125th Anniversary Review: The Role of Hops in Brewing

C. Schönberger[1,*] and T. Kostelecky[2]

ABSTRACT

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Although hop technology has been a substantial part of brewing science for the last 130 years, we are still far from claiming to know everything about hops. As hops are considered primarily as a flavour ingredient for beer, with the added benefit of having anti-microbial effects, hop research is focused on hops as a bittering agent, as an aroma contributor and as a preservative. Newer fields in hop research are directed toward the relevance of hops in flavour stability, brewing process utilisation, the technological benefits of hops in brewing as well as hops as a source of various substances with many health benefits. However the more we find out about the so-called "spirit of beer" the more questions emerge that demand answers. While hop research was only an ancillary research field for decades, during the last ten years more universities and breweries have determined that hops must play a meaningful role in their research efforts. This article gives an overview of the up-to-date knowledge on hop aroma, hop derived bitterness, and the role of hops in flavour stability as well as light stability. Hop research is a wide field, therefore in this review only selected topics are reviewed. Other research areas such as hops utilisation, the antifoam potential of hops, or the advances in knowledge pertaining to the physiological valuable substances of hops go beyond the scope of this article.

Key words: flavour stability, hop aroma, hop bitterness, hop flavour, hop products, hops, light struck flavour.

ROLE OF HOPS

Introduction

So much in life is complex and so is hop aroma. Verzele wrote in 1986 that "Hops are much more important for beer than is generally estimated, even in brewery circles"[58]. This is still true, however recently we have experienced some notable changes. With the current revival of very hoppy beers, predominantly in the U.S. craft beer market (also increasingly in Europe), the need to decipher the mystery of hops and especially that of hop aroma is again on the list of priorities in brewing research.

[1] Barth Innovations, Freiligrathstr. 7/9, 90482 Nuremberg, Germany.
[2] John I. Haas, Inc., 5185 MacArthur Blvd NW, Washington, DC 20016, USA.
[*] Corresponding author. E-mail: Christina.Schoenberger@johnbarth.de

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Potent aroma compounds in hops

The first hop oil fractions were obtained by steam distillation in 1819[17]. But only at the end of the 19th century were the first six hop aroma compounds, including myrcene and humulene, identified by Chapman[7]. Chapman described back then that linalool and myrcene elicit the typical scent of hops. In 1966, Buttery and Ling[6] were able by means of capillary column chromatography to resolve about 100 hop oil components. Twelve years later Tressel et al.[55] investigated the beer aroma constituents. Within the 110 components, he was able to identify 47 that were shown to be hop derived. Figure 1 shows the classification of hop oil according to Sharpe and Laws[47], where 50–80% of the hop oil is comprised of hydrocarbons.

In 2000, Steinhaus and Schieberle[51] found 23 potent aroma compounds in the hop variety Spalter Select that were subsequently categorised by flavour dilution factors. The most potent aroma constituents were *trans*-4,5-epoxy-(E)-2-decenal (which confers a metallic note), linalool (flowery) and myrcene (geranium like). The researchers were also able to identify four previously unknown compounds in hop oil, namely 4,5-epoxy-(E)-2-decenal; 1,(Z)5-octadien-3-one; 1,(E)3,(Z)5-undecatriene and 1,(E)3,(Z)5,9-undecatetraene. In similar work, Kishimoto et al.[31] discovered 4-mercapto-4-methylpentan-2-one (4MMP) as a potent odorant in American, Australian and New Zealand cultivars that contributed to the fruity aroma from these hops.

Hop aroma in beer

As approximately 97% of the world hop crop finds its way into beer, the aroma properties of hops in beer are of much greater importance to the brewer than the hop aroma of the original raw hops. Still many brewers select their hops by manual sensory evaluation, knowing by experience what characteristics in raw hops they are looking for that will ensure the aroma characteristics of their beers. The question of how the raw hop characteristics correlate with the hop aroma characteristics in beer cannot be answered satisfactorily, as the brewing process and the hopping regimes offer so many parameters to consider that general conclusions cannot be drawn. However, with the current capability to identify hundreds of hop oil compounds, it has become possible to track the fate of individual compounds during the brewing process.

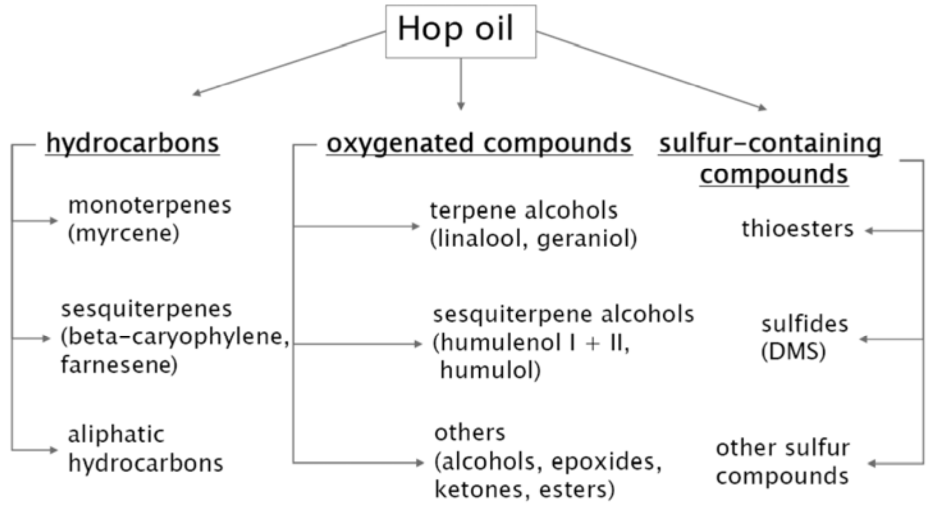

Fig. 1. Classification of hop oil according to Sharpe and Laws[47].

Table I. Identified aroma relevant compounds in strong hopped beers by Kishimoto et al.[31], Nielsen[43] and Lermusieau and Collin[34].

Sensory character	Compound	Threshold in beer
Black currant	4 MMP	10–50 ppb
Black currant, muscat	3 MH	55 ppb
Resinous	Myrcene	30–1,000 ppm
Floral, citrus	Linalool	8–80 ppm
Floral, rose like	Geraniol	4–40 ppm
	Ethyl 2-methyl-butanoate	
	Ethyl 4-methyl-pentanoate	1 ppm
Fruity, herbal	*cis*-Rose oxide	5–50 ppb
Hoppy, pineapple	(e,z)1,3,5-Undecatriene	no data
Cheesy	2-Methylbutyric acid	no data
Grape tobacco, black tea	Beta damascenone/phenyl ethyl alcohol	no data
Cedarwood	Caryophylla-3,8-dien-(13)-dien-5-beta-ol	no data
Cheesy/onion/garlic	Various sulfur compounds	no data

To define a flavour impact in a specific food type, for instance beer, the relevant threshold of the substance must be known. However, the threshold value depends very much on the medium analyzed (water, acidified water, beer, unhopped beer) and can vary considerably. Also, interactions between different compounds that lead to additive, synergistic or masking sensory impression are difficult to evaluate. While the analytical means to effectively define hop aroma impact compounds in beer had not yet been established prior to 1980, various researchers claimed in the 80s and 90s that linalool oxide, citronellol, geraniol, geranyl acetate, α-terpineol, α-eudesmol, t-cadinol, humulenepoxide I, humulenol II and humuladienone and other substances were responsible for the hoppy aroma in beer[40]. Steinhaus and Schieberle[51] showed that by using aroma extract dilution analysis (AEDA), most of these compounds were not responsible for a hoppy aroma in beer. Only linalool was confirmed in various works to significantly contribute to the hoppy aroma in beer[45]. Takoi et al.[52] found that linalool acts synergistically with geraniol and citronellol. They also discovered that the presence of β-citronellol (lime aroma) depends on geraniol metabolism by the yeast. Kishimoto et al.[31] identified 19 hop derived components in hopped beers using GC-olfactometry. Within these, 4-mercapto-4-methylpentan-2-one (4MMP, blackcurrant-like) and 3-mercaptohexan-1-ol (muscat-, blackcurrant-like) proved to contribute to the hoppy aroma. Nielsen[43] was also able to identify important contributors to a hoppy aroma (Table I).

The current knowledge about hop aroma in beer can be summarised as follows:

- Green and grassy flavours can be attributed to aldehydes, e.g., hexanal
- Citrus flavours can be attributed to esters, nerol and linalool
- Floral and fruity flavours can be attributed to linalool, geraniol, β-ionone, citronellol, to 4MMP and 3 MH and other ketones, epoxides and esters[37]
- Herbal flavours can be attributed to oxidised sesquiterpenes[32].

With ongoing research in the field of hop aroma it becomes more evident that hop aroma character impact compounds are variety specific. While some results deny various hop aroma compounds any relevance, additive or even synergistic effects (as well as masking) may still change the picture. Hanke et al.[18] studied the effect on threshold values of binary mixtures of hop aroma compounds. As an example, he found that a mixture of caryophyllene and nerol was found to have a flavour threshold of 170 µg/L whereas the single thresholds are 210 mg/L and 1,200 µg/L, respectively. The addition of linalool with farnesene resulted in a common threshold of 500 μ/L while farnesene alone has a threshold of about 2,000 μg/L. Furthermore, the ratio of the relevant compounds proved to be of importance in these mixtures which confirms the remarkable complexity of hop aroma.

A hoppy aroma in the final beer is most noticeable when late-hopping or dry-hopping is applied. Late-hop addition means a hop addition at the end of boil or in the whirlpool where the hops are (still) subject to a temperature treatment, without unnecessary evaporation of many valuable aroma compounds. In order to determine the aroma potential of hops, Hanke et al.[19,20] were able to show that different hop varieties had different transfer rates of linalool and other aroma compounds into beer. The behaviour of each aroma compound was unique and compound specific. The transfer rates of linalool proved to be between 50 and 110% depending on the hop variety. For geraniol, the rates were between 100 and 240%, which means that both compounds were additionally released or generated during processing. The specific influence of yeast and yeast metabolism is also of importance in terms of generation and release of hop aroma compounds, as important biotransformation reactions may take place during fermentation[52]. The late-hop addition process is paradoxically often still based on the alpha acid content. To provide a measure with which to dose hops with hop aroma in mind, in 1992, Nickerson and Van Engel[42] attempted to establish the Hop Aroma Unit (HAU) based on the quantitation of selected hop aroma compounds in beer that were regarded as important at that time. But as the linalool content does not necessarily correlate with the total hop oil content (nor does the content of other compounds), and the hop oil content does not necessarily correlate with the alpha acid content, a consistent hop aroma in a moderately to strongly traditionally hopped beer can still be considered a masterstroke of achievement (if you are not using hop aroma downstream products).

With the success of U.S. craft beers, where a substantial number of beers are dry-hopped, this technique is gaining much of the focus of hop research. Dry-hopping is mainly applied during lagering. Dry-hopping can be seen as a cold extraction of hop material into an alcoholic solution. Though only relatively little research has been carried out concerning dry-hopping, some studies have shown that the dry-hop character is very sensitive in regard to changes. It has been shown that a different picking date can have a significant impact on the dry-hop flavour in beer and it was also shown that the location where the hops are grown can have as much importance as the picking date[2]. But in regard to very high hop additions, particularly above 500 g/hL (for dry-hopping only), saturation effects in terms of maximum hop flavours became clear. It is obvious that the flavour results from late-hopping versus dry-hopping regimes are totally different and that very often in craft brewing, extreme hopping additions in total of about 500–800 g/hL can be applied.

However, with the work more recently conducted, we now have a much better understanding about hop aroma and hop aroma in beer and which molecules contribute to it. The more we understand, the more we have to admit how complex hop aroma is and that in the end, we may never gain a complete understanding of it.

Hop derived bitterness

One of the primary aspects of flavour contributed to beer by hops is bitterness. Research into the physiology of bitterness during the last decade has revealed the complexity of bitterness perception, but riddles still remain. The bitterness research in brewing revealed that iso-alpha acids, though the main contributor to beer bitterness, are not the only source for bitterness in beer. Hops were used for centuries as the bittering agent for beer and also as a preservative agent. However, during the last 25 years, the consumers' appreciation of bitterness in beer has significantly declined. For most beers, the range of bitterness was once between 20 and 60 bitterness units (BU), but for the majority of beers today it is between approximately 6 and 30 BU.

Because humans through history have evolved to be alert to bitter foods as being a possible dietary danger, the physiology of bitter taste reception is different from the reception of the other four basic taste qualities, which are defined as sour, sweet, salty and umami. Despite this, bitter flavours contribute to the palatability and digestibility of food and beverages[46].

Table II shows the identified hop derived bitter components, their thresholds, and the average concentration in commercial beers types.

Looking at the threshold values of the single compounds and their typical concentration in a lager beer, it is evident that the isohumulones are the primary contributor to the bitter taste in beer, however it is likely that other bitter components have an additive effect. Although isohumulones are normally regarded as an entity in terms of bitterness, it has to be noted that the individual isomers have different bitterness threshold intensities. The *cis*-isomers are generally more bitter than the *trans*-isomers as described by Hughes and Simpson[25]. Looking at example concentrations using U.S. craft beers, where hops were added various times during boiling, it can be seen that non-isomerised humulones may contribute to beer bitterness, though their flavour thresholds are rarely reached in conventional brewing.

The beta-acids were never regarded as contributing to beer bitterness as the general opinion was that they were lost in the brewing process. Haseleu et al.[21] were able to identify a number of bitter tasting beta-acid transformation products that were generated during the wort boil, such as cohulupone, hulupinic acid, nortricyclocolupone, two tricyclocolupone epimers, two dehydrotricyclocolupone epimers, two hydroxytricyclocolupone epimers, and two hydroperoxytricyclocolupone epimers. With thresholds ranging from 7.9 to 90.3 μmol/L, it is likely that some of these contribute to beer bitterness[21].

Also, hop polyphenols can contribute to bitterness and astringency, depending on their degree of polymerization and concentration in the beer. As polyphenols comprise a vast group of different reactive substances, this contribution is hard to assess. Recent studies have shown that the bitterness of polyphenols derived from spent hop material (sourced from CO_2 extraction) interact with the bitterness

Table II. Bitter compounds in beer, threshold and typical concentration[21].

	Threshold in µm/L	Typical concentration in lager beer	Concentration in a hop pronounced US Craft beer
Cohumulone	17	1	10
Humulone	21	2	10
Adhumulone	21	1	2
cis-Isocohumulone	7	31	15
cis-Isohumulone	10	33	18
cis-Isoadhumulone	8	11	10
trans-Isocohumulone	19	15	9
trans-Isohumulone	20	14	12
trans-Isoadhumulone	15	5	2
Colupulone	39.3	0	1
Lupulone	35	0	Unknown
Adlupulone	37	0	Unknown
Cohulupone	7.9	7	7
Hulupinic Acid	68.5	0	Unknown
Nortricyclocohulupone	90.3	0	Unknown
Dehydrotricyclocolupulone	40.6	0	Unknown
Tricyclocolupulone	37.9	3	Unknown
Hydroperoxytricyclocolupulone	20.7	0	Unknown
Hydroxytricyclocolupulone	14.7	8	Unknown
Xanthohumol	10	0	2
Isoxanthohumol	16	2	5
8-Prenylnaringenin	7.5	0	Unknown

Table III. Descriptive sensory analysis of bitter acids[15].

	Description of bitterness
Iso-alpha acids	astringent, chalky, not medicinal, not metallic, less fruity and vegetative
Tetrahydro-iso-alpha acids	medicinal, metallic, sharp, astringent, not dull, not flat
Rho-iso-alpha acids	less medicinal, more vegetative and fruity, flat, dull
Hexahydro-iso-alpha acids	medicinal, metallic, aspirin, vegetative, green

of iso-alpha acids in beer. For these trials, 10 mg of iso-alpha acids were combined with either 100 mg or 200 mg/L of polyphenols. It was found that the addition of polyphenols in these concentrations increased bitterness intensity and duration and also resulted in astringent and harsher notes at higher concentrations. It was found that beers with 200 mg/L of polyphenols were rated as more bitter than beers with 10 mg/L iso-alpha acids[36].

Further, bittering compounds are derived from the reduced hop products containing rho-iso-alpha acids (RIAA), tetrahydro-iso-alpha acids (TIAA) and hexahydro-iso-alpha acids (HIAA) which are normally dosed into the beer prior to final filtration. These products are produced by means of hydrogenation and/or reduction using sodium borohydride. When these products came to the market, their relative bitterness compared with iso-alpha acids was described as 0.67× for RIAA, 2.03× for TIAA, and 1.15× for HIAA. However these factors were determined in water[54]. Although a similar bitterness perception could be confirmed for RIAA in beer, investigations with TIAA and HIAA in beer revealed that they had a more comparable bitterness intensity to iso-alpha acids[16]. These different findings were investigated and could be attributed to the influence of the beer matrix, namely the content of residual extract, the ethanol content, the sweetness and the acidity[48]. Though bitterness intensities might be equal, the bitterness profiles of RIAA, TIAA and HIAA are very different. Table III shows the results of a descriptive analysis of these bitter acids.

Bitter perception can vary considerably from person to person, as some individuals are very sensitive to bitter taste, whereas others can show a marked insensitivity. As the bitter perception is triggered by various receptors, individuals can be sensitive to certain bitter compounds but not to others[46]. It was recently shown that certain taste receptors react with isohumulones, whereas different taste receptors react with humulones[28].

Another topic of considerable debate in terms of bitterness is the contribution and quality of the co-isomer, iso-cohumolone. Iso-cohumulone was said to elicit a harsh and unpleasant bitterness, however this was a conclusion of a series of works from the 1950s to the 1970s where the quality of bitterness in beers was assessed by comparing beers with different levels of bitterness. What has been established is the fact that the yields of cohumulone and iso-cohumulone are higher during the brewing process than those of humulone and iso-humulones, particularly during fermentation. This can be explained by the more polar character and better solubility of the co-isomers. Recent studies have been able to confirm that the bitterness quality of iso-cohumulone is not inferior to that of other homologues, however the cohumulone content in hop varieties still seems to be a parameter of concern to brewers and has influenced the hop breeding programs of the last decades[49].

Hops and flavour stability

Obviously, there is a benefit to having stable beer flavour, and beer flavour is subject to influences and change throughout the brewing process to the point of bottling and beyond. It is the objective of the brewer to retain fresh beer flavour and inhibit the development of stale flavour for as long as possible. Within brewing research, flavour stability is one of the major areas of concern, however, many of the results in regard to the reaction pathways involved in stale flavour generation have been somewhat contradictory. Lipid oxidation and the free radical-mediated oxidative chain reaction of various beer constituents can be seen as the major causes for beer staling[4,56]. The key contributors to the aged flavour were found to be (E)-2-nonenal, methional, 3-methylbutanal, 2-furfuryl ethyl ether, beta-damascenone and acetaldehyde[44].

The role of hops in flavour stability is somewhat controversial, though it is generally accepted that hops play a major role in flavour stability in various ways. Hop polyphenols are generally accepted as improving flavour stability by having antioxidant capabilities. As antioxidants they react as free radicals scavengers, enzyme mediators and inhibitors, or metal chelators[41]. Different methods are available to evaluate the antioxidant activity of polyphenolic compounds and do not always lead to comparable findings, e.g., ESR (electron spin resonance) measurements, DPPH (2,2-diphenyl-1-picrylhydrazyl) measurements or FRAP (ferric reducing activity of plasma) measurements. The identity of hop compounds responsible for free radical scavenging activity was not clearly established until recently. Various researchers found hop derived polyphenols including proanthocyanidins, flavanols, phenolic acids, stilbenes, flavonols, multifidols and prenylated flavonoids to be powerful antioxidants able to scavenge peroxyl radicals and to prevent formation of hydroxyl radicals[38].

The antioxidant potential of hops is influenced by processing and it remains unclear to what extent the drying process of fresh hops diminishes the antioxidant capacity of hops[60].

Newer findings confirm the highly anti-radical protective effects of alpha acids. Ting et al.[53] suggest that alpha acids can form stable transit phenoxyl radicals that act directly as antioxidants and that these can also suppress the initiation of the oxidative chain reaction. Hops also seem to prevent the formation of alpha-dicarbonyl compounds that are related to stale flavours, by forming complexes with ortho-phenylenediamine[53]. In contrast, iso-alpha acids were found to be slightly pro-oxidative by acting as electron donors and thereby leading to the formation of hydrogen peroxide, which is in contrast to other studies, where iso-alpha acids were considered to be antioxidants[11]. Hense et al.[22] confirmed that alpha and beta acids showed similarly significant radical quenching abilities, while iso-alpha acids displayed a negligible effect. They concluded that in order to increase the oxidative wort stability, there should be an incremental hop dosage regime during the boil or in the whirlpool. Though there can be a loss in bitter yield, the radical content can decrease by up to 28% this way. In addition, they found that the higher amount of alpha acids also resulted in a higher formation of SO_2 during fermentation, which again improved the flavour stability[23]. Mikyška et al.[39] found that beers hopped with aroma hops showed a better flavour stability compared to beers hopped with bitter hops and attributed this finding to the higher levels of polyphenols in the aroma hops.

A rather novel approach in this regard was taken by Hioe et al.[24] in the use of hop leaves to improve flavour stability, as hop leaves were shown to improve the endogenous antioxidant content of the beer.

Many hop aroma compounds are effective in masking the development of stale flavours, but if present in too high a concentration may augment off-flavours[19]. Furthermore, hop aroma itself is subject to changes during beer storage, but studies have shown that dry-hopping can add to increased flavour stability[13].

Iso-alpha acids and bitterness stability

Hop-derived beer bitterness is a crucial part of the beer flavour and is itself subject to changes over time. A conventional hopping in wort boiling will result with a ratio of *cis*-isohumulones to *trans*-isohumulones of roughly 70:30[59]. Various studies have shown that the *trans*-isohumulones are less stable that the *cis*-humulones and deteriorate much faster than *cis*-isohumulones in the course of beer aging[8]. Along with this degradation, the perceived bitterness can also decline to some extent. The ratio of concentration of *trans/cis*-isomers has therefore been proposed as a good marker for flavour deterioration in beer[1]. The use of pre-isomerised hop products is a tool to obtain a more stable bitterness, as the percentage of the *cis*-isohumulones is higher with pre-isomerisation. Jaskula et al.[30] found that apart from the use of TIAA or pre-isomerized hop products, an additional late-hopping in the whirlpool can help to increase the bitterness stability in the finished beer. In addition, they proposed that mashing at a higher temperature leads to more coagulated protein prior to wort boiling and thus less loss of humulones in the trub, resulting in higher hop utilisation and improved bitter stability[29]. The decomposition of the hops *trans*-isomers in beer was only recently found to be an acid catalytic decomposition of *trans*-isohumulones into tri- and tetra-cyclic degradation products, where the pH value plays an important role[27]. A question of ongoing debate is the role of oxidised isohumulones as precursors of carbonyls, e.g., 3-methyl-butanal, that act as stale flavours[12].

If we were to fully utilize our gained knowledge about hops and flavour stability in beer, a sensible hopping regime would be to use hop polyphenols in the beginning of boil (or even in the mash) in the form of spent hops or aroma hops, then dose a significant portion of aroma hops or bitter hops at the end of boil or in the whirlpool to contribute a high amount of residual alpha acids, beta acids, and hop aroma compounds. The bittering would be accomplished with isomerised products to achieve a better bitter stability due to a better *cis/trans* ratio. A further additional dry-hopping could be implemented to further enhance flavour stability.

Hops as a foam enhancer

There are two important parameters that affect foam development and its retention in beer – the content and ratio of foam positive substances, and the physics of foam[3]. The key events involved in foam formation and retention are as follows:

1. Bubble formation
2. Drainage (of liquid from foam into beer)
3. Bubble coalescence (merging of two bubbles through the rupture of the film between them)
4. Disproportionation (the passage of gas from a small bubble to an adjacent larger one).

Foam positive substances can be hydrophobic, film stabilizing, or may increase the viscosity. Foam positive substances are as follows.

1. Malt-derived proteins with specific molecular weights that form a strong, flexible and cohesive film in order to reduce gas permeability and to inhibit coalescence and disproportionation.
2. Metal cations (derived from malt or water) forming foam stabilising complexes with iso-alpha acids.
3. Natural stabilisers (polysaccharides derived from malt increasing viscosity and inhibiting drainage; iso-alpha acids).

Foam negative substances include fatty acids (lipids), basic amino acids (both derived from malt) and a too high content (above 5%) of ethanol.

The role of the hop acids for beer foam is to stabilise the foam complexes. Each of the different iso-alpha acids acts in a slightly different manner to produce varying degrees of foam depending on the surface activities[14]. It is worthwhile to note that the various homologues and isomers of the iso-alpha acids and reduced iso-alpha acids have different foam properties. Hughes[26] found that the *trans*-isomers in foam are enriched relative to *cis*-isomers. Often neglected are the very foam positive hop derived substances known as abeo-isohumulones described by Verzele[57]. They are said to have almost no bitterness but have very good foam properties and are also very unstable. Siebert[50] was able to show that an increase in either proteins or iso-alpha acids in a model beer led to a greater foam. He was also able to show that the pH value and the content of ethanol could have a major impact on beer foam.

Many beer styles around the globe continue to become lighter in body and flavour and as a result, they are lower in foam-positive protein and in the isomerised hop acid content. This adversely affects the foam stability of the

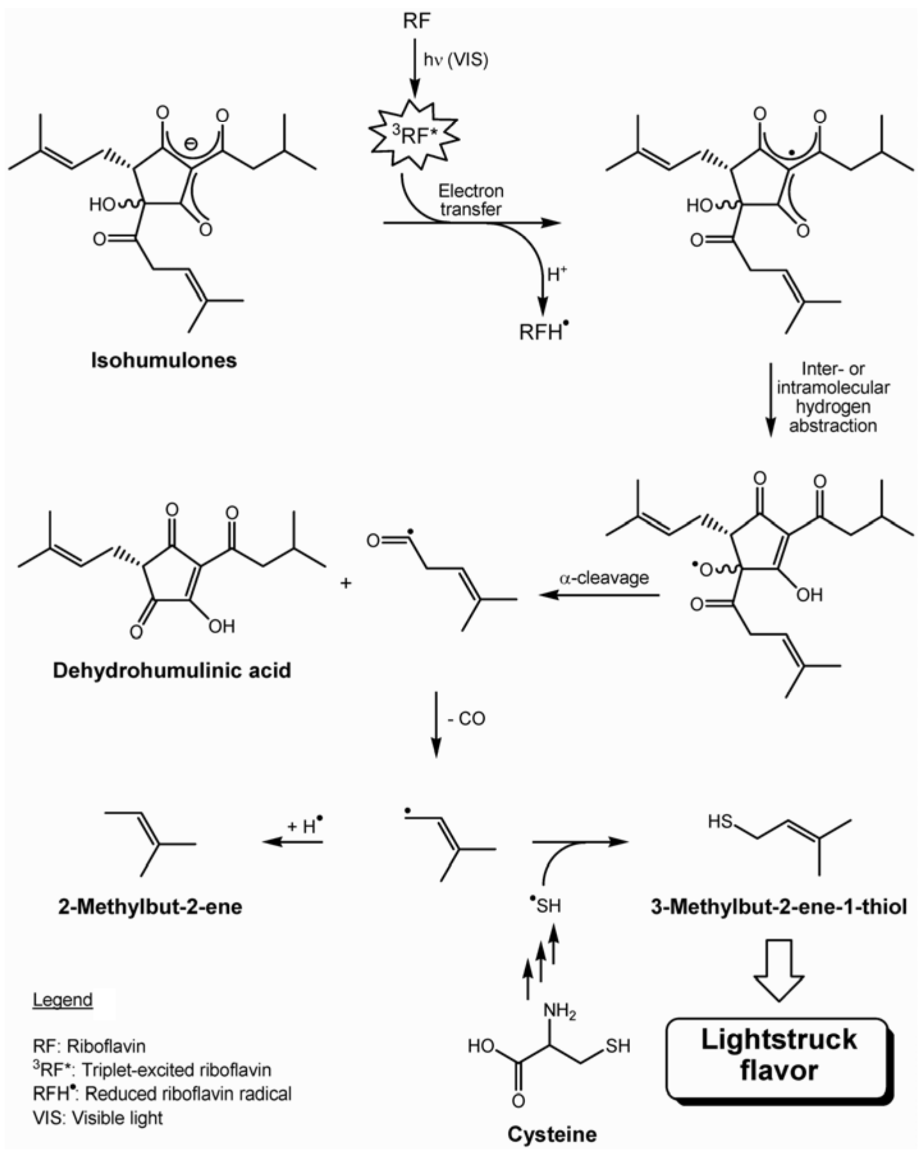

Fig. 2. Mechanism for light-induced formation of 3-methylbut-2-ene-1-thiol (MBT) from isohumulones on sensitized radiation in the presence of a sulfur source, cysteine[9].

beer. Therefore the use of tetrahydro-iso-alpha acids in beer as an alternative to alginate products as a foam enhancer/stabiliser is well established. The hydrogenation step in the production of tetrahydro-iso-alpha acids and hexahydro-iso-alpha acids is the crucial part to further increase the foam enhancing ability of the iso-alpha acids.

Using the NIBEM foam stability method, Kunimune and Shellhammer[33] found that the foam-stabilizing effects of iso-alpha-acids and the reduced forms were, from the strongest to the weakest: TIAA, HIAA, IAA, and RIAA. The effects of foam cling were shown, but interestingly, no corresponding increase in the amount of cling was evident with increased hop acid concentrations, but the qualitative appearance of the cling patterns was influenced. At higher concentrations, above five parts per million, the patterns presented a more powdery appearance. Tetra showed a greater ability to produce cling beginning with the lowest concentration and very small amounts of TIAA and HIAA (approximately two and four ppm, respectively) were sufficient to create a substantial amount of cling[33].

Hops as the cause and a solution to light struck flavour?

That beer is sensitive to light is a well-known fact. In terms of flavour, one of the most detrimental reactions is the formation of light-struck flavour, resulting in the so-called skunking of beer (because the flavour resembles that of the secretion from the anal glands of skunks). Though already recognized by Lintner in 1875, the basic science explaining light-struck formation was not clearly understood until the 1960s, when it was found to be a non-enzymatic light-induced reaction involving a photosensitizer compound (riboflavin), a sulphur containing compound and isohumulones. This skunky flavour is attributed to 3-methyl-2-butene-1-thiol (3-MBT) having a very low aroma threshold of about 4–7 ng/L. As the predominantly blue part of the visible spectrum (350–500 nm wavelength) was found to be responsible for this reaction, brown glass acts as a good protector, significantly cutting off light below approximately 500 nm. Figure 2 shows the reaction responsible for the formation of the light struck flavour. Various polyphenolic substances are described in the literature as 3-MBT inhibitors[10]. Primarily through the work of de Keukeleire et al.[9] during the last 10 years, the mechanism of the formation of 3-MBT is now well understood. It was found that the photo-decomposition of isohumulones by visible light occurs via one-electron oxidation of the beta-tricarbonyl chromophore, which is a common structural element not only of the isohumulones but also of the reduced isohumulones. With the recombination of radicals derived from isohumulones and reduced isohumulones with sulphur-based radicals, different off-flavours are formed (not only 3-MBT)[9]. Therefore so-called light-stable hop reduced hop acids, TIAA and RIAA, are not fully light stable, but they are effective in preventing the formation of the most prominent and offensive compound, 3-MBT. Lusk et al.[35] were able to identify two additional "skunky" aroma compounds derived from light-exposed iso-alpha acid bittered beer. The exact identity and structure of the compounds are yet to be elucidated, but they were shown to exhibit similar sensory effects as 3-MBT.

Many commercial product specifications for TIAA and RIAA light-stable hop products allow residual isohumulones to a level of 0.1–0.2% in the finished hop product. To assess the risk of these residual isohumulones in reduced hop products, theoretical calculations showed that the amount of 3-MBT, which can be formed in beer using a worst-case scenario of excessive light exposure and the highest allowable residual IAA in light-stable extracts, is close to the sensory threshold for 3-MBT[5]. This study did not take into account the possible formation of other off-flavours formed in beer from exposure to light, only the formation of 3-MBT.

Zufall et al.[61] investigated the sensory attributes of beers brewed with RIAA and TIAA in conventionally brewed beers. The beers with RIAA or TIAA proved to be superior in terms of flavour stability and a strong tendency was found for improved beer stability with hop products having a higher degree of reduction, i.e., from RIAA to TIAA to HIAA. Though the staling developed more slowly, it could of course not be prevented. Zufall et al.[61] found that the flavour characteristics of aged beers brewed with reduced hop products differed significantly from conventional beers yielding a more pronounced bready, sweet or caramel notes, but not the typical cardboard staling flavours.

SUMMARY

Research in the area of hop aroma in beer has revealed that in addition to known flavour impact compounds such as predominantly linalool, other substances can contribute to a hoppy aroma in beer due to additive and synergistic effects. The hopping regime used determines the resulting hoppy aroma and fermentation can also play an important role in terms of flavour release or biotransformation reactions. Bitterness research has gained immense new insights, not only in bitterness perception mechanisms, but also in identifying new hop derived bitter compounds (e.g., tricyclocolupulones) and in evaluating the contribution of polyphenols to beer bitterness. Also, the hopping regime can significantly affect the composition of bittering compounds in the final beer and which, in part, explains the variety of perceived types of bitterness in different beer styles.

The flavour stability of beer is positively influenced by hops in a number of ways including the influence of polyphenols, but also potentially with non-isomerized alpha acids. Improved bitter stability can be achieved with a higher content of *cis*-isohumulones, and it has been shown that an enhanced hop aroma can be beneficial for stability. Hops are important for beer foam, and tetra- or hexa iso-alpha acids can be useful tools in contributing to more stable beer foam and are suitable as substitutes for other foam stabilizers such as alginates. Also the formation of the light-struck flavour is now better understood. It has become clear that 3-MBT is not the only off-flavour that can be formed in hopped beer upon exposure to irradiation and that reduced isohumulones were found to be photoreactive, therefore the term light-stable hop products can be somewhat misleading.

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