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## Identification and characterization of 1,3-pentadiene in commercially produced hop extract and its potential impact on hop product and lager beer quality.

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## Abstract

The authors have identified a previously un-reported compound in commercially produced supercritical $CO_2$ hop extracts. The compound, initially thought to be a contaminant from either the process or packaging, was positively identified by GCTOF-MS and SPME-GC-MS to be a naturally derived degradation product of hop acids. A cross-functional investigation into raw materials, $CO_2$ processing and storage liners (Py-GC/MS) was conducted to reveal its identity as 1,3-pentadiene. A mechanism has been proposed for the formation of 1,3-pentadiene from the degradation of side chains of both alpha and beta hop acids. Further investigation revealed that 1,3-pentadiene is either carried into or formed in lager beer produced with commercial hop extracts. The authors propose that 1,3-pentadiene content in pellets, hop extracts and lager beer may give insight into hop and beer quality pertaining to flavor stability.

## Background

Quality of brewing raw materials correlates to the overall quality of finished beer. Analytical assessment of supercritical $CO_2$ hop extracts (cv. Cascade) by GC-MS FID revealed a compound not previously identified. The compound was initially thought to be a contaminant from either the process or packaging, which concentrated during fractionation or distillation into hop oils, and presented great difficulty for removal from the extract. The compound was originally identified as ethylidene cyclopropane. The presence of this compound caused considerable concern in terms of product quality and safety. Researchers at MillerCoors sought to collaborate with hop supplier Yakima Chief to investigate the absolute identity of the compound, its origin and any effects it may have on product quality or safety.

## Methods and Results

**Cascade Hop Extract:** Analysis of the extract was originally conducted via GC-MS: 0.1 g Cascade extract was dissolved in 1.0g of methanol. A 1.0uL sample was injected into the GC and separated using a DB-1 column (30x0.32x1m). The carrier gas was helium and the split was set at 100mL/m, flow rate set at 1.5mL/m. Spectra of the unknown peak was recorded at 1.776 mins.

**Analysis of the Liner:** Pyrolysis gas-chromatographic mass spectrometry (Py-GC/MS) was applied for analysis of the plastic liner material. Results indicated that the component of interest was either 1,3-pentadiene or ethylidene cyclopropane. Analysis of the sample liner by Thermal Desorption of the total sample was unable to identify the ethylidene cyclopropane, when desorbed at 180 °F (83°C), the recommended maximum fill temperature, for a period of 15 minutes.

## Methods and Results

Method:

| | |
|---|---|
| Start temp | 60’C |
| Hold | 1.5min |
| Ramp rate | 4’/min |
| End temp | 280’C |
| Hold | 15mins |
| Inj temp | 250’C |
| Line temp | 280’C |
| Inj volume | 1ul |

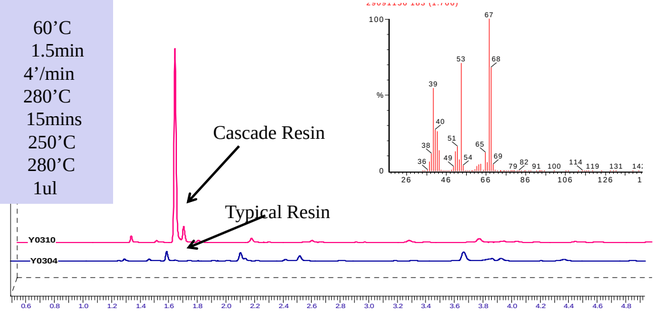
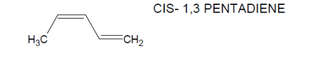
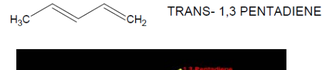



**Figure 1. Cascade Hop Extract Analysis by GC-MS**

**Analysis of the Liner (cont.):**. The remaining sample from the desorption was pyrolized at a temperature of 550°C to decompose the sample. Upon examination of the ion extraction for the pyrolysis, both **1,3 pentadiene** and ethylidene cyclopropane were found to be matches at the same retention time.

**Analysis of Other Hop Extracts and Pellets:** Purified standards of cis-1,3 pentadiene (TCI America) and trans- 1,3 pentadiene (Sigma Aldrich) were used to confirm the identity of the unknown compound found in the cascade extract. Retain lots of the same extract as well as different extracts (not packaged in the same liner) were also analyzed: Herkules, Tomahawk, Saaz, and Cascade.



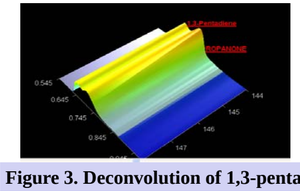



**Figure 3. Deconvolution of 1,3-pentadiene using the LECO ChromaTOF® software.**

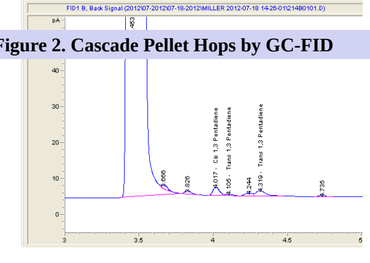


**Figure 2. Cascade Pellet Hops by GC-FID**

## Methods and Results

**Analysis of Other Hop Extracts and Pellets (cont.):** Using the extract ion chromatograms, it was thus determined that in all samples tested, 1,3-pentadiene is the most likely compounds of interest. NIST match potential for 1,3 – pentadiene average >925 for all samples analyzed. Cascade pellets were extracted using methanol and analyzed via GC-FID.

**Analysis of Advanced Hop Products:** Potassium isomerized kettle extract (PIKE) and Tetrahydro-iso-alpha acids were analyzed via SBSE-GC-MS-TOF:0.1 g/1.0mL MeOH, 15 minutes exposure with the stir bar in the headspace. Spent hop material was analyzed after being macerated with methanol via stir bar (1.0g/1.0mL, 1cm PDMS stir bar). GC-MS-TOF showed a best match for the mixed isomer 1.3-Pentadiene for PIKE, best match for the cis isomer in the spent hop material and no 1,3-pentadiene was detected in tetrahydroisoalpha acids.

**Analysis of 2 Commercial Lager Beers:** SBSE-GC-MS-TOF was used to identify 1,3-pentadiene in two commercial lager beers. 5 g of cold beer was extracted using 2 stir bars (one in the liquid, one in the head space) in a 20mL headspace vial and extracted for 1 hour, then simultaneously desorbed. Lager Beer A, bittered with PIKE (9.0 BUs) and Light Lager Beer B, bittered to 6 BUs with pellet hops both contain 1,3-pentadiene, with the pellet hopped beer (~316 ppb)having roughly twice the concentration as the beer hopped with PIKE (12 BUs).

## Discussion and Conclusion

Results confirm that the component of interest was 1,3-pentadiene, and that it is naturally occurring in hop pellets, $CO_2$ hop extracts, as well as some advanced hop products, as well as beers made with these hop products. The 1,3 pentadiene is proposed to result from the degradation hop acids or components of the hop oil fraction. Future steps would be to look more in depthly at concentration of 1,3 –pentadiene in hop oils, and other beers, particularly pellet hopped beers. According to the CDC, 1,3-pentadiene is not harmful and poses no health threat to humans. However 1,3-pentadiene is a known off-flavor found in cider (kerosene, fusel oil off odor). Thus, it would be of interest to determine the threshold for flavor and aroma detection in beer and to monitor any concentration changes during beer aging. Because 1,3-pentadiene is likely a product of hop oil/hop resin degradation, it may also be of merit to determine rates of formation in hop pellets or advanced hop products to better understand its potential to be a marker of hop product quality.

## References and Contacts

**References**:

1. CRC Report on 1,3-pentadiene: http://www.inchem.org/documents/sids/sids/504609.pdf
2. Azhu Valappil, Z. et al. *Impact of thermal and nonthermal processing technologies on unfermented apple cider aroma volatiles*. **J. Agric. Food Chem**. (2009) Feb 11; 57(3): 924-929

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