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

- **Hop oil**
  - **Hydrocarbons**
    - Monoterpenes (Myrcene)
    - Sesquiterpenes (β-Caryophyllene, α Humulene, Farnesene)
    - Aliphatic hydrocarbons
  - **Oxygen compounds**
    - Terpene alcohols (linalool, geraniol)
    - Sesquiterpene alcohols (humulenol I +II, humulol)
    - Others (alcohols, epoxides, ketones, esters)
  - **Sulfur compounds**
    - Thioesters
    - Sulfides (DMS)
    - Others

Sharpe and Laws
<table>
<thead>
<tr>
<th>Substance Grouping</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monoterpenes</td>
<td>~ 40 %</td>
</tr>
<tr>
<td>Sesquiterpenes</td>
<td>~ 40 %</td>
</tr>
<tr>
<td>Carboxylic acid esters</td>
<td>~ 15 %</td>
</tr>
<tr>
<td>Carboxylic acids</td>
<td>~ 1 %</td>
</tr>
<tr>
<td>Monoterpenoxides</td>
<td>~ 1 %</td>
</tr>
<tr>
<td>Sesquiterpenoxides</td>
<td>~ 1 %</td>
</tr>
<tr>
<td>Aldehydes, Ketones</td>
<td>~ 1 %</td>
</tr>
<tr>
<td>Aliphatic hydrocarbons</td>
<td>&lt; 1 %</td>
</tr>
<tr>
<td>Sulfur containing compounds</td>
<td>&lt; 0,1 %</td>
</tr>
<tr>
<td>Glycosidically bound aroma compounds</td>
<td>?</td>
</tr>
</tbody>
</table>
Examples for Monoterpenes and Sesquiterpenes

Monoterpenes

- Myrcene
- Linalool
- Geraniol
- Limonene
- beta-Pinene

Sesquiterpenes

- Humulene
- beta-caryophyllene

Humulene and beta-Caryophyllene together can represent more than 50% of the hop oil.
Hop Aroma Research

- 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

- Myrcene: 53.12%
- Caryophyllene Oxide: 0.8%
- Caryophyllene: 8.59%
- Farnesene: 6.5%
- Humulene: 22.58%
- Linalool: 0.6%
- Citronellol: 0.9%
- Epoxide II: 1.6%
- Methyl heptonoate: 0.8%
- Other: 9.2%

Minor components: 3.6%

Shellhammer MBAA 2011
Minor Hop Components

- Unknown 1, 0.31%
- Eudesmol, 0.30%
- Citral, 0.27%
- Limonene, 0.23%
- Unknown 3, 0.25%
- Unknown 4, 0.23%
- Unknown 2, 0.4%
- Farnesol, 0.36%
- Geranyl Acetate, 0.53%
- Ethyl 2-methyl butyrate, 0.01%
- Isobutyl isobutyrate, 0.03%
- Nerol, 0.03%
- Citronellal, 0.03%
- p-cymene, 0.06%
- b-ionone, 0.07%
- a-pinene, 0.11%
- Geraniol, 0.12%
- Hexanal, 0.12%
- Epoxide I, 0.19%
Traditional Hop Profiles and Aroma

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

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

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

<sup>a</sup> Source: Deutscher-Hopfen (4).

<sup>b</sup> Source: New Zealand Hops Limited (18).
**Traditional Hop Variety Descriptions**

**Citra™**

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.

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

**Cascade**

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.

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

- As described in Barth Hop Aroma Compendium:

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

- Menthol
- Floral
- Tea
- Green fruits
- Sweet fruits
- Citrus
- Red berries
- Green
- Woody aromatic
- Spicy/herbal
- Cream caramel
- Vegetal

- Mosaic® (cold infusion®)
- Mosaic® (raw hops)

- 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 monoterpenic alcohols (µg/g of hop) before and after the boil (data of the HHT hop was previously reported in reference 27).
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

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

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 ≠ 2
Synergistic Effects of Hop Aroma Compounds

Concentration

No perceptible flavor

Threshold concentration

perceptible flavor

Substance A

Substance B

Beer 1

Beer 2

Beer 3
<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>Linalool</td>
<td>27</td>
<td>104&lt;sup&gt;a&lt;/sup&gt;; 133&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>493&lt;sup&gt;c&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>Geraniol</td>
<td>104&lt;sup&gt;a&lt;/sup&gt;; 133&lt;sup&gt;b&lt;/sup&gt;</td>
<td>90</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2304&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>Humulene</td>
<td></td>
<td></td>
<td>3483</td>
<td>4346&lt;sup&gt;e&lt;/sup&gt;</td>
<td>1843&lt;sup&gt;f&lt;/sup&gt;</td>
<td>5668&lt;sup&gt;g&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Caryophyllene</td>
<td>4346&lt;sup&gt;e&lt;/sup&gt;</td>
<td></td>
<td>239</td>
<td>147&lt;sup&gt;h&lt;/sup&gt;</td>
<td>1297&lt;sup&gt;i&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nerol</td>
<td></td>
<td></td>
<td></td>
<td>1843&lt;sup&gt;f&lt;/sup&gt;</td>
<td>147&lt;sup&gt;h&lt;/sup&gt;</td>
<td>1206</td>
<td>2699&lt;sup&gt;j&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>Terpineol</td>
<td></td>
<td></td>
<td></td>
<td>5668&lt;sup&gt;g&lt;/sup&gt;</td>
<td></td>
<td>1297&lt;sup&gt;i&lt;/sup&gt;</td>
<td>2699&lt;sup&gt;j&lt;/sup&gt;</td>
<td>1076</td>
</tr>
<tr>
<td>Myrcene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>119</td>
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<tr>
<td>Farnesene</td>
<td>493&lt;sup&gt;c&lt;/sup&gt;</td>
<td>2304&lt;sup&gt;d&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2020</td>
</tr>
</tbody>
</table>
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
bad | good

depending on configuration, concentration, interaction and perception
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 and concentration of bitter compounds in beer

Hofmann, 2011
Threshold Ranges of Hop Bitter Acids

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

<table>
<thead>
<tr>
<th>Threshold ranges in mg/l</th>
<th>In beer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iso-alpha acids</td>
<td>3-8 mg/l</td>
</tr>
<tr>
<td>Tetrahydro-iso-alpha acids</td>
<td>2-9 mg/l</td>
</tr>
<tr>
<td>Rho-iso-alpha acids</td>
<td>6-12 mg/l</td>
</tr>
<tr>
<td>Hexahydro-iso-alpha acids</td>
<td>2-10 mg/l</td>
</tr>
</tbody>
</table>
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!

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