

# Applications of Metabolomics in Hop and Beer Analysis



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## Abstract

Metabolomics is a growing application able to generate a global snapshot of metabolites present in a given sample. Prior research has demonstrated the possibility of distinguishing between hop varieties on the basis of their metabolic profile, however how this plays out in a typical fermentation has yet to be elucidated. Our research has used nuclear magnetic resonance (NMR) to monitor the small molecule profiles of different hop varieties and commercially produced beer.

It has been hypothesized that different metabolites will be present in beer that has been produced using dry hopping techniques versus that which has been late hopped. We analyzed two commercial beers known to be late-hopped with Cascade and dry-hopped with Magnum, respectively. We also analyzed chloroform-methanol extracted hop compounds via NMR and were able to obtain global snapshots of ~40 metabolites and quantify their presence via the Chenomx Metabolite Database. Differences can primarily be seen between beers, but less so between hop varieties. Novel compounds were found to carry over from hop material into the final beer.

## Objective

To use metabolomics to profile beer and to observe the small molecule contributions made by different varieties of hops added at different times during the brewing and fermentation processes.

## Materials & Methods

- Hops used were Cascade and Magnum varieties from 2013.
- Hop and beer samples were obtained from Sierra Nevada and kept cold until analysis.
- Liquid samples for NMR were filtered through 3K MWCO filters, brought to a pH of 6.8, and spiked with 5 mM standard.
- Hops aqueous and non-polar extractions were performed using a 2:1 chloroform-methanol extraction.
- NMR spectra were acquired using a Bruker Avance 600 MHz NMR spectrometer
- Metabolites were assigned using Chenomx NMRSuite.

## Conclusions & Future Directions

NMR Metabolomics can be used to elucidate small molecule composition and differences in hop samples and commercially produced beer. Though spectra of Magnum and Cascade hops are not distinctly different, the dry-hopped beer contained various peaks that are absent in the late hopped beer. Novel compounds such as trigonelline have been found in hops and are transmitted into the final beer. Current work focuses on identifying and assigning metabolites to unknown peaks and analyzing beers brewed on UC Davis' 5-gallon system using both varieties of hops in late and dry hopping scenarios.

## Results & Discussion

Figure 1: Nonpolar <sup>1</sup>H NMR Spectrum of Hop Metabolites

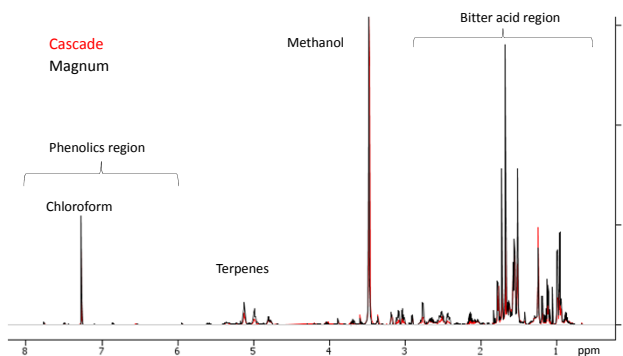
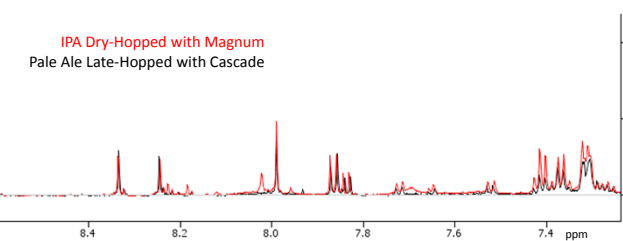


Figure 2: Aqueous <sup>1</sup>H NMR Spectrum of Beer Metabolites



Sample	Pale Ale	IPA	Sample	Pale Ale	IPA
2'-Deoxyadenosine	171	203	Isoleucine	37	164
2-Oxoglutarate	74	74	Lactate	1038	1083
4-Aminobutyrate	467	690	Leucine	59	236
4-Hydroxyphenyllactate	58	58	Maltose	8218	10443
4-Pyridoxate	24	18	Methanol	48	97
Acetate	654	901	Nicotinate	0	29
Acetone	10	20	Phenylacetate	111	139
Adenosine	246	213	Phenylalanine	202	465
Alanine	650	1472	Proline	4788	4889
Allantoin	598	1141	Pyridoxine	15	0
Arabinose	366	366	Pyroglutamate	1559	1845
Betaine	865	1491	Pyruvate	2068	2130
Choline	719	1026	Succinate	695	818
Creatinine	20	14	Thymidine	73	102
Cytidine	211	281	Trehalose	335	1222
Ethanol	910418	1182957	Trigonelline	25	39
Ethanolamine	130	198	Tryptophan	135	179
Fumarate	30	53	Tyrosine	289	541
Glycerol	12750	14567	Uridine	281	451
Guanosine	358	467	Valine	392	758
Histidine	0	213	sn-Glycero-3-phosphocholine	648	788
Hypoxanthine	25	26	trans-Aconitate	28	30
Inosine	24	30			

Figure 3: Aqueous <sup>1</sup>H NMR Spectrum of Beer and Hop Metabolites

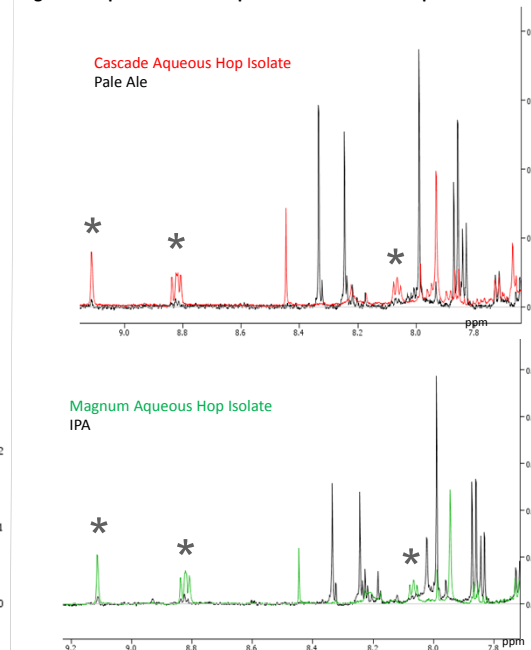


Figure 1: Overlay of Nonpolar NMR Spectra of Cascade and Magnum Hop Extracts. (General peak assignments were made based on Farag et al., 2012)

Figure 2: Overlay of IPA and Pale Ale Beer NMR Spectra.

Figure 3: Overlay of aqueous hop fraction and corresponding beer spectra (Cascade and late-hopped Pale Ale, Magnum and dry-hopped IPA). Spectra of novel compound trigonelline marked with \*.

Table 1: Identified metabolites in commercial beer samples and corresponding concentrations (µM)

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