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Linalool—A Key Contributor to Hop Aroma

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The hop aroma of beer can reveal different characteristics. Green, grass-like notes are due to aldehydes like hexanal and hexenal (1). Citrusy notes are generated by esters, nerol, and linalool (1), and flowery and fruity impressions are derived from linalool, geraniol, beta-ionon, citronellol, and a variety of ketones, epoxides, and esters (1–3). In the 1980s, Kowaka et al. (4) divided hop aroma into three main characteristics (dry hop, hop oil, and kettle hop). Kettle hop was defined as the flavor of boiled hops. This herbal flavor was postulated as an essential flavor impression, and humulene epoxide II was believed to be the key indicator substance (4). However, in further trials, the role of humulene epoxide II could not be confirmed, and it is not suitable as an indicator for herbal flavor (5). In 1991 Sakuma et al. (6) detected linalool as an important substance in hoppy flavor. These observations were confirmed by Kaltner (7) who postulated that linalool is an indicator substance. No influence of oxygenated compounds was found (8). However, different opinions about the contributing compounds are due to different definitions of hoppy flavor. When added at late stages of wort boiling, the resulting hop flavor differs from that of the green flavor of raw hops/hop pellets.

Today, it is accepted that linalool is a key contributor to hoppy flavor. On the one side, there is a good correlation between linalool content and perceived fruity-flowery flavor (6,7,9–11). On the other hand, linalool exceeds its threshold and, therefore, contributes actively to the aroma of hoppy beers (7,11,12). Only linalool has such an active aroma contribution. Previously published flavor thresholds differ, ranging from 8 µg/L (8) to 80 µg/L (13). According to Kaltner a hoppy flavor in beer is perceived at linalool concentrations above 20 µg/L. This coincides with the results of Hanke et al. (11,14) who found a flavor threshold of 27 µg/L in beer. Linalool is a chirale compound, and the chirale distribution is stable during processing from hop cones to all conventional hop products (9,15). The more odor potent (R)-form dominates as 92–94% of the total linalool content (7,16,17).

The use of a single hop variety results in individual flavor characteristics (1,18–21). The occurrence of “hop aroma” compounds is not limited to hops. The fruity flavor of Riesling and Muscat wines evolves from the combination of alpha-terpineol, geraniol, citronellol, nerol, linalool with 2-phenyl ethanol, ethyl acetate, and isoamylacetate (22–25). The linalool content of these wines ranges from 120 to 230 µg/L (25). So, although linalool is a perfect indicator substance for hoppy flavor in beer, this flavor perception is generated by a multitude of different aroma compounds. To date, more than 300 volatile compounds have been identified in hop oils. Most of these compounds, as well as their derivates, have flavor effects even at subthreshold concentrations. Such subthreshold effects have been assumed for complex foods like beer and could be confirmed for different flavor compounds in beer (11,26–28). In addition to the positive contribution of linalool to beer flavor, the thresholds of diacetyl and other off-flavors have been found to decrease at higher linalool concentrations (11).

Recent publications report increasing linalool levels during fermentation (7,29,30). This is believed to be due to a breakdown of glycosides (29). Glycosides originate from a protective mechanism of plants and consist of a sugar moiety, mostly beta-D-glucose, and “aglycon.” In hops, different aroma compounds act as aglycon. The content of glycosides is variety dependent (31,32). Figure 1 shows a linalool glycoside.
Glycosides are water soluble and odorless (29). Using glycosidic enzymes or heat or acidic treatment, glycosides can be split into the sugar moiety and odor active compound (e.g., linalool, geraniol) (31). The glycosides nerol and geraniol are heat stable and stable in diluted acid (33). Daenen et al. (29) showed that different yeast strains have different glycosidic enzymes. Different yeast strains cause individual cleavage of glycosides and, therefore, varying aroma release during fermentation (29). Aroma compounds are partially transformed during fermentation. Geraniol can be transformed into citronellol and nerol by yeast (20,34). alpha-Terpineol can be formed from linalool. Linalool is also a product of geraniol degradation (33–35). Steinhaus et al. (21) found that aroma compounds partially evaporate during fermentation.

A perceptible hoppy flavor can enhance beer quality. Contradictory results have been published regarding flavor stability, however. Schur (36) found a negative impact of hoppy flavor, but this could not be confirmed by Kaltner (7) and Hanke (11), who found masking effects that resulted in better sensorial results. The correlation between aging acceptance of beers and linalool content is shown in Figure 2.

Linalool is a suitable indicator substance for hoppy flavor in beer, especially in late-hopped brews. Dry-hopped beers however show a hop flavor that is very different from the hop aroma perceived in lager beers. Therefore, further investigations are necessary to determine indicator substances for dry-hopped beers. An increased linalool content in beer results in a fruity-flowery and citrusy character and potentially increases the aging stability of the beer. To minimize evaporation of aroma substances during wort boiling, late-hop addition is needed for beers with an intense hoppy flavor. Alternatively, hops can also be added during the whirlpool rest. Until now, most brewers have added hops according to their alpha-acid content, even if a hoppy flavor is desired. Dosing hops according to their linalool content should be a future approach used to create hoppy beers.
References