Hop Chemistry

DISCLAIMER

1) I am not a hop chemist
2) The field of hop chemistry is vast
3) Some of the published science is sloppy
4) Hop flavors and aromas are **subjective**

Why are hops added to beer?

- They add bitterness to balance malt sweetness
- They contribute to foam stability
- Aroma
- Microbiological stability

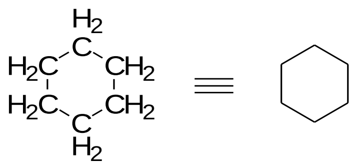
Chemical Composition of Dried Hops

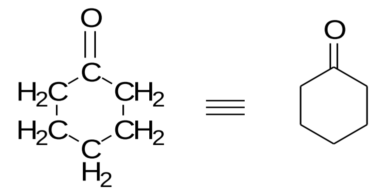
Constituent	Percentage
Water	6-12
Soft Resins	
Alpha acids	2-16
Beta acids	1-10
Essence Oil	0.5-2.5
Hard Resins (Tannins & polyphenols)	2-5
Amino acids	0.1
Simple Sugars	2
Pectin	2
Oils & Fatty acids (unseeded hops)	0-2.5
Protein & non-Cellulose Carbohydrate	15
Ash (Mineral content)	8-10

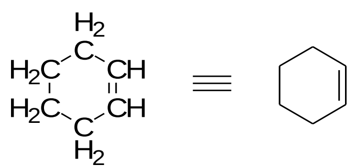
Many chemical compounds are responsible for the properties of hops:

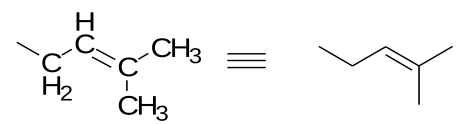
- α-acids (humulones)
- β-acids (lupulones)
- Hop oils (or essential oils)
- Polyphenols (tannins)

An Organic Chemistry Primer—Representing Structures





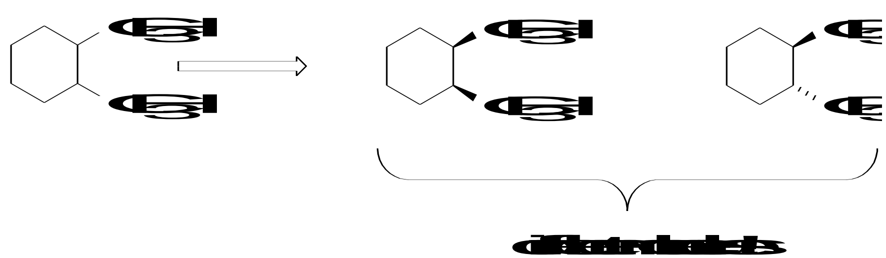




- Lines represent bonds
- Carbon atoms are present where lines intersect or end
- Each carbon will form four bonds
- Heteroatoms (O, N) are shown; hydrogens are implied

An Organic Chemistry Primer—Representing Structures

- Organic molecules are three-dimensional
- This can be represented in two-dimensional drawings using wedge-shaped or dashed bonds
- Molecules that are identical except in three dimensions are called stereoisomers
- Stereoisomers can have different physical properties



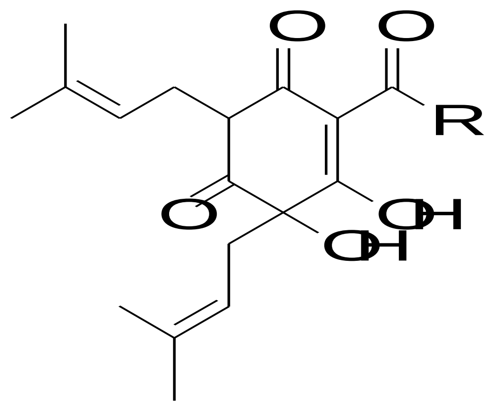
α-Acids

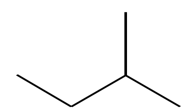
- First isolated as lead compounds in 1887 by German chemists
- Humulone was isolated in 1904 as a pure compound
- In 1925 a structure for humulone was proposed—turned out to be incorrect
- The correct structure was elucidated in 1950

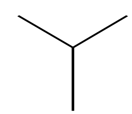
α-Acids

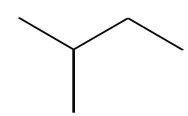
- In 1952 the existence of additional α-acids was proposed
- Cohumulone was isolated in 1952, and the structure confirmed in 1954
- Adhumolone was characterized the same year
- Humulone, cohumulone, and adhumulone make up 95% of the α-acids in hops
- The structural differences between the three major α-acids are relatively small

α-Acid Structures-The Big Three



Humulone R= 

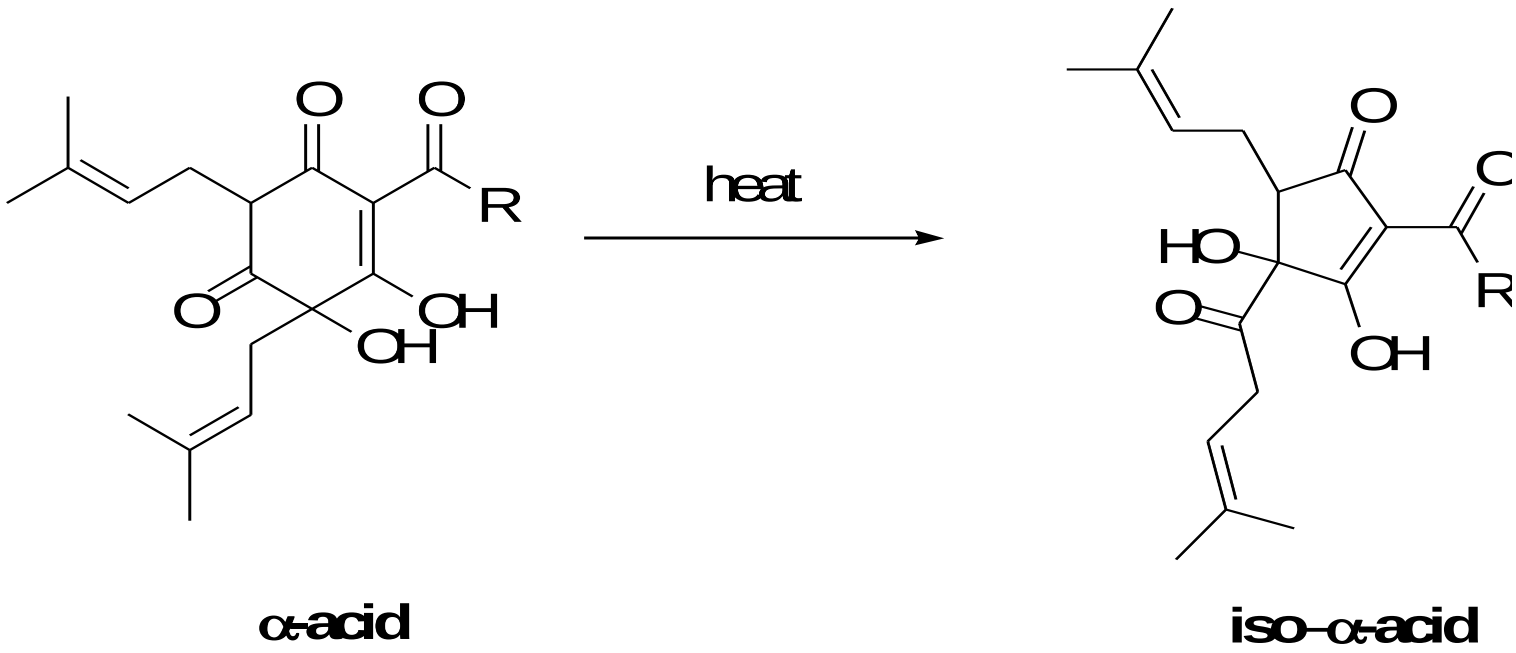
Cohumulone R= 

Adhumulone R= 

α-Acid Isomerization

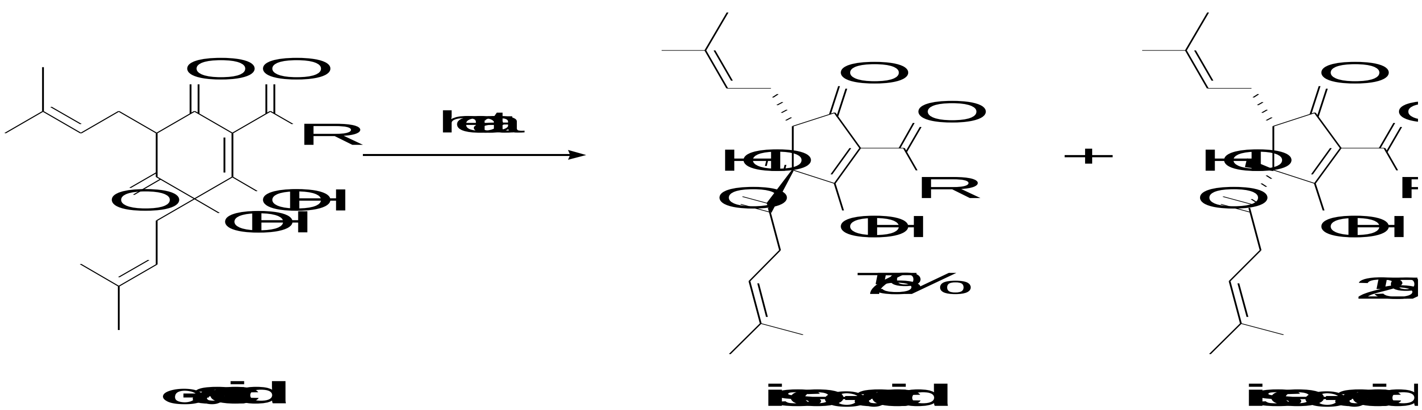
- α-acids are not themselves bitter
- α-acids have low aqueous solubility (pH-dependent)—6 mg/L
- For bittering, α-acids have to be *isomerized*
- This can occur at temperatures >100°C (212°F)
- The higher the pH the faster the isomerization
- Also catalyzed by some metal ions (e.g., Mg)
- Photoisomerization (light) is possible--slow

Structural Changes in Isomerization



Isomerized α-acids

- When an α-acid isomerizes it generates two iso-α-acids
- The two iso-α-acids are stereoisomers and have different properties—bitterness, stability



Isomerized α-acids

- Isomerized α-acids are much more soluble in wort than α-acids
- Maximum conversion from α-acid to iso-α-acid is 60-65% at atmospheric boil
- Utilization is 30-40% (T90 pellets)
- Utilization can be affected by boil time, gravity, pH, oxidation, adsorption, foaming
- More losses occur in fermentation, filtration

Isomerized α-acids

- The concentration of iso-α-acids in beer is low—15-80 ppm (15-80 mg/L)
- But 80% of beer's bitterness is derived from iso-α-acids
- Degradation of the iso-α-acids leads to compounds that aren't as bitter
- This explains the decrease in hoppiness in beers that are mishandled

Isomerized α-acids

- Iso-α-acids are also sensitive to light
- These degradation products are responsible for the skunky taste of light-struck beer
- But iso-α-acids can be chemically modified to increase their stability
- This allows certain macro beers to be packaged in colorless glass bottles instead of amber bottles
- More on this later

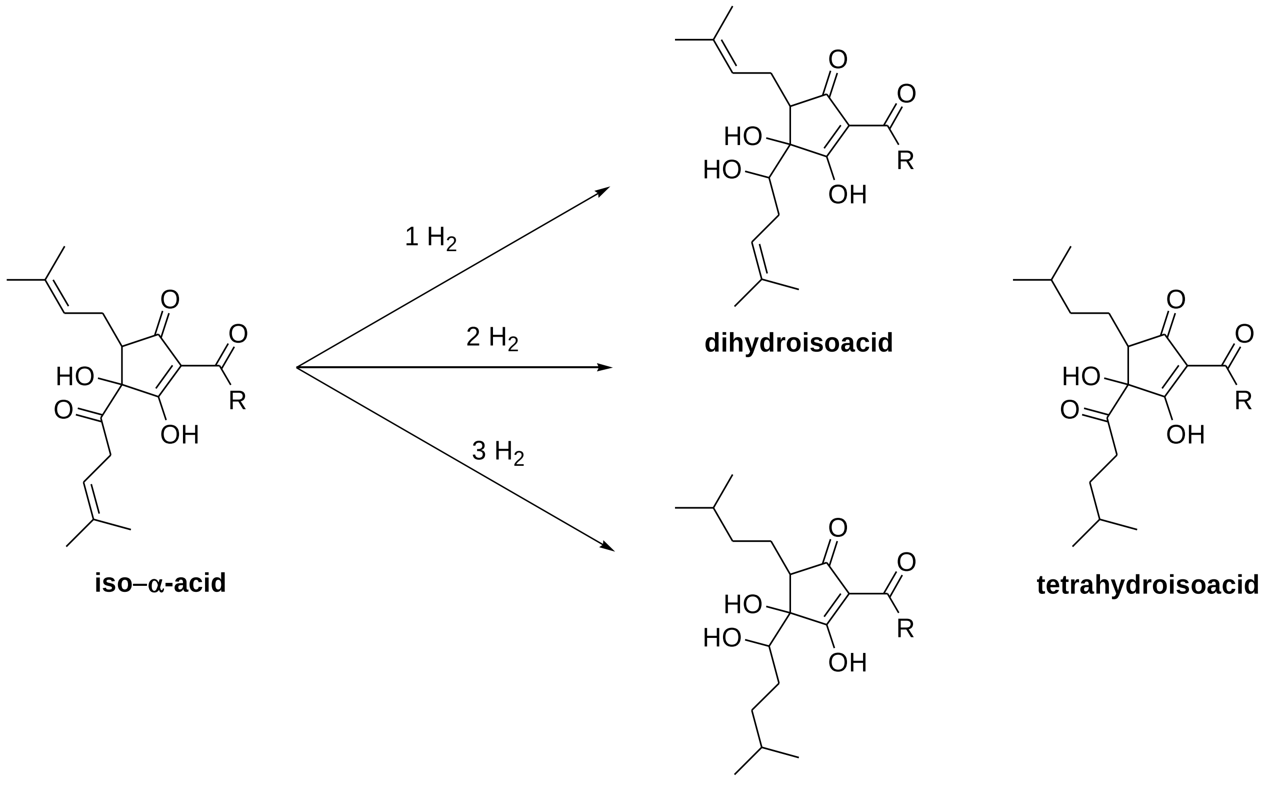
Isomerized α-acids

- Iso-α-acids stabilize beer foam
- They inhibit the growth of gram-positive bacteria, but lactic acid bacteria in beer are not affected by iso-α-acids (they've adapted)
- The iso-α-acids derived from cohumulone stabilizes foam less than the iso-α-acids derived from the other α-acids, and reportedly have a lower and less-pleasant bitterness than the other iso-α-acids
- Thus cohumulone levels in hops can be an important consideration—more later

Reduced Iso-α-acids

- The term “reduction” in organic chemistry can be defined in several ways
- For our discussion of hops chemistry the best definition will be reduction = the addition of hydrogen (H_2) across bonds
- There are several bonds in iso-α-acids where hydrogen can be added
- Reduction of iso-α-acids can be carried out to different degrees
- The reduced iso-α-acids have useful properties in the production of beer

Reduced Iso-α-acids



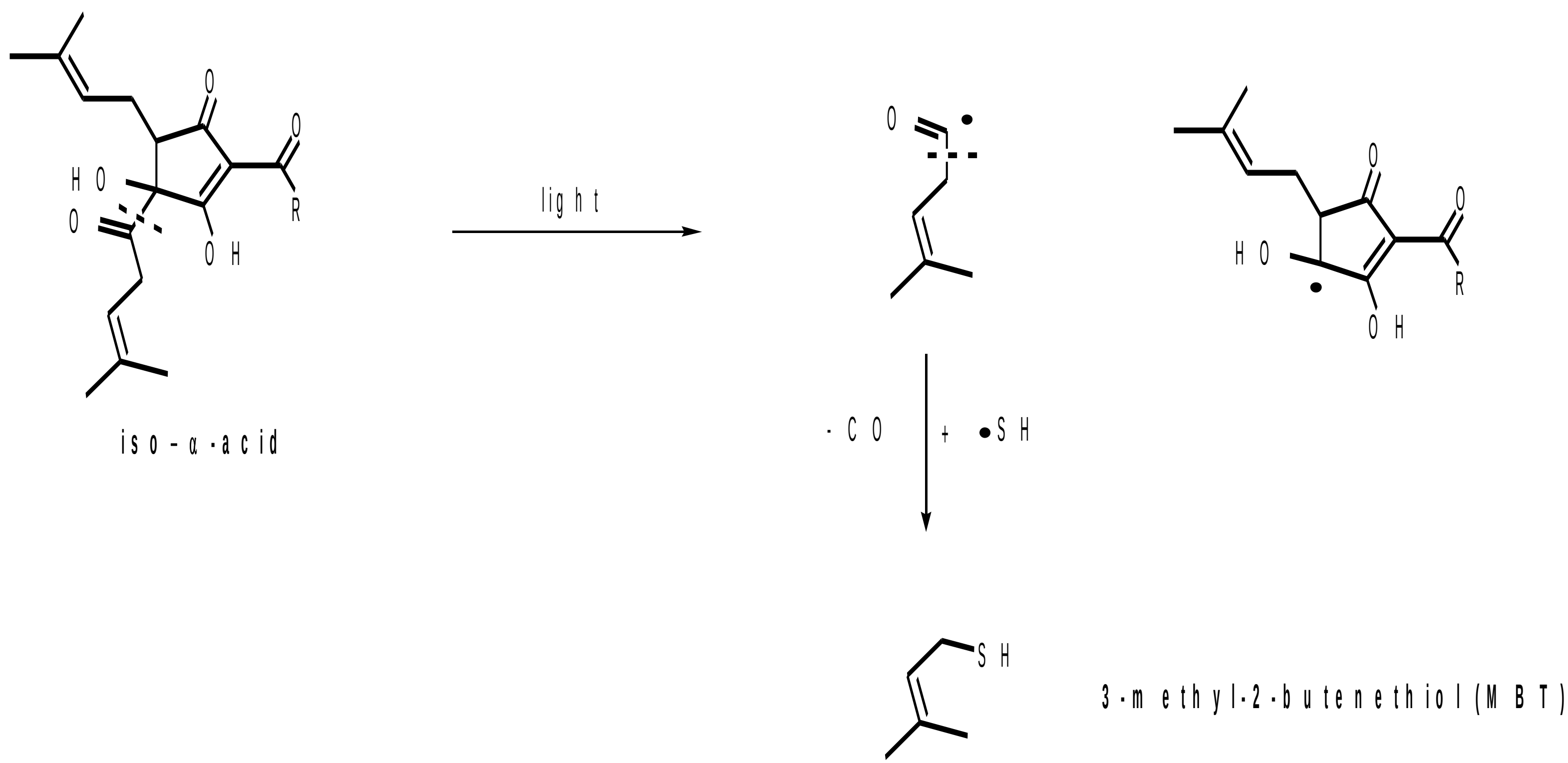
Reduced Iso-α-acids

- Reduction of iso-α-acids improves their stability to light exposure
- Reduced iso-α-acids improve foam stability (more hydrophobic)
- Reduction can also increase the level of bitterness
- Skunk odor formation is prevented

Skunking of Beer

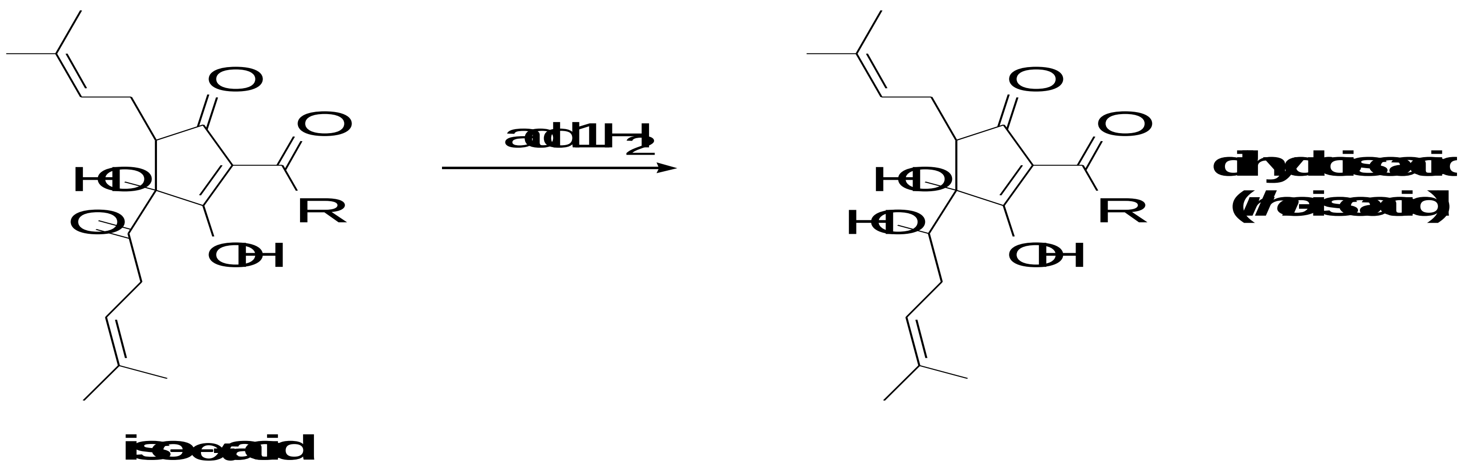
- The skunk odor in light-struck beer is due to a sulfur-containing compound called 3-methyl-2-butene-1-thiol (MBT)
- It’s generated when light of a certain wavelength interacts with an iso-α-acids
- The immediate degradation products pick up sulfur from another source in beer (cysteine)
- MBT is one component (of seven) in skunk spray (taste threshold ~1 ppt)

Skunking of Beer



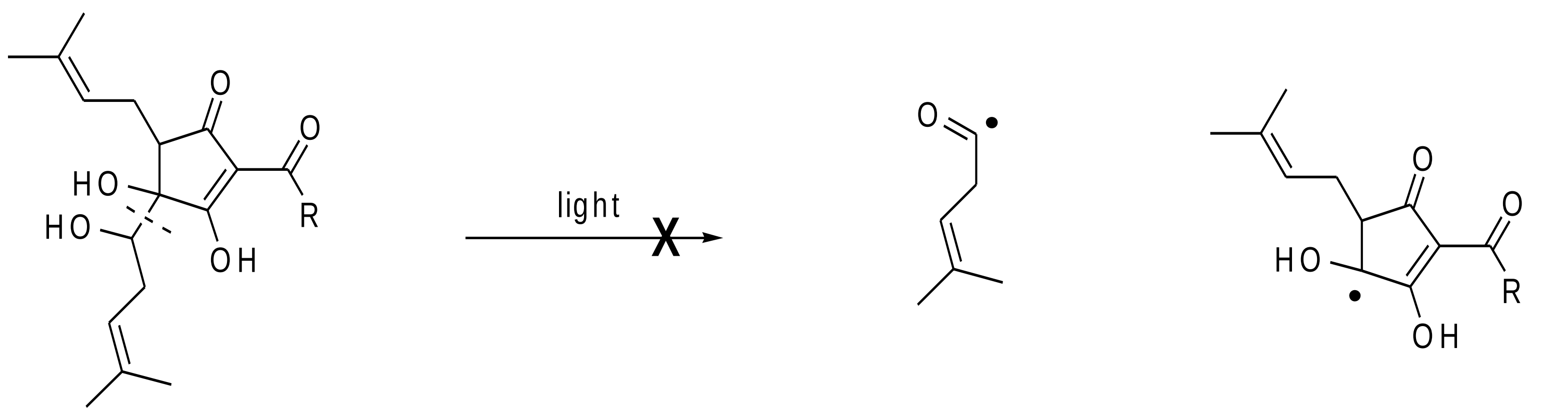
Skunking of Beer

- Reduction prevents the photo reaction:



Skunking of Beer

- Reduction prevents the photo reaction:



rho-isoacid

Skunking of Beer

- Miller High Life is packaged in colorless glass bottles
- It doesn’t take a lot of light exposure to bring about the skunking reaction—it can occur in as little as 30 seconds
- Miller uses a reduced iso-α-acid—a tetrahydroiso-α-acid—to bitter High Life
- This prevents the skunk formation

β-acids

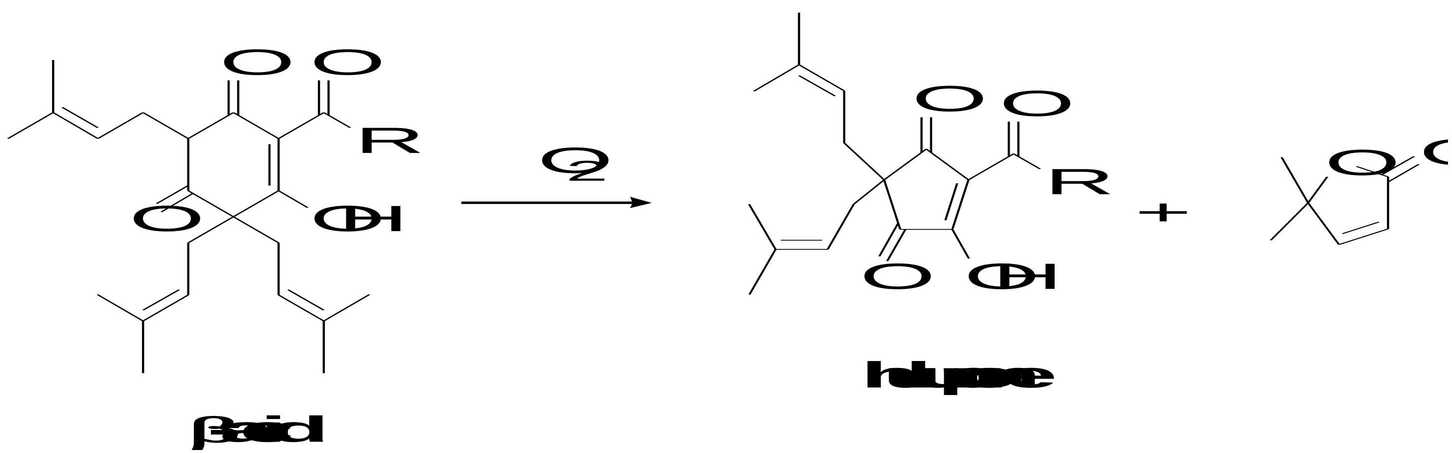
- Lupulone was first isolated in pure form in 1863
- Its structure wasn't confirmed until 1952
- Colupulone and Adlupulone were identified in 1955
- Structurally α-acids and β-acids resemble each other, but their chemical properties are very different

β-acids

β-acids

- β-acids are not themselves very bitter
- Their solubility is lower than that of α-acids, so most of the β-acid charged to the boil is lost on the kettle walls or with the trub
- Unlike α-acids, they don't isomerize upon heating in wort
- Instead, they oxidize to form bitter compounds—the hulupones

β-acids



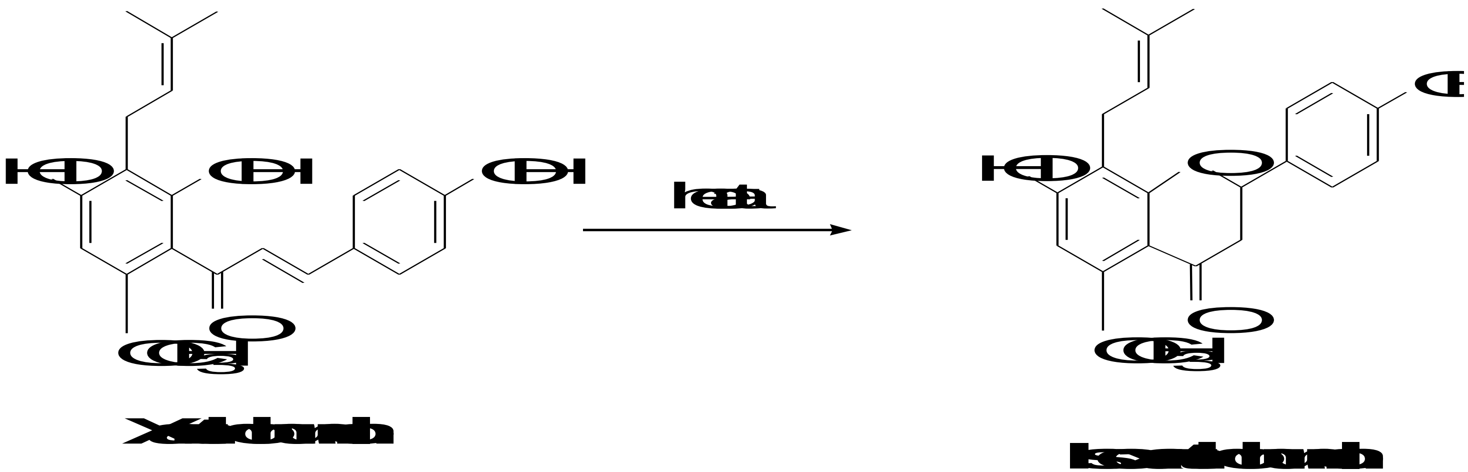
β-acids

- Hulupones will also form in stored hops from exposure to oxygen
- Their bitterness is only slightly less than that of iso-α-acids
- The quality of the bittering varies—some beer drinkers like it, some don’t
- This oxidation process can explain why old hops can still produce bitter beer

Another Source of Bittering

- There is another minor source of bittering in hops: Xanthohumol
- Xanthohumol is a polyphenol, but it undergoes a change during the boil that converts it to a bitter substance, Isoxanthohumol
- Isoxanthohumol is 8-30% as bitter as iso-α-acids

Another Source of Bittering



- Note the lack of a five-membered ring—compare to iso-α-acids and hulupones

Hop Oil

- Hop oil (essential oil) constitutes typically 0.5-2.5% of hops by weight
- There are between 400 and 1000 different compounds in hop oil
- Because they are volatile relative to α-acids and β-acids they are responsible for the aroma of hops
- There are three main types of compounds in hop oil:

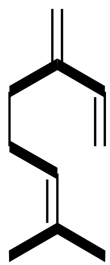
Hop Oil

1) Hydrocarbons (major)
2) Oxygen-containing compounds
3) Sulfur-containing compounds

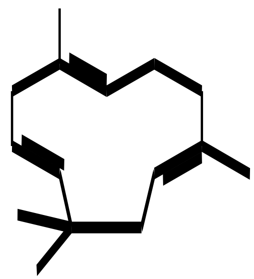
- An entire series of lectures could be devoted to hop oil constituents
- We'll only discuss a few—those found on a typical hop certificate of analysis

Hop Oil: Hydrocarbons

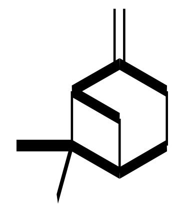
- Composed of carbon and hydrogen only



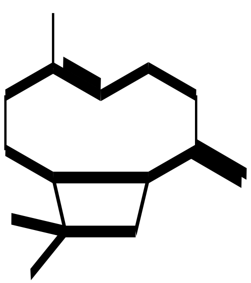
myrcene



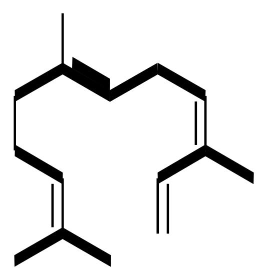
humulene



β-pinene



caryophyllene



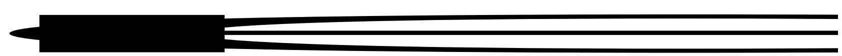
farnesene

Hop Oil: Hydrocarbon Aromas

• Myrcene	green, balsam, slightly metallic
• Humulene	woody
• β-pinene	coniferous pine, woody
• Caryophyllene	woody, carrot
• Farnesene	green, woody, weedy, herbal, pine, gin

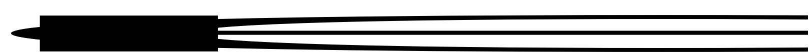
Hop Oil: Oxygenated Compounds

- These are derived from hydrocarbons by oxidation (addition of oxygen)



Hop Oil: O.C. Aromas

- Geraniol — sweet floral, perfumy
- Linalool — floral, orange



Hop Oil Volatility

- The hydrocarbon aroma compounds are quite volatile and will not survive the boil and fermentation
- They will distill off during the boil, and be sparged off by CO_2 during fermentation
- Most oxygen- and sulfur-containing compounds will survive the boil and fermentation

Hop Oil Volatility

- Bitterness is a function of α-acid levels and boil time
- Aroma level is a function of volatilization

	Floral	Citrus	Spicy	Resinous
Kettle hop	+	+		
Late hop	++	++	++	
Dry hop	+++	+++	+++	+

From Shellhammer 2014

Hop Certificates of Analysis

- Hop Cs of A will show you the content of certain chemical compounds for a given lot of hops
- Typically 10 or so compounds are included: α-acids, β-acids, cohumulone, β-pinene, myrcene, linalool, caryophyllene, farnesene, humulene, and geraniol
- Total oil (mL/100 g) is also included

Hop Certificates of Analysis

- Aroma Hop: Cascade (YCH)

Alpha Acid 5.5 - 9% **Beta Acid** 6 - 7.5% **Cohumulone** 30 - 35% **Total Oil** 0.8 - 2.5 mL/100g **β-Pinene** 0.5 - 0.8% of total oil **Myrcene** 45 - 60% of total oil	**Linalool** 0.3 - 0.6% of total oil **Caryophyllene** 5 - 9% of total oil **Farnesene** 6 - 9% of total oil **Humulene** 14 - 20% of total oil **Geraniol** 0.2 - 0.2% of total oil

Hop Certificates of Analysis

- Bittering Hop: Warrior

Alpha Acid 15.5 - 18% **Beta Acid** 4.4 - 6% **Cohumulone** 25 - 28% **Total Oil** 1 - 2.5 mL/100g **B-Pinene** 0.5 - 0.7% of total oil **Myrcene** 40 - 50% of total oil	**Linalool** 0.4 - 0.7% of total oil **Caryophyllene** 11 - 14% of total oil **Farnesene** < 1.0% of total oil **Humulene** 15 - 18% of total oil **Geraniol** 0.4 - 0.8% of total oil

Hop Certificates of Analysis

Major differences between Warrior (l) and Cascade (r)

Alpha Acid 15.5 - 18%	**Alpha Acid 5.5 – 9%**
Beta Acid 4.4 - 6%	**Beta Acid 6 – 7.5%**
Cohumulone 25 - 28%	**Cohumulone 30 – 35%**
Myrcene 40 - 50%	**Myrcene 45 - 60%**
Caryophyllene 11 - 14%	**Caryophyllene 5 - 9%**
Farnesene < 1.0%	**Farnesene 6 - 9%**

Hop Certificates of Analysis

- Chemistry will only get you so far when deciding what hops and how much hops to use in a beer
- Many of the most interesting aroma compounds aren’t included on Cs of A
- Smelling and tasting hops still has great value in brewing

Questions?