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Dry hopping potential of Eureka!, a new hop variety

To monitor the dry hopping potential of the new hop variety Eureka!, brewing trials were performed and observed in detail. Static dry hopping was done for 1, 2, 4, and 8 days. Beers were analyzed using published methods to have an insight into the transfer of 4-MMP (GC×GC-TOFMS, published by *Reglitz* et al. in BrewingScience 71, 2018), selected hop aroma compounds (EBC 9.49) and hop derived bitter substances (EBC 9.47). Major transfer of 4-MMP and the aroma compounds myrcene, linalool, geraniol, and 2-methylbutyl isobutanoate happened during the first two days of dry hopping with only slight further increase between days 2 and 8. The same behavior could be found for the bitter components alpha-acids and humulinones, whereas xanthohumol increased until day 4. All results of dry-hopped beers allowed a comparison with a lab scale cold-water extraction which was tested as a possible prediction tool for dry hopping of a selected hop variety. In addition to analytics, sensory evaluations were carried out for the beers with help of descriptive analysis. With focus on fruity, especially black currant-like, aroma in beer, the received findings suggest a hop contact time of 2 days of dry hopping with the hop variety Eureka!.

Descriptors: dry hopping, 4-mercapto-4-methylpentan-2-one (4-MMP), hop aroma components, hop bitter compounds, brewing trials, cold-water extraction

1 Introduction

A multitude of hop varieties are present on the market which are traditionally classified as aroma or bitter hops. However, all hop varieties contain compounds that are contributing to aroma and bitterness of beer (hop essential oils and hop bitter acids).

The hop variety Eureka! originated from a cross between Apollo and a male developed in the Hopsteiner breeding program. Maturating in late-season, its average yield ranges from 2,800 to more than 3,000 kg/ha. The Eureka! hops offer both, a high total hop oil content (up to 4 mL/100 g) as well as a high content of bitter components (alpha-acids between 17 and 20 % and beta-acids up to 6 %) (Table 1).

A detailed aroma evaluation of the smell of raw hops of Eureka! gave resinous, strong herbal, spicy, and fruity notes. Even though the fruity notes are less distinct, they could be specified from tropical-citrus to dark stone fruit with a special attention on black currant aroma impression (Fig. 1, [1]).

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The black currant-like smelling hop odorant 4-mercapto-4-methylpentan-2-one (4-MMP) also known as 4-methyl-4-sulfanylpentan-2-one (4-MSP) was described for the first time in Cascade hops [2, 3]. In 2017, *Steinhaus* and Reglitz studied the influence of variety, provenance, harvest year, and processing on 4-MMP concentra-

Table 1 Chemical ingredients of hop variety Eureka! [1]

Components	
Alpha-acids in %	17.0–20.0
Beta-acids in %	4.5–6.0
Co-Humulone % rel.	28–30
Xanthohumol	0.5–0.6
Total Oil in mL/100 g	2.5–4.5

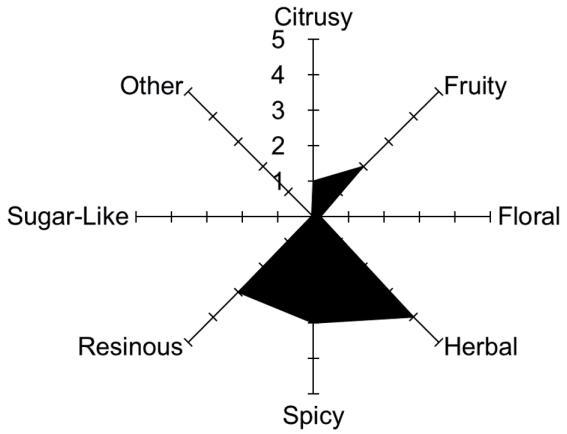

Fig. 1 Aroma evaluation of Eureka! (rated by smell of raw hops on a 0-5 scale)

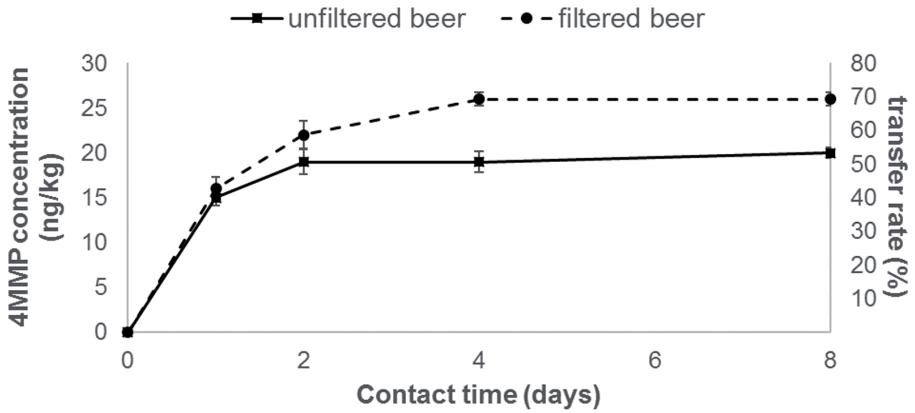

Fig. 2 **Transfer of 4-MMP from hops into beer during dry hopping with Eureka!, published in [5] (Error bars represent ± standard deviation of triplicate analyses)**

tions [4]. To get the exact amount of this thiol, the authors developed a stable isotope dilution assay, with selective isolation of thiols by mercurated agarose and in combination with GC×GC-TOFMS and applied the method to 53 different hop samples. The value of 4-MMP in this study ranged from <1 to 114 µg/kg. High concentrations could be found in hop varieties from the United States, with the highest level in Citra (114 µg/kg) followed by Eureka! (59.1 µg/kg), Simcoe (51.2 µg/kg) and Apollo (28.6 µg/kg). 4-MMP was absent from traditional German and English varieties. The study also showed that hop processing such as drying and pelletizing had only a minor impact on this compound but the harvest year as well as the storage influenced the amount. In the next step, the developed analytical method [4] was also used by Reglitz et al. to study the behavior of this hop odorant during dry hopping with the hop variety Eureka! [5]. Therefore, the transfer of 4-MMP was observed during static dry hopping. The results (Fig. 2) showed that the major transfer happened during the first two days of dry hopping, whereas only slight further increase between days 2 and 8 was detected [5].

Even if 4-MMP is an important hop odorant with a very low odor threshold in beer (0.5–1.5 ng/L [6]), there are other relevant key hop derived aroma compounds in beer. It is known from literature that linalool is responsible for the citrusy and floral aroma impressions in late hopped beers [7, 8]. It is also present in high concentrations in dry-hopped beers. For the monoterpene myrcene an aroma contribution to dry-hopped beer could also be observed [7]. Like 4-MMP, the terpene alcohol geraniol with an odor threshold of 4 µg/L [2] is described to be more varietal specific than linalool [3]. The ester 2-methylbutyl 2-methylpropanoate, also known as 2-methylbutyl isobutanoate, was identified by *Takoi* et al. in 2009 as a specific flavor compound derived from Nelson Sauvin hop with an odor threshold of 78 µg/L in beer imparting a green apple-like and/or apricot-like flavor [9].

Besides hop derived aroma compounds, many other hop ingredients dissolve into beer when the dry hopping technique is used. Isohumulones are known to be the main contributors to beer bitterness. But in the last years research was focused on the identification, quantitation, and the evaluation of the bitterness intensity of oxidized hop acids like humulinones [10-12]. *Algazzali* and *Shellhammer* reported in 2016 that humulinones have a relative bitterness intensity of 66 (± 13) % in comparison to isohumulones [12]. Depending on the hop variety, hops may contain up to a maximum of 1 % of the prenylflavonoid xanthohumol. The natural yellow substance was discovered more than 100 years ago. The ratio of xanthohumol to alpha-acids serves as a characteristic of each variety. Xanthohumol shows a very mild bitterness [13]. Prenylflavonoids continue to draw attention of more and more research groups. Several positive physiological and pharmacological properties have been reported for xanthohumol and other prenylflavonoids from hops [14-17].

The aim of the present work was to study the dry hopping potential of the new hop variety Eureka!. Therefore, brewing trials were carried out and several hop derived aroma and bitter compounds were evaluated in the final beers with help of analytical methods together with a sensory approach. In addition, a lab scale cold-water extraction method was performed, and the corresponding results were compared to the findings of the real brewing trials. In this work, the same beers were analyzed as published recently by Reglitz et al. (2018) where the authors focused on 4-MMP only [5].

2 Materials and methods

2.1 Beer samples

The base beer for the dry hopping experiments was a German Pilsner type beer. The hopping regime was a single hop addition at the beginning of wort boiling with pellets of the varieties Perle and Hallertauer Tradition as well as ethanol extract made of Herkules, Hallertauer Magnum and Hallertauer Taurus. The beer was centrifuged but not filtered. The analytical parameters of the beer were as followed: 11.6 % original gravity, 5.0 vol% Ethanol, pH 4.5, and 35 International Bitter Units (IBU). The dry hopping procedure was done side by side in four cylindroconical vessels (10 hL) at –1 °C. Each vessel contained the base beer from one batch. The pellets type 90 of US Eureka! hops (harvest 2016) were added from the top of the vessels and the total amount was 250 g hops/hL beer. The dry hopping was done in a static way. After the contact time of 24 h, the hop sediment was removed from the bottom of the first vessel. In the same way, vessel 2 (after 2 days), vessel 3 (after 4 days), and vessel 4 (after 8 days) were treated. Each vessel was separated into 2 parts and one part was filtered using diatomaceous earth (100 g/hL) as filter aid. Filtered and unfiltered beers were bottled after air removal and closed with crown corks with oxygen scavenging properties. The bottles were stored at 4 °C. The finished beers were analyzed direct after the brewing trials.

2.2 Lab scale cold-water extraction

The hop amount used in the brewing trial was 250 g/hL. Therefore, the same hop amount as well as the same batch of hop pellets type 90 of US Eureka! (harvest 2016) were used for the lab scale method. The extraction solvent was a 5 % ethanol (v/v) buffered water with a pH 4.5. Citrate buffer (0.05 M) was used and the pH was adjusted with 45 % (w/w) potassium hydroxide solution.