ARTICLE

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.

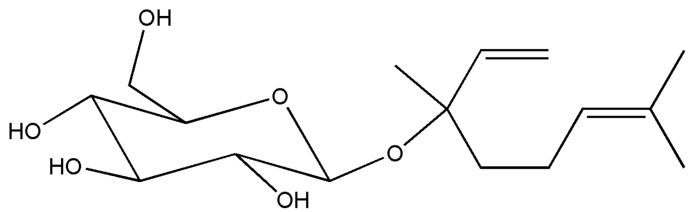

Figure 1. Glycoside from beta-D-glucose and linalool.

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.

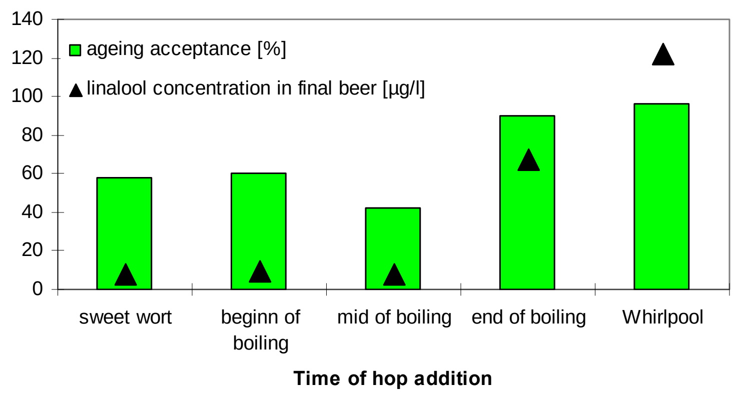

Figure 1. Correlation between linalool content in final beer and aging acceptance of forced-aged beers (7).

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

1. Kishimoto, T., Wanikawa, A., Kono, K., and Shibata, K. (2006). Comparison of the odor-active compounds in unhopped beer and beers hopped with different hop varieties. J. Agric. Food Chem. 54:8855-8861.
2. Marriott, R. (2001). Hop aroma products and their application in brewing. In: European Brewery Convention Monograph 31: Symposium on Flavor and Flavor Stability, pp. 137-142. Fachverlag Hans Carl, Nürnberg, Germany.
3. Van Opstaele, F., Goiris, K., Syryn, E., De Rouck, G., Jaskula, B., De Clippeleer, J., Aerts, G., and De Cooman, L. (2007). Hop: Aroma and bitterness perception. Cerevisia 31:167-188.
4. Kowaka, K., Fukuoka, Y., Kawasaki, H., and Asano, K. (1983). The true value of aroma hops in brewing. In: 19th European Brewery Convention Congress, London, pp. 71-78.
5. Fukuoka, Y., and Kowaka, M. (1983). Identification of compounds imparting hoppy flavor to beer. Rep. Res. Lab. Kirin Brew. Co. 26:31-36.
6. Sakuma, S., Hayashi, S., and Kobayashi, K. (1991). Analytical methods for beer flavor control. J. Am. Soc. Brew. Chem. 49:1-3.
7. Kaltner, D. (2000). Untersuchungen zur Ausbildung des Hopfenaromas und technologische Maßnahmen zur Erzeugung hopfenaromatischer Biere. Ph.D. dissertation. Freising, Technische Universität München, Fakultät Wissenschaftszentrum Weihenstephan für Ernährung, Landnutzung und Umwelt.
8. Kaltner, D., Thum, B., Forster, C., and Back, W. (2000). Hopfen. Brauwelt 140:704-709.
9. Fritsch, H., and Schieberle, P. (2003). Changes in key aroma compounds during boiling of unhopped and hopped wort. In: 29th European Brewery Convention Congress, Dublin, pp. 259-267. Fachverlag Hans Carl, Nürnberg, Germany.
10. Fritsch, H. T., and Schieberle, P. (2005). Identification based on quantitative measurements and aroma recombination of the character impact odorants in a Bavarian Pilsner-type beer. J. Agric. Food Chem. 53:7544-7551.
11. Hanke, S. (2009). Untersuchungen zum Einfluss der Hopfungstechnologie auf die Geschmacksstabilität und Harmonie untergäriger Biere. Ph.D. dissertation. Freising, Technische Universität München, Wissenschaftszentrum Weihenstephan für Ernährung, Landnutzung und Umwelt.
12. Peacock, V. E., and Deinzer, M. L. (1981). Chemistry of hop aroma in beer. J. Am. Soc. Brew. Chem. 39:136-141.
13. Meilgaard, M. C. (1975). Flavor chemistry of beer. II. Flavor and threshold of 239 aroma volatiles. Tech. Q. Master Brew. Assoc. Am. 12:151-168.
14. Hanke, S., Seidl, J., and Back, W. (2008). Bedeutung und Einfluss von Hopfenaromastoffen. Weihenstephaner 76:121-123.
15. Kaltner, D., Steinhaus, M., Mitter, W., Biendl, M., and Schieberle, P. (2003). (R)-Linalool als Schlüsselaromastoff für das Hopfenaroma in Bier und sein Verhalten während der Bieralterung. Monatsschr. Brauwissenschaft 56:192-196.
16. Steinhaus, M., Fritsch, H. T., and Schieberle, P. (2003). Quantitation of (R)- and (S)-linalool in beer using solid phase microextraction (SPME) in combination with a stable isotope dilution assay (SIDA). J. Agric. Food Chem. 51:7100-7105.
17. Steinhaus, M., and Schieberle, P. (2000). 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. 48:1776-1783.
18. Back, W. (2000). Aromatherapie—Einflußmöglichkeiten auf das Hopfenaroma. Brauindustrie 85:138-140.
19. Kaltner, D. (2005). Moderne Hopfenprodukte—Aus vielen guten Zutaten kann der Brauer ein spitzen Bier-Image brauen. Getränkeherstellung, August:25-27.
20. Steinhaus, M., and Schieberle, P.(2007). Transfer of potent hop odorants linalool, geraniol and 4-methyl-4-sulfanyl-2-pentanone from hops into beer. In: 31st European Brewery Convention Congress, Venice, pp. 1004-1011. Fachverlag Hans Carl, Nürnberg, Germany.
21. Steinhaus, M., Wilhelm, W., and Schieberle, P. (2007). Comparison of the most odour-active volatiles in different hop varieties by application of a comparative aroma extract dilution analysis. Eur. Food Res. Technol. 226:45-55.
22. Van Wyk, C. J., Kepner, R. E., and Webb, A. D. (1967). Volatile components of *Vitis vinifera* variety White Riesling. III. Neutral components extracted from wine. J. Food Sci. 32:669-674.
23. Van Wyk, C. J., Webb, A. D., and Kepner, R. E. (1967). Volatile components of *Vitis vinifera* variety White Riesling. I. Grape juice. J. Food Sci. 32:660-664.
24. Webb, A. D., and Muller, C. J. (1972). Volatile aroma components of wines and other fermented beverages. In: (Hrsg.): Advances in Applied Microbiology, pp. 75-146. Academic Press.
25. Wenzel, K. W. O., and De Vries, M. J. (1968). Investigation of Muscat aroma. S.-Afr. Tydskr. Landbouwet. 11:273-279.

26. Hanke, S., Herrmann, M., and Back, W. (2008). Interactive effects of flavor compounds in beer. In: 1st International Symposium for Young Scientists and Technologists in Malting, Brewing and Distilling, Cork, P20.
27. Hanke, S., Herrmann, M., Back, W., Becker, T., and Krottenthaler, M. (2009). Synergistic and suppression effects of flavor compounds in beer. In: 32nd European Brewery Convention Congress, Hamburg, L21.
28. Herrmann, M., Klotzbücher, B., Wurzbacher, M., Hanke, S., Kattein, U., Back, W., and Krottenthaler, M. A new validation of relevant substances for the evaluation of beer aging depending on the employed boiling system. J. Inst. Brew. *Submitted.*
29. Daenen, L., Saison, D., De Cooman, L., Derdelinckx, G., Verachtert, H., and Delvaux, F. R. (2007). Flavor enhancement in beer: Hydrolysis of hop glycosides by yeast beta-glucosidase. Cerevisia 32:24-36.
30. Hanke, S., Herrmann, M., Rückerl, J., Schönberger, C., and Back, W. (2008). Hop volatile compounds. Part II: Transfer rates of hop compounds from hop pellets to wort and beer. Brew. Sci. 52(July/August):140-147.
31. Biendl, M., Kollmannsberger, H., and Nitz, S. (2003). Occurrence of glycosidically bound flavor compounds in different hop products. In: 29th European Brewery Convention Congress, Dublin, pp. 252-258. Fachverlag Hans Carl, Nürnberg, Germany.
32. Kollmannsberger, H., Biendl, M., and Nitz, S. (2006). Occurrence of glycosidically bound flavor compounds in hops, hop products and beer. Monatsschr. Brauwissenschaft 59(May/June):83-89.
33. Ohta, T., Morimitsu, Y., Sameshima, Y., Samuta, T., and Ohba, T. (1991). Transformation from geraniol, nerol and their glucosides into linalool and alpha-terpineol during Shochu distillation. J. Ferment. Bioeng. 72:347-351.
34. King, A. J., and Dickinson, J. R. (2003). Biotransformation of hop aroma terpenoids by ale and lager yeasts. FEMS Yeast Res. 3:53-62.
35. Baxter, R. L., Laurie, W. A., and McHale, D. (1978). Transformations of monoterpenoids in aqueous acids—Reactions of linalool, geraniol, nerol and their acetates in aqueous citric-acid. Tetrahedron 34:2195-2199.
36. Schur, F. (1976). Auswirkungen der Hopfung auf Technologie und Bierqualität. Schweiz. Brau.-Rundsch. 87:19-29.