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2015 ASBC Annual Meeting

Sensory Bitterness Quality of Oxidized Hop Acids: Humulinones and Hulupones

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2015 ASBC Annual Meeting
June 14–17, 2015
La Quinta Resort and Club
La Quinta, CA

Study Objectives:

- To what extent do oxidized hop acids (addition of old/aged hops) effect bitterness quality in late hop additions?
- Build upon previous studies that found that the bitterness intensity of known oxidized α-acids (humulinones) and oxidized β-acids (hulupones) to be greater than previously expected.

Project Background:

Hop-derived bitterness balances sweet malted barley in the production of beer. Fresh hops contain α- and β-acids, neither of which are bitter. To generate bitterness brewers add hops to the brew kettle where α-acids are thermally isomerized into bitter isohumulones (iso-α-acid, iso). 'Bittering additions' involve the inclusion of hops at the beginning of the boil whereas 'aroma additions' are added later in the process where the oils are better protected from volatilization. Yet, modern trends of adding hops on the cold side of the process (dry-hopping) has the potential to add bitterness depending on the age and quality of the hops used.

Vs.

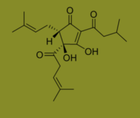
Hop quality can quickly decline during aging, mainly due to contact with oxygen. Auto-oxidation of hop acids can lead to formation of many, potentially bitter, compounds. Two such oxidation products that have been found to be bitter are hulupones (oxidized β-acids) and humulinones (oxidized α-acids).

Our lab previously determined the relative bitterness intensity of hulupone and humulinone compared to isohumulone by linearly regressing hop acid concentration against bitterness scores using a trained descriptive panel, experienced in bitterness evaluation. Hulupones were found to be on average 84% as bitter as iso-α-acid (±10%) and humulinones 66% as bitter as iso-α-acids (±13%). The variation in the ratios of oxidized hop acids to isohumulones is due to the panelist-dependent nature of relative bitterness perception of hop acids.

Experimental Method:

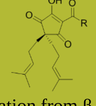
Extract Preparation

Figure 1. **Isohumulone**
product of α-acid isomerization



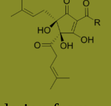
Commercially obtained extract of 30% purity

Figure 2. **Hulupones**
product of β-acid oxidation



Isolation from β-acid extract (92.5% purity) using method by Wright 1963.

Figure 3. **Humulinones**
product of α-acid oxidation



Isolation from α-acid extract (93.7% purity) using method by Cook *et al*. 1955

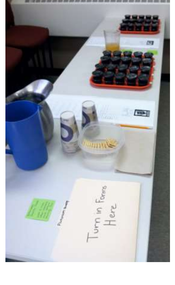
Beer Production

An unhopped lager beer (70% P2R, 30% Adjunct) was brewed in the Oregon State University pilot brewery. The wort was fermented with Wyeast lager strain 2124 at 55° C. The final beer specifications were 5% ABV, 2.5% real extract and 2 volumes of CO_2.

Descriptive Analysis

Table 1. Definitions of terms used in this study for characterizing bitterness

Terms	Definitions
Peak Bitterness	Maximum intensity of bitterness
Duration	Length of time it takes the bitterness to dissipate
Metallic	Reminiscent of aluminum or tin
Medicinal/Harsh	Aspirin, acrid, chalky, unpleasant
Vegetative	Plant-like, bitter greens, arugula, endive, dandelion



- Ten experienced panelists
- Two training sessions
- Six independent replications
- Three treatments
  - **Warm Up: Isohumulone** (12 mg/L)
  - **Isohumulone** (18.8 mg/L)
  - **Hulupones** (22.5 mg/L)
  - **Humulinones** (28.8 mg/L)
- Five descriptive terms
  - **Peak bitterness, duration, metallic, medicinal/harsh, vegetative**
- Categorical 0-7 scale

Results and Discussion:

Figure 4. PCA of bitterness quality scores averaged across panelists and replications

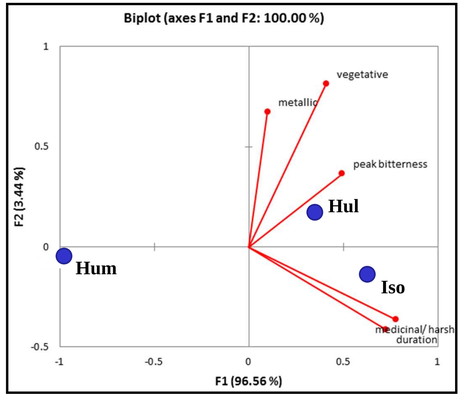


Table 2. Sensory bitterness quality scores of beer treatments

Treatment	Peak Bitterness	Duration	Metallic	Medicinal / Harsh	Vegetative
Iso 19ppm	5.4^{A}	5.2^{A}	2.3	3.7^{A}	2.5^{AB}
Hul 23ppm	5.4^{A}	4.9^{A}	2.5	3.5^{A}	2.6^{A}
Hum 29ppm	4.8^{B}	4.2^{B}	2.2	2.7^{B}	2.1^{B}

Treatments with different superscripts are significantly different within each attribute using Tukey's Honestly Significant Difference (HSD) at α = 0.05.

Table 3. Correlation matrix (Pearson) summary of p-values

	Peak Bitterness	Duration	Metallic	Medicinal / Harsh	Vegetative
Peak Bitterness	**0**				
Duration	**< 0.0001**	**0**			
Metallic	0.211	0.173	**0**		
Medicinal / Harsh	**0.001**	**< 0.0001**	0.013	**0**	
Vegetative	**0.001**	**0.005**	0.638	0.201	**0**

Values in bold are significant at p<0.05.

Humulinones were significantly different than hulupones and isohumulone in four out of five bitterness quality attributes. However all terms used in the study were highly correlated; therefore evidence suggests that humulinones were not different in bitterness quality but rather different in overall intensity compared to the other treatments.

Conclusions:

- Dry hopping has the potential to add bitterness to beer.
- Oxidized hop acids humulinones and hulupones are bitter.
- Hulupones were confirmed to be 84% as bitter as isohumulone.
- Humulinones are >66% as bitter as isohumulone and contribute to bitterness in dry hopped beers.
- Evidence suggests hulupones and humulinones are not different than isohumulone in bitterness quality.
- Future work should consider whether other oxidized hop acids, carried into beer, are different in bitterness quality.

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