Auxiliary bitter compounds in hops and the quality of bitterness in beer

IMPROVING THE HARMONY | The term "auxiliary bitter compounds" in hops refers to all bitter compounds in the hop resin which are transferred to the beer and are not iso-α-acids. The majority of these substances are considered desirable from a sensory perspective. The ratio of the non-specific EBC bittering units (spectrophotometric method) to the specific iso-α-acids (HPLC method) serves as an indicator for the amount of auxiliary bitter compounds in beer. The evaluation of various existing data demonstrates: adding larger amounts of aroma hops over several additions not only influences the aroma but also serves to improve the harmony of the beer bitterness.

THE ESSENTIAL BITTER compounds in hops are the α-acids. They undergo isomerization during wort boiling. Depending on the duration of the boil and the type of hop product employed, up to 45 % of the α-acids are converted to readily soluble iso-α-acids. The latter are primarily responsible for the bitterness in beer. Many brewers consider iso-α-acids to be the only relevant bitter compounds in beer, and therefore, they do not attribute any value to other bitter compounds introduced through the addition of hops.

However, aside from α-acids, hops also contain numerous other compounds, such as β-acids. Opinions differ regarding their contribution to bitterness in beer. Since they are soluble in wort only to a limited degree, do not undergo isomerization and are present merely in trace amounts in beer, their sensory contribution is frequently questioned.

Defining auxiliary bitter compounds in hops

In recent years, a variety of terms have emerged for the bitter compounds found in beer which are not iso-α-acids. These include "non-iso- α-acid bitter substances" (or compounds) or "accompanying bitter substances". The term "auxiliary bitter compounds" will be used in subsequent passages to refer to all of the substances in beer which are not characterized as iso-α-acids. Based on this definition, unisomerized α-acids are considered auxiliary bitter compounds.

It has been demonstrated that α-acids and β-acids in hops are unstable in the presence of the oxygen in air, which causes an increase in the quantity of auxiliary bitter compounds in hops and subsequently in beer. Aging compounds created through oxidation are not addressed here. All con-

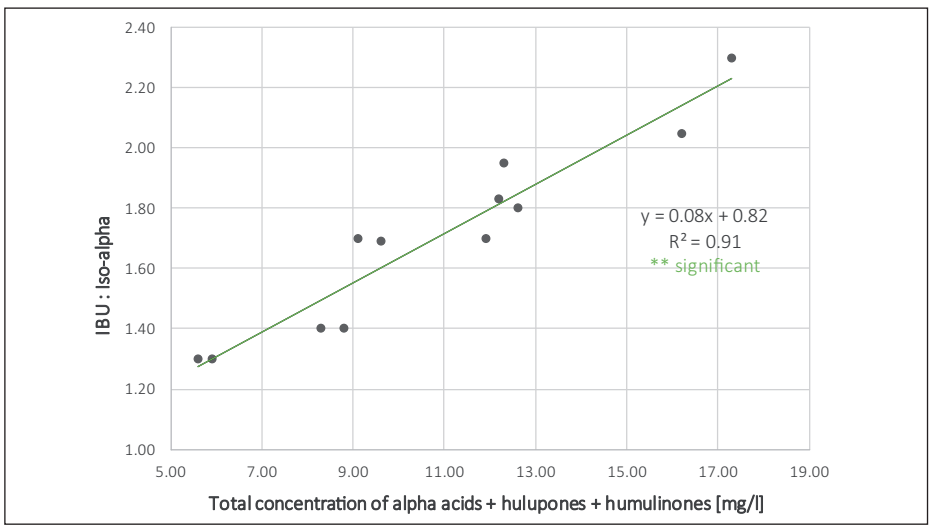


Fig. 1 IBU to iso-α-acids as a function of the concentration of α-acids, humulinones and hulupones in 12 beers

Authors: Dr. Adrian Forster, Dr. Florian Schüll, both HVG Hopfenverwertungsgenossenschaft e.G., Wolnzach; Andreas Gahr, Forschungsbrauerei der Hopfenveredlung St. Johann GmbH, Train – St. Johann; all from Germany

clusions and research results are based on "fresh" hops. The term "fresh" is explained in [1, pp.152] and can be simplified as follows: after harvesting, hops are stored in a normal atmosphere (with exposure to air) for a period of one to up to eight months before being processed to a product (extract, pellets) which is protected against exposure to oxygen. If the hops are stored at a low temperature (< 5 °C) prior to processing, the losses in quality are tolerable and consequently the product is considered "fresh".

Analysis of bitter compounds in beer

The current method of choice is HPLC. Earlier, HPLC was limited to the determination of α-acids and β-acids in hops [EBC 7.7], but has since been utilized for the separation of numerous compounds [e.g. 2].

Important findings were reported by the work group headed by T. Hofmann (TU München-Weihenstephan) regarding bitter compounds in hops [3]. A summary of these findings can be also found in [1, p. 225]. A great number of compounds have been found in beer which can be grouped as follows:

- Compounds present in hops, for example, deoxyhumulone;
- compounds with a polyphenolic character such as xanthohumol, which is converted to isoxanthohumol similar to the isomerization of acids during wort boiling;
- compounds which are formed in conjunction with α-acids, for example humulinones;
- compounds partly formed from β-acids during wort boiling such as hulupones, hulupinic acids or hydroxytricyclolupulones.

Along with these compounds, unisomerized α-acids may also be present, depending on when the hops are added in the brewing process. With a hop addition at the beginning of the boil, only traces of α-acids are detectable in beer, with the concentration increasing to several mg/l for the corresponding additions later in the boiling process.

The majority of these compounds were described as pleasantly bitter by Haseleu [3]. Although the concentrations of these

BITTERING UNITS (IBU), ISO-α-ACID CONTENT, ...

... IBU to iso-α, IBU minus iso-α = non-iso-α-bittering units

IBU	iso-α	IBU:iso-α	non-iso-α-BU
20	20	1	0
25	20	1.25	5
30	20	1.33	10

Table 1

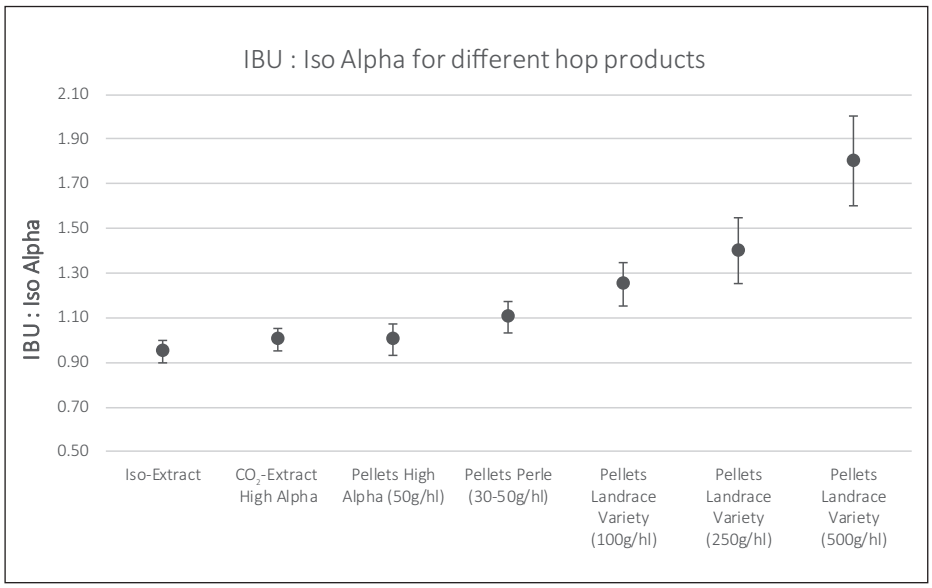


Fig. 2 Ranges of IBU to iso-α-acid ratios for different hop products

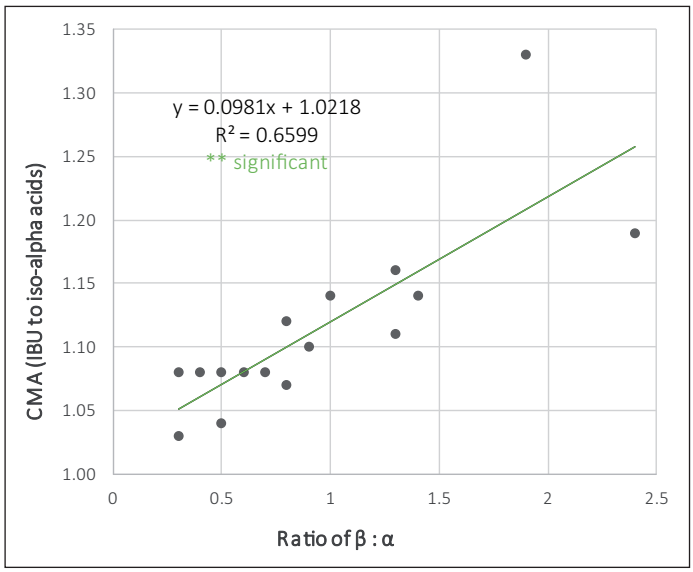


Fig. 3 IBU to iso-α-acid ratios in beer plotted against the ratio of β-acids to α-acids in the hops (16 single-hop beers)

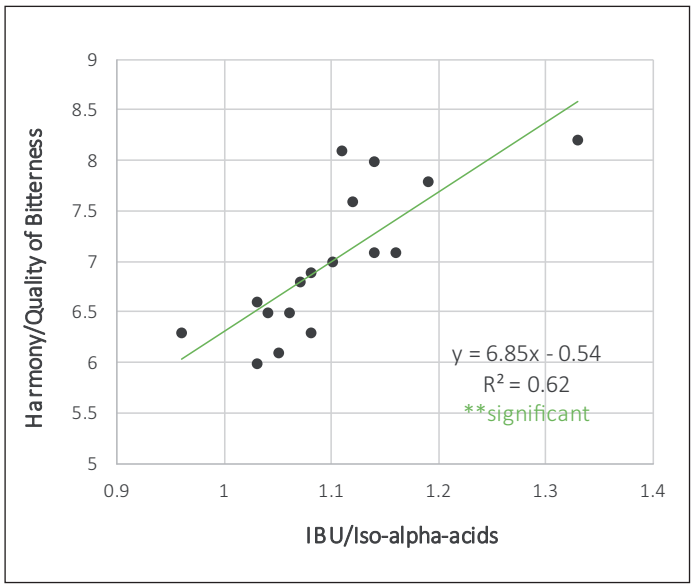


Fig. 4 Quality of the bitterness in 16 single-hop and one control beer plotted against the ratio of IBU to iso-α-acids

compounds are often lower than the respective sensory thresholds in beer, additive and synergistic effects occur, contributing to the overall sensory perception.

Despite the fact that HPLC is a very suitable method for determining auxiliary hop bitter compounds in beer, only a few research institutes possess the resources to perform this complex analysis. One, therefore, wonders whether other tools are available to assist brewers in estimating the quantity of the auxiliary bitter compounds present in their beer.

Evaluating the quantity of auxiliary bitter compounds from hops

As strongly hopped beers continue to rise in popularity, it is clear that auxiliary bitter compounds will play an increasingly greater role in the view on the quality of beer bitterness. This presents two challenges:

- Defining a simple method, which can serve as an indicator for the general quantity of non-iso-α acid bitter compounds in beer;
- finding a figure in hops which corresponds to this indicator in beer.

Two methods are available for the determination of bitterness in beer. The specific method described in EBC 9.47 utilizes HPLC to determine the concentration of iso-α-acids (IAA). The other is a non-specific spectrophotometric method which measures the absorption of all substances dissolved in iso-octane at a wavelength of 275 nm (EBC 9.8). This includes α-acids and other bitter compounds in addition to iso-α-acids. The ratio of the value obtained for bittering units (IBU) for unspecific compounds to the concentration of specific iso-α-acids (measured by means of HPLC) represents the relative quantity of auxiliary bitter compounds. The greater the difference between the unspecific bittering units and the specific iso-α-acids is, the more the other bitter compounds contribute to measured value for IBU.

It should be noted that the ratio of IBU to iso-α-acids is not an absolute measure but rather serves as a reference for the relative contribution made by the auxiliary hop bitter compounds to the corresponding level of bitterness. This relationship is shown in table 1. Although all three beers contain 20 mg/l iso-α-acids, each yields a different IBU to IAA ratio: 1.0, 1.25 and 1.5. This difference in IBU corresponds to 0, 5 and 10 bittering units, respectively, which are

not attributable to iso-α acids. The results of a series of brews are plotted in figure 1. In the graph, the ratios of IBU to iso-α-acids were plotted against the values obtained by HPLC for non-iso-α-acid bitter compounds which include α-acids, hulupones and humulinones. The results show a significant relationship and a correlation confirming the initial assumption. The ratio of IBU to iso-α-acids represents a viable indicator for the quantity of auxiliary bitter compounds present in beer.

A further relationship can be found in the following empirical observation. Depending on the kind of hop product and the hop variety, beers are produced containing varying ratios of IBU to iso-α-acids [1, p. 226]. The ratios of IBU to iso-α-acids according to the kind of hop product and the respective range of variation are provided in figure 2. If iso-extract is used exclusively, the value is below 1. Extract from high hops yielded values around 1.0, while the values measured in beers produced with high pellets are calculated to be somewhat higher (approx. 1.03). A value of around 1.1 was measured for pellets of the hop variety Perle. Additions at a rate of 100 g/hl with traditional aroma varieties (e.g. Tettnanger, Spalter, Hallertauer Mfr.) resulted in values near 1.3. If the hopping rate is increased to 500 g/hl, for example, IBU to iso-α-acids values closer to 2.0 can be achieved. Delaying the hop addition until the end of the boil brought the ratio to above 2.0. The more complex the aroma hop additions are, the greater the amount of auxiliary hop bitter compounds.

Since Haseleu [3] reported that many bitter compounds are derived from β-acids, it was only logical to look for a relationship between the β-acid content in hops and the IBU to iso-α ratio. This was done as part of the brewing trials with single hop varieties supported by the CMA [4] in 2005. A total of 16 beers were produced at that time.

Figure 3 shows a graph of the ratio of IBU to iso-α-acids measured in the beers plotted against the ratios of β-acids to α-acids in the hops. A significant correlation was observed between hops and auxiliary hop bitter compounds in beer. For this reason, including the ratio of β-acids to α-acids in information brochures describing individual hop varieties is helpful [1, p. 146].

Sensory analysis results for auxiliary bitter compounds in hops

The sensory attributes of single hop batches brewed for the CMA variety portfolio [4] were evaluated according to a rating system developed by the participating organizations. Members of a trained tasting panel scored the beer samples for harmony/quality of the bitterness on a scale of 1 to 10. Figure 4 shows the sensory evaluation results for the ratio of bittering units to iso-α-acids. A high degree of correlation was observed. The harmonious aspect of bitterness increased with the quantity of auxiliary hop bitter compounds. In figure 5 results of several test series with 16 beers are combined [5, 6]. A strong correlation of the quality of bitterness and the ratio of IBU to iso-α-acids is evident. In essence, these practical brewing trials confirm the fundamentals established by Haseleu. If undamaged by oxygen, auxiliary bitter compounds from fresh hops round out the bitterness in beer.

The impact of brewing procedures

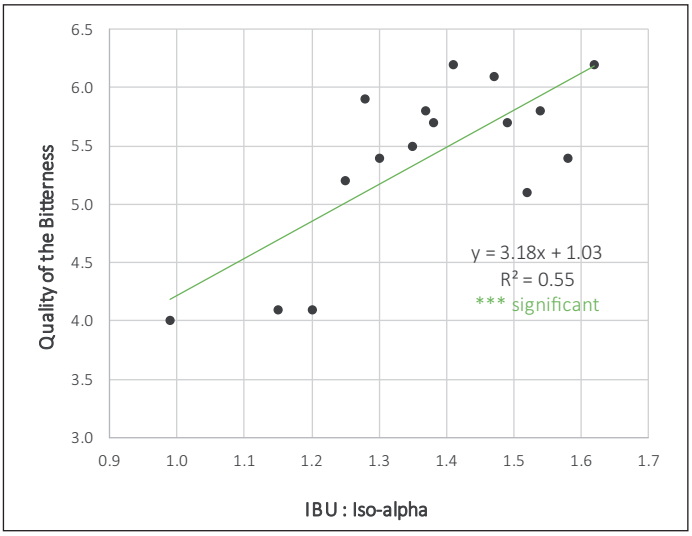
Several factors influence the amount of auxiliary hop bitter compounds in beer:

- Using hops with a higher β:α ratio leads to higher concentrations of auxiliary bitter compounds in beer. This is primarily true of aroma hops. Along with traditional landrace aroma hop varieties such as Saazer, Spalter, Tettnanger, Hallertauer Mfr. and Hersbrucker with β:α ratios of 1.3 to 2.4, Saphir also exhibits a high value of 1.9, while those for Hallertau Tradition, Spalter Select, Opal and Smaragd range from 0.8 to 1.0.
- Contrary to aroma hops, bitter varieties are utilized at considerably lower rates (20 to 50 g/hl) and the β to α ratio is only 0.4. Thus, the potential of bitter varieties contributing relevant amounts of auxiliary bitter compounds is limited.
- Short boiling times increase the ratio of IBU to iso-α-acids, because many of the auxiliary bitter compounds are extracted easily.
- Late hop additions with a high potential for auxiliary bitter compounds, such as the case with most aroma hops, have a direct effect on the non-iso-α-acid compounds in beer [7].
- However, the qualitative, positive effect is countered by an economic aspect, namely poorer utilization of the α-acids.
- The practice of dry hopping also transfers bitter compounds to the beer without the formation of iso-α-acids. In beers exclusively dry hopped at a rate of 500 g of hops per hl of beer, bitterness values of up to 28 IBU were measured with iso-α-acid concentrations of slightly more than 1 mg/l [7].

Summary

The term auxiliary bitter compounds in hops refers to all bitter compounds in the hop resin which are transferred to the beer and are not iso-α-acids. This includes all such components found in fresh hops and excludes those formed through oxidative aging reactions. There are numerous auxiliary bitter compounds found in hops that are either present in a directly soluble form in hops or are formed from α-acids and β-acids during the wort boiling process.

Fig. 5
Quality of the bitterness in 16 beers plotted against the ratio of IBU to iso-α-acids



The majority of these substances are considered desirable from a sensory perspective. They reduce a lingering character of bitterness and make a positive contribution to the quality and harmony of the bitterness in beer. The ratio of the non-specific EBC bittering units (spectrophotometric method) to the specific iso-α-acids (HPLC method) serves as an indicator for the amount of auxiliary bitter compounds in beer. This ratio is equal to 1 in beers brewed with only one hop addition of high-α hops at the beginning of the boil.

By contrast, beers brewed with a complex hopping regimen, e.g. with several additions of aroma hops, exhibit significantly higher levels of bittering units than iso-α-acids. Here, the values for IBU to iso-α-acids have been measured as even higher than 2. In this situation, the iso-α-acids are present in comparable quantities to the non-iso-α bittering units. Thus, auxiliary bitter compounds make up a sizable portion of the bittering units.

The results from the brewing trials described previously show that the bitterness of beers with higher ratios of IBU to iso-α-acids is less harsh and lingering, while the overall impression is more balanced and pleasant. Adding larger amounts of aroma hops over several additions not only influences the aroma but also serves to improve the harmony of the beer bitterness. ■

Literature

1. Biendl, M.; Engelhard, B.; Forster, A.; Gahr, A.; Lutz A.; Mitter, W.; Schmidt, R.; Schönberger, C.: "Hops – Their Cultivation, Composition and Usage"; Fachverlag Hans Carl, 09/2014, ISBN: 978-3-418-00823-3.
2. Dresel M.; Vogt C.; Dunkel A.; Hofmann T.: "The Bitter Chemodiversity of Hops (Humulus lupulus L.)", J. Agric. Food Chem. 64 (2016), pp. 7789-7799.
3. Haseleu G.; Intelmann D.; Hofmann, T.: "Structure, determination and sensory evaluation of novel bitter compounds formed from α-acids of hop (Humulus Lupulus L.) upon wort boiling", Journal of Food Chemistry 116 (2009), pp. 71-81.
4. Hopfen aus Deutschland, Sortenmappe der Centralen Marketing-Gesellschaft der deutschen Agrarwirtschaft (CMA), 2005.
5. Forster, A.; Gahr, A.: "Der Einfluss der Hopfung auf die Bierqualität", BRAUWELT 150 (2010), pp. 1547-1551.
6. Forster, A., Gahr, A.: "Hopping of Low Alcohol Beers"; BrewingScience 65 (2012), pp. 72-82.
7. Forster, A., Schüll, F.; Gahr, A.: "Geringe Bittere und volles Hopfenaroma – ein Widerspruch?", Brauindustrie 102 (2017), pp. 24-27.