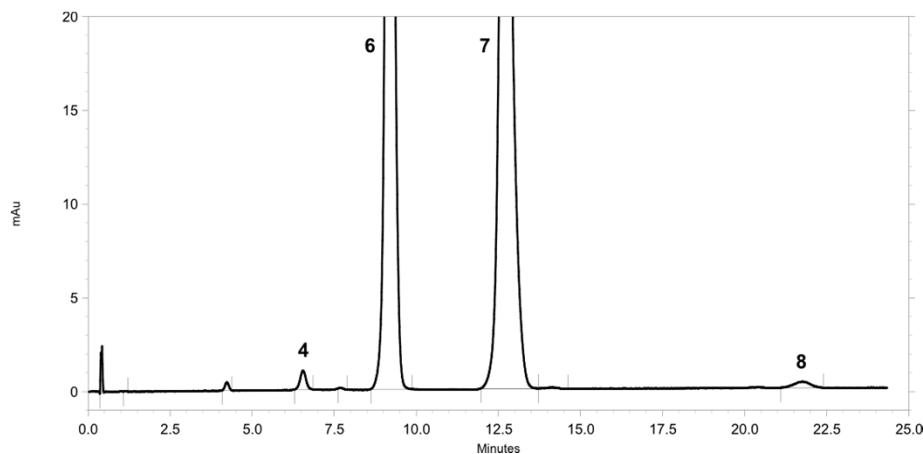
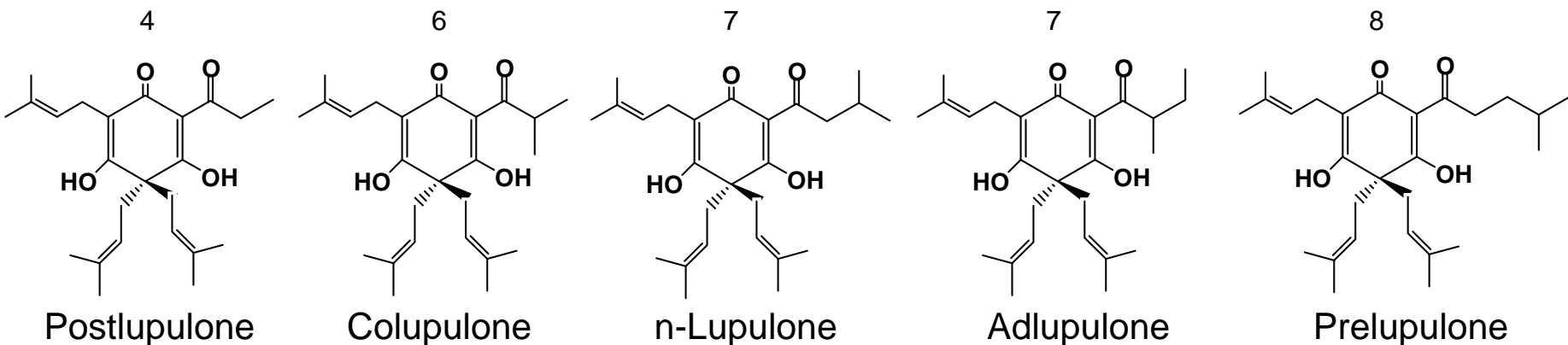


HPLC Allows Quantitative Analysis of Beers Made With Multiple Hop Acids





The Five Beta Acids

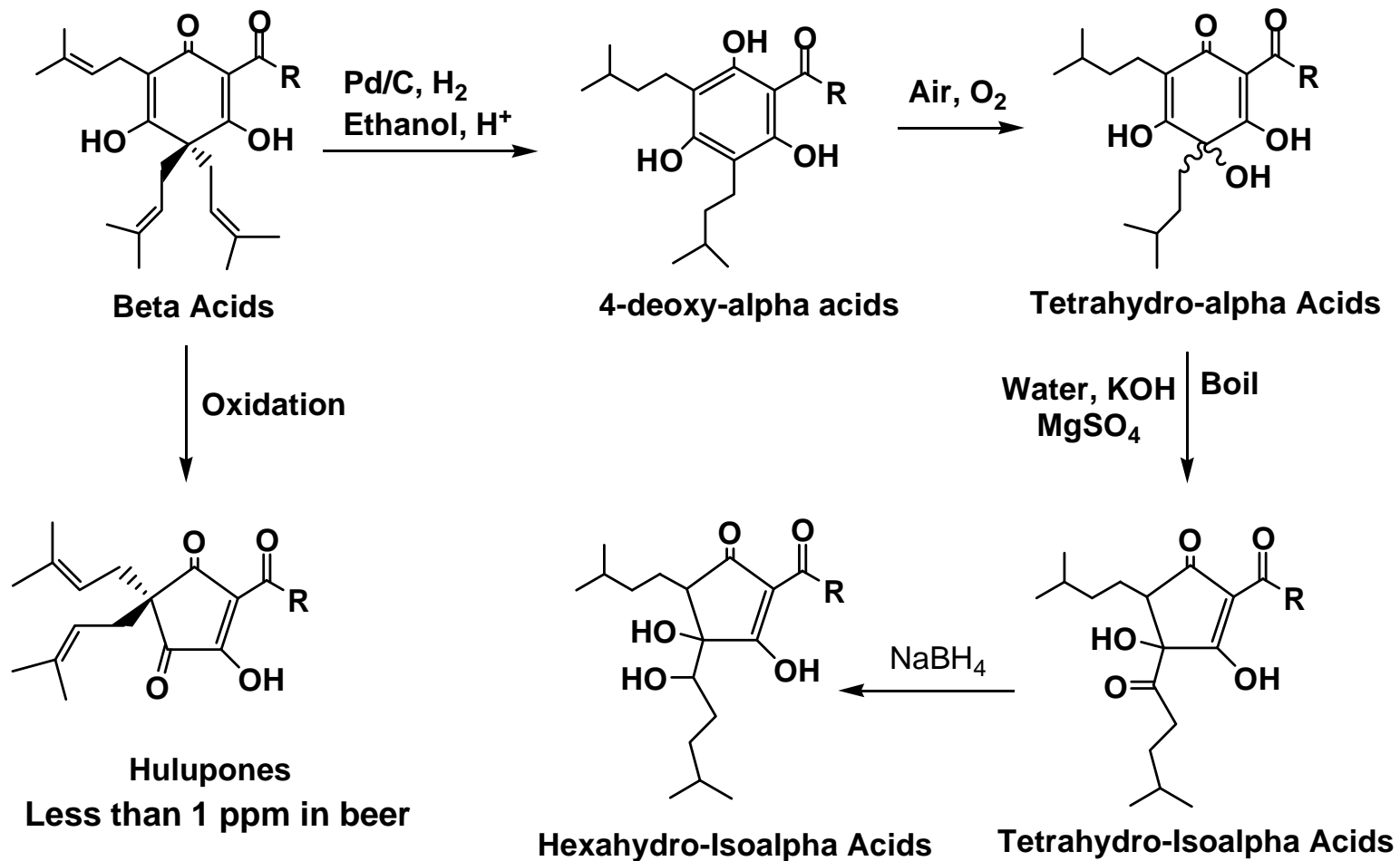


Properties

Found in Hops 2-8% w/w
Solubility in beer < 0.5 ppm
Very Antibacterial
Flavor Threshold ~ 20 ppm



Beta Acid Chemistry





The Antibacterial Properties of Hop Acids

<u>Hop Acid</u>	<u>MIC (ppm)</u>
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Beta Acid	0.5
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Alpha Acids	2
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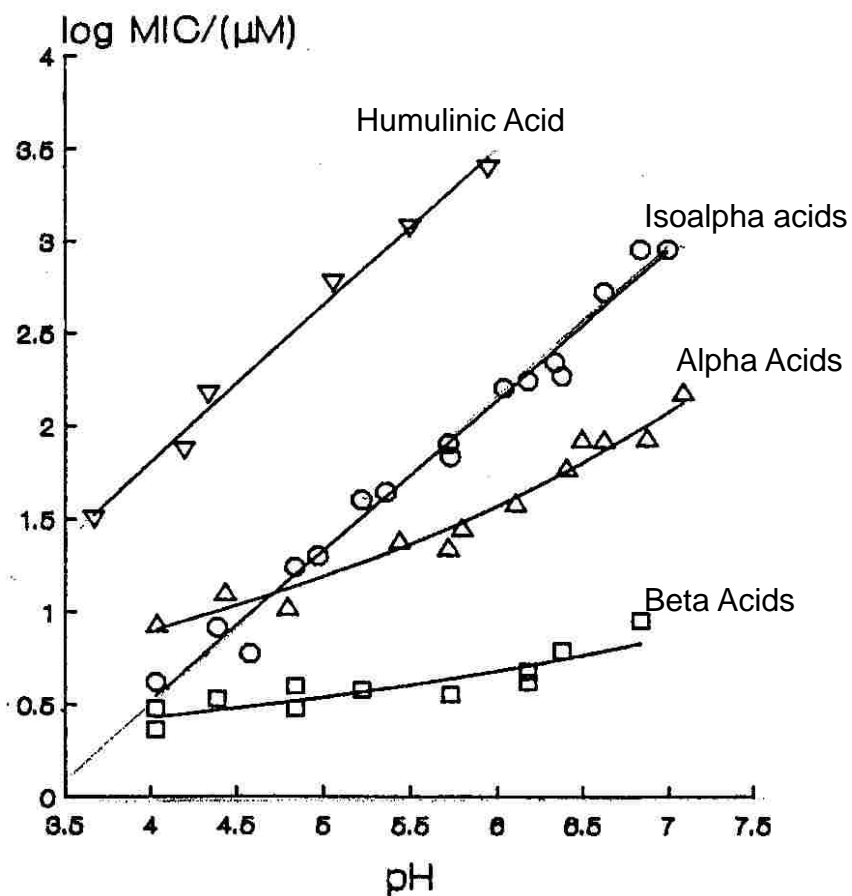
Iso-alpha Acids	8
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Tetrahydro-IAA	4
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Hexahydro-IAA	4
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Rho-IAA	12
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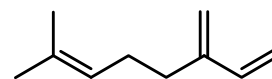
Effective against gram+ bacteria only!



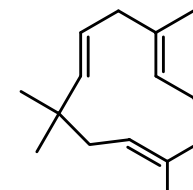


Hop Oil and Hop Aroma

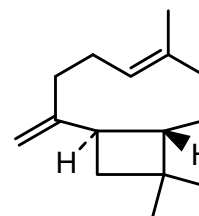
	<u>Area % by Steam-Distilled</u>
1 α -Pinene	0.06
2 β -Pinene	0.60
3 Myrcene	45.53
4 Limonene	0.28
5 Copaene	0.24
6 Linalool	0.76
7 Caryophyllene	9.23
8 Methyl dec-4-enoate	0.79
9 Farnesene	0.00
10 Humulene	32.00
11 β -Muurolene/cadinene	0.82
12 Selinene	0.34
13 β -Cadinene	1.52
14 α -Cadinene	0.88
15 Geranyl acetate	0.13
16 Geranyl isobutyrate	0.28
17 Geraniol	0.08
18 Caryophyllene oxide	0.17
19 Humulene monoepoxide I	0.16
20 Humulene monoepoxide II	0.67
21 Humulene diepoxide A	0.12
Humulene/ Caryophyllene ratio	3.47
(corrected for relative response)	3.80
Oil content (% , v/w)	0.9



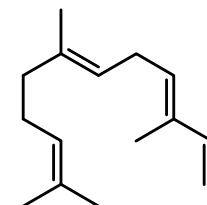
Myrcene



Humulene



Caryophyllene



Farnesene

Properties

Found in Hops 0.5 – 3 mL/100g

Over 250 identified hop oil compounds

Less than 10 ppm found in beer

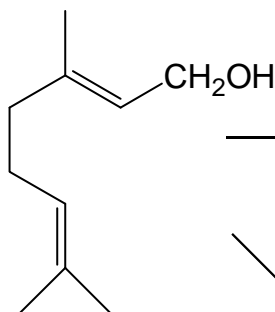
Citrus, Floral, Spicy, Herbal

Transformed by yeast & oxidation

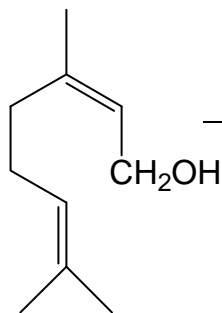
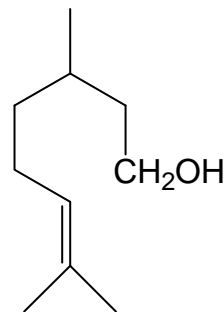


Biotransformation of Hop Oil By Yeast

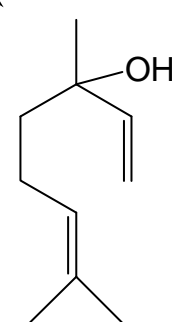
Geranol



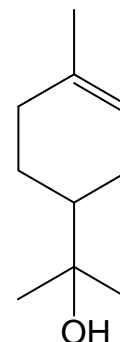
β -Citronellol ~ 0% in hops and wort...



Nerol



Linalool



α -Terpineol

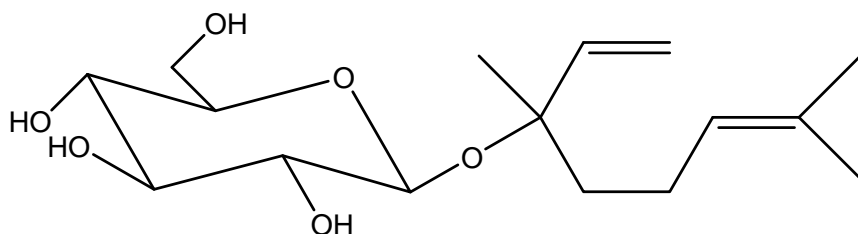
Yeast can produce over 500 aroma and flavor Compounds !



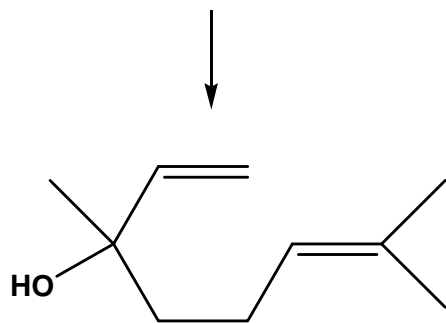
Compounds Found In The Bract And Their Chemistry



Glycosides and Hop Aroma



Linalool Glycoside



Properties

Glucose – Aromatic Compounds

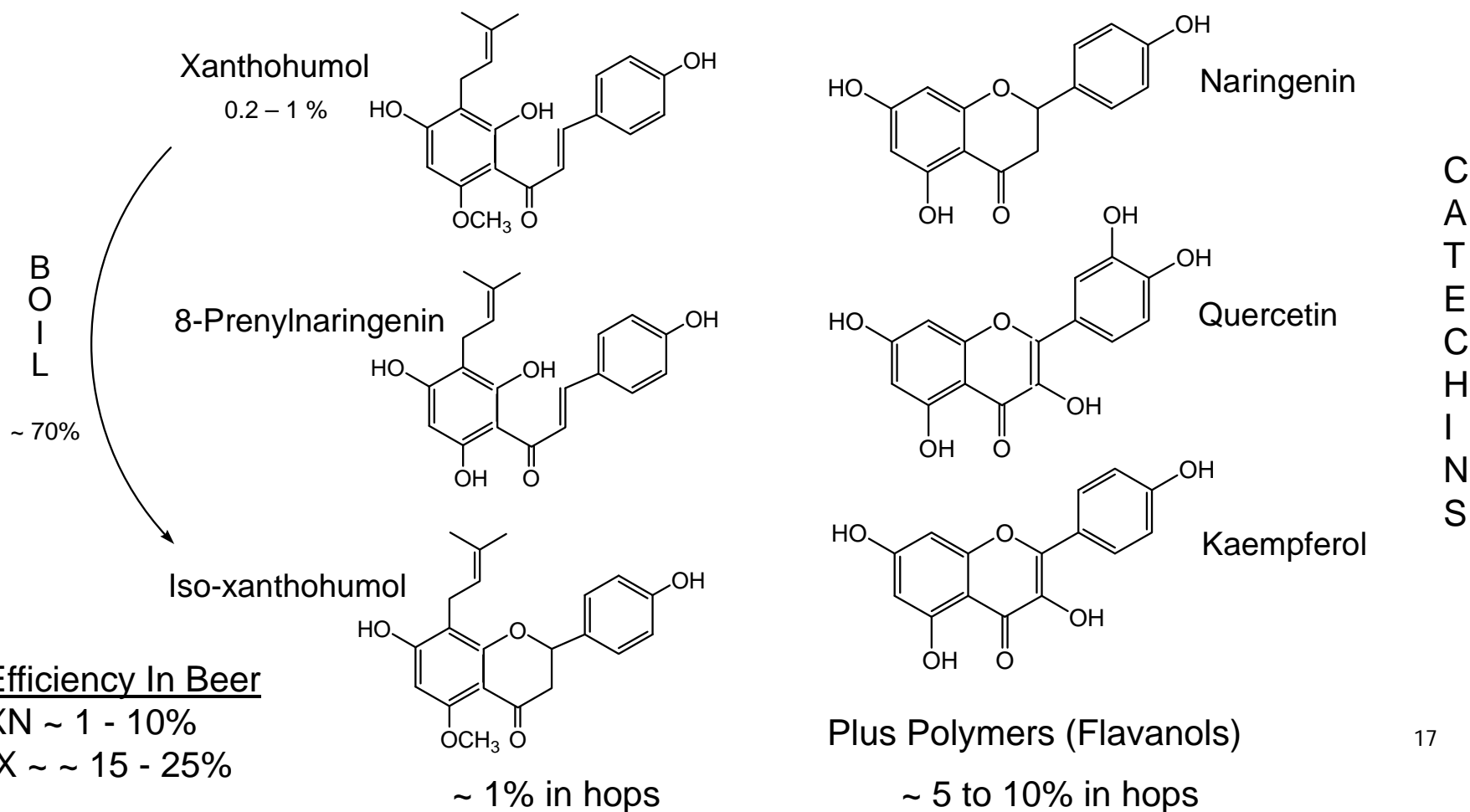
Water Soluble

Hydrolysis by yeast enzymes
or acid and heat.

Glycosides of linalool, geranoil, nerol, vanillin, benzaldehyde, phenylacetate as well as many other ketones, aldehydes and alcohols have been discovered.



Prenylated Polyphenols (Lupulin) & Polyphenols (Bract) - Antioxidants





EPR Spectroscopy & Hydroxyl Free Radicals

EPR is used to measure the antioxidant content of beer. Oxidative staling of beer occurs by free radicals. Hydroxyl free radicals rapidly oxidizes compounds in beer and catalyzes further radical reactions which results in cardboard-like flavor and staling of beer, thus shortening shelf-life.

HORAC – Hydroxyl Radical Scavenging Capacity

<u>Compound</u>	<u>Antioxidant Capacity</u> ($\mu\text{mol Trolox/g}$)
Grape OPC Extract	11,906
Quercetin-(H ₂ O) ₂	5,610
Xanthohumol	72,245
Iso-Xanthohumol	29,600
Alpha Acids	1,230
Beta Acids	2,115
Iso-alpha Acids	493



Conclusion

The organic acids in hops provide bitterness, foam, lacing and antibacterial protection to beer.

The hop oils, aromatic glycosides along with yeast are responsible for the aroma compounds in beer.

The hop polyphenols are responsible for the antioxidant protection of beer which can improve beer shelf-life.