

The Effects of Polyphenols Extracted during Dry Hopping on Beer Flavor Stability

Brad Titus Dr. Anita Oberholster

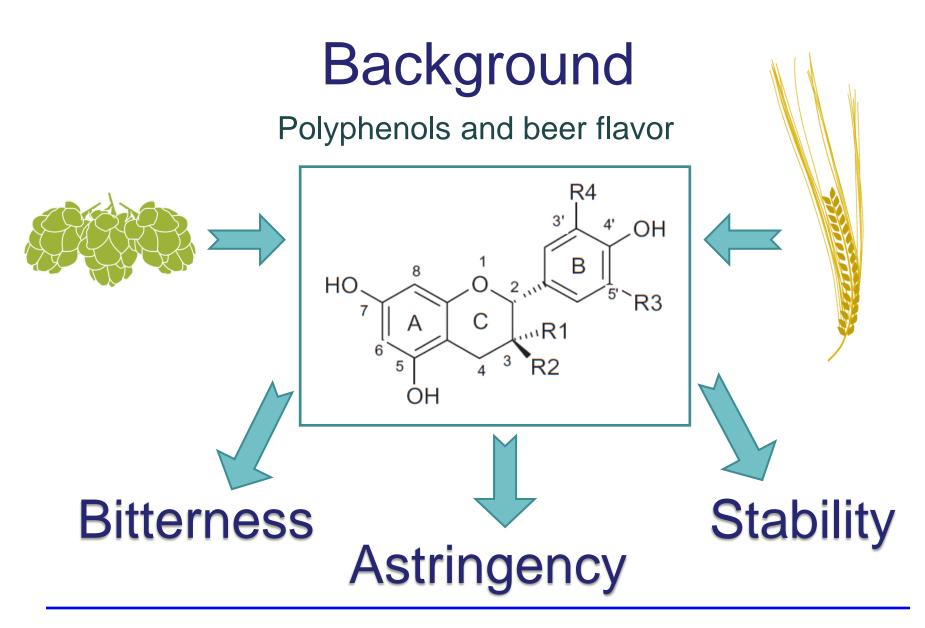
Contents

- Specific aims
- Background
 - Polyphenols and beer flavor
 - Chemical ageing markers
- Experimental Design
 - Experimental beer
 - GC analysis
 - HPLC analysis
 - Descriptive analysis
- Results
- Acknowledgements and References

Specific Aims

- Determine impact of dry hopping on flavor stability of beer in relation to polyphenol extraction
- Observe extraction rates of hop-derived flavor-active compounds during dry hopping





Background

Chemical Aging Markers

Alde	nydes	t/c- <i>iso-</i> α-acid ratio			
Sources	Compounds				
Amino acid degradation (Strecker)	phenylacetaldehyde methional 3-methylbutanal 2-methylbutanal 2-methylpropanal	HO = 4 OH + HO = 4 OH			
Maillard reactions	Furfural				
Oxidative degradation of lipids	hexanal pentanal	(de Clippeleer et al. 2010; Malfliet et al. 2008;			
Aldol condensation	(E)-2-nonenal	De Cooman et al. 2000)			

Experimental beer



August Busch III Pilot Brewery – UC Davis

- 1.7 hL batch
- 12.5°P
- 5.0% ABV
- Rahr Pale Ale Malt
- Rahr Caramel 20L
- 30 IBUs
- Wyeast 1056
- 18°C fermentation for 4 days
- Sterile filtered

Experimental process



Experimental process



Experimental process

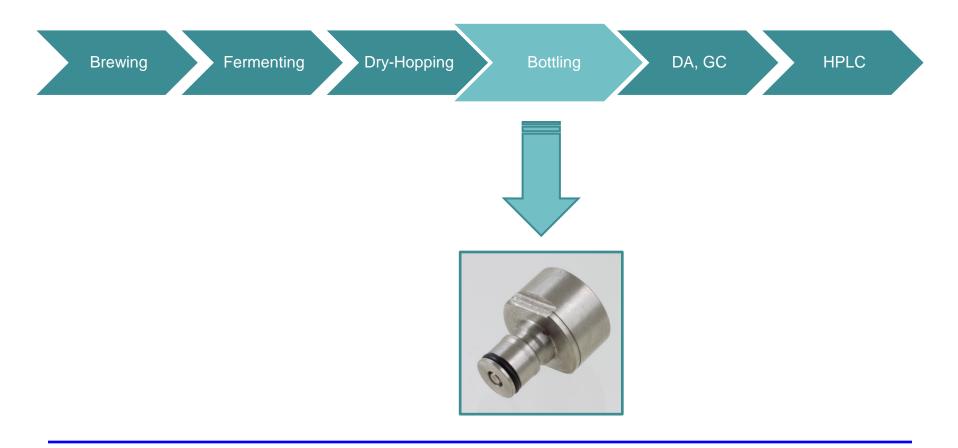


Experimental process



Hop varietal	Cascade (BSG)
Hop type	Pellets (T-90)
Dry hop amount	1/2 lbs/bbl
Contact time	0-96 hr

Experimental process



Experimental process

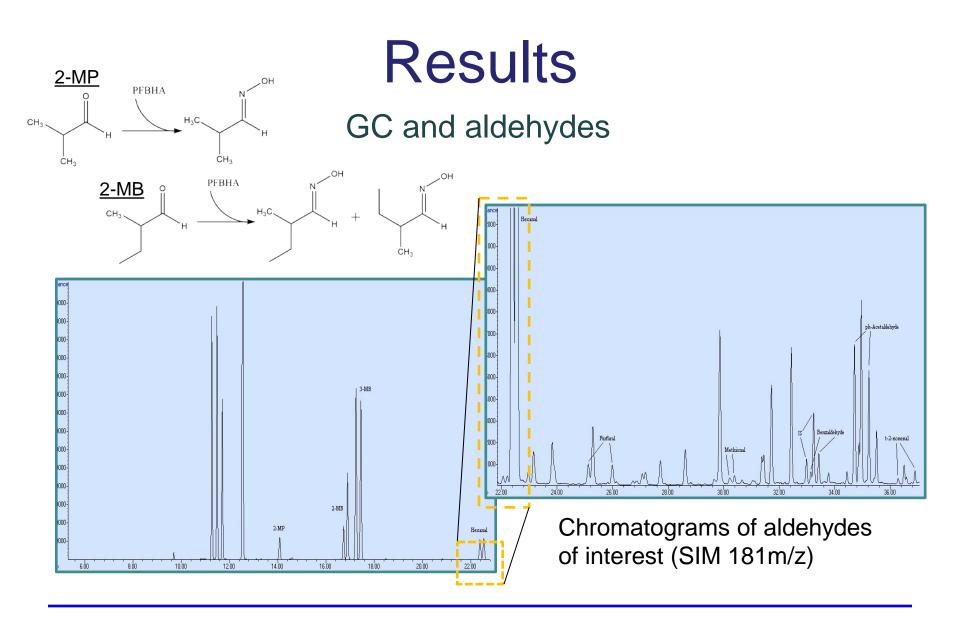




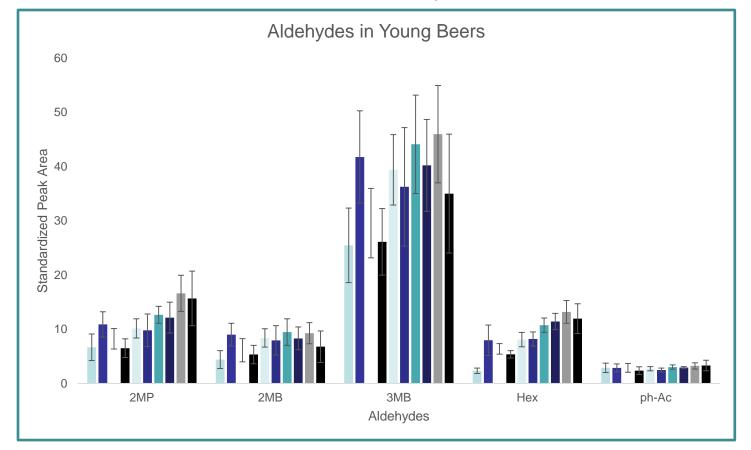


Experimental process

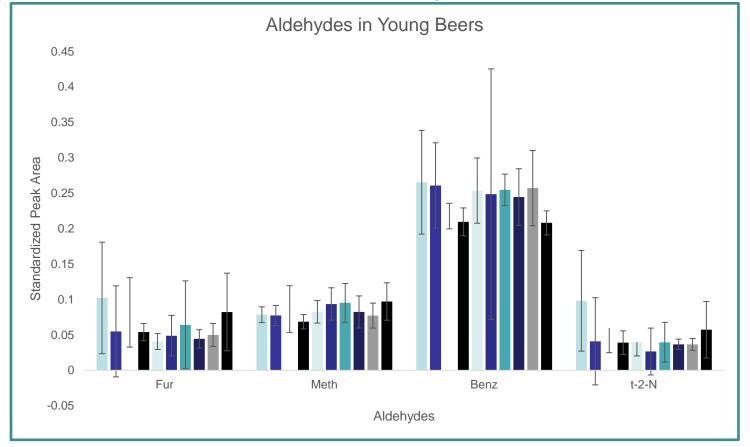




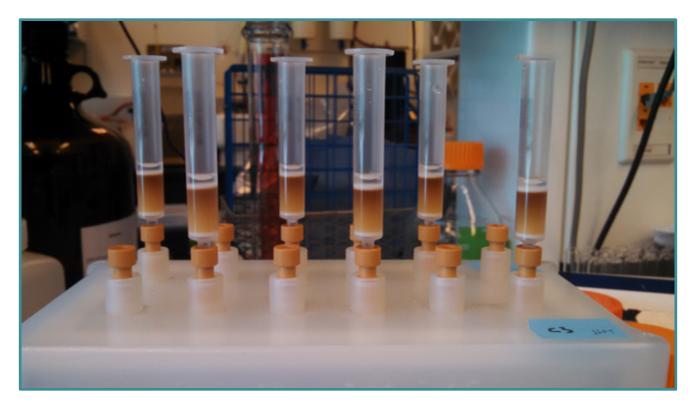
GC and aldehydes

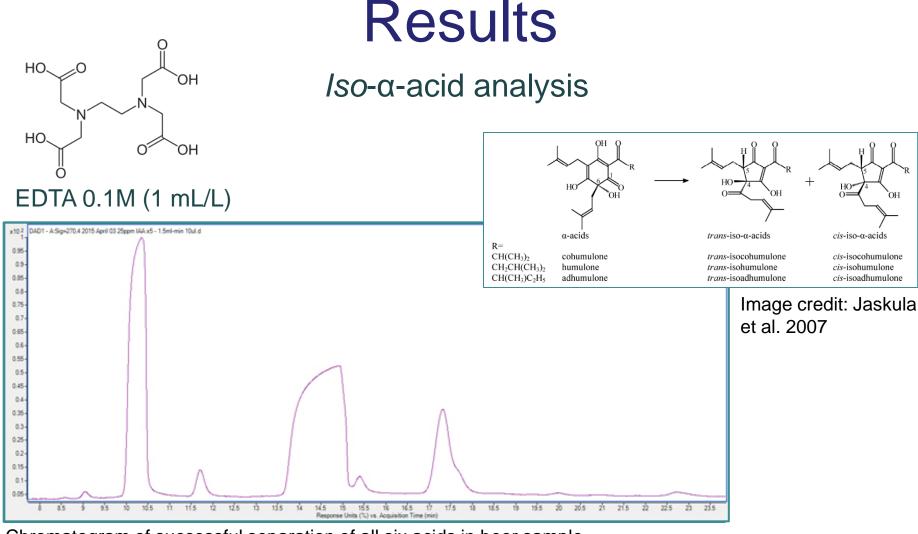


GC and aldehydes



Iso-α-acid analysis

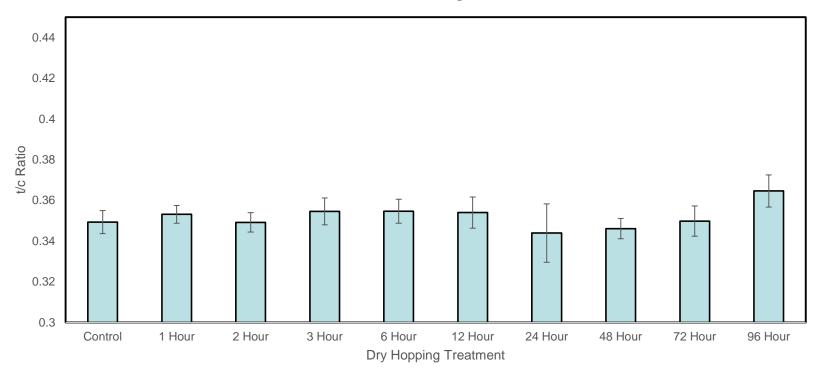




Chromatogram of successful separation of all six acids in beer sample.

Iso-α-acid analysis

t/c IAA ratio - Young Beers



Polyphenol analysis

mAU - 4.198				~~~					
		~				-			
40 - 0joo ojileo 30	protocatechuic acid	p-hydroxybenzoic acid t3.362 catechin		21.848 EC/C	p-coumaric acid	30.006 ferulic acid 32.350 ECG 32.350 Tavonol(quer-glucoside)	34.965 TIavonoi (quer-rham)	39.792 flavonol (myr)	
	10	1 . 1	1 X	20		30	r	40	
Chromatogram showing polyphenols of interest									

Descriptive analysis

DA Design

- Modified ballot design
- Treatments evaluated in triplicate
- 10 treatments x 3 dry hop reps x 3 sensory reps = **90 beers**
- DA done in two weeks
- Thank you panelists!



Descriptive analysis

Attributes

- Pine
- Grapefruit
- Pineapple
- Citrus
- Stone Fruit
- Dried Fruit
- Cedar
- Floral
- Passion fruit
- Herbal
- Onion/Garlic
- Earthy
- Vegetal



Expectations

- Correlations between sensory and chemical data
- Lower t/c ratios in aged beer with shorter dry hop time
- Changes in aldehyde profiles indicating lipid oxidation and deterioration of flavor compounds
- Correlation between polyphenol concentrations and aging markers

Acknowledgements

Dr. Anita Oberholster Dr. Larry Lerno Dr. Charles Bamforth Joe Williams Dr. Nadia Byrnes Dr. Hildegarde Heymann Cary Doyle Katherine Neuhaus Vinnie Cilurzo Anna Hjelmeland Barth Haas Group





BARTH-HAAS GROUP

Agricultural & Environmental Chemistry Graduate Group



- (1) De Clippeleer, J.; de Rouck, G.; de Cooman, L.; Aerts, G. Influence of the Hopping Technology on the Storage Induced Appearance of Staling Aldehydes in Beer. J. Inst. Brew. **2010**, *116*, 381–398.
- (2) Steinhaus, M.; Schieberle, P. Comparison of the Most Odor-Active Compounds in Fresh and Dried Hop Cones (Humulus Lupulus L. Variety Spalter Select) Based on GC-Olfactometry and Odor Dilution Techniques. J. Agric. Food Chem. **2000**, 48, 1776–1783.
- (3) Malfliet, S.; Opstaele, F. Van; Clippeleer, J. De; Syryn, E.; Goiris, K.; de Cooman, L.; Aerts, G. Flavour Instability of Pale Lager Beers : Determination of Analytical Markers in Relation to Sensory Ageing. *J. Inst. Brew.* **2008**, *114*, 180–192.
- (4) Vesely, P.; Lusk, L.; Basarova, G.; Seabrooks, J.; Ryder, D. Analysis of Aldehydes in Beer Using Solid-Phase Microextraction with on-Fiber Derivatization and Gas Chromatography/mass Spectrometry. J. Agric. Food Chem. 2003, 51, 6941–6944.
- (5) Saison, D.; De Schutter, D. P.; Delvaux, F.; Delvaux, F. R. Optimisation of a Complete Method for the Analysis of Volatiles Involved in the Flavour Stability of Beer by Solid-Phase Microextraction in Combination with Gas Chromatography and Mass Spectrometry. J. Chromatogr. A 2008, 1190, 342–349.
- (6) Jaskula, B.; Goiris, K.; De Rouck, G.; Aerts, G.; De Cooman, L. Enhanced Quantitative Extraction and HPLC Determination of Hop and Beer Bitter Acids. *J. Inst. Brew.* **2007**, *113*, 381–390.
- (7) Dvořáková, M.; Hulín, P.; Karabín, M.; Dostálek, P. Determination of Polyphenols in Beer by an Effective Method Based on Solid-Phase Extraction and High Performance Liquid Chromatography with Diode-Array Detection. *Czech J. Food Sci.* **2007**, *25*, 182–188.
- Quifer-Rada, P.; Vallverdú-Queralt, A.; Martínez-Huélamo, M.; Chiva-Blanch, G.; Jáuregui, O.;
 Estruch, R.; Lamuela-Raventós, R. A Comprehensive Characterisation of Beer Polyphenols by High Resolution Mass Spectrometry (LC–ESI-LTQ-Orbitrap-MS). *Food Chem.* 2015, 169, 336–343.

THANK YOU!

Questions?