The Versatility of Hops

Introduction

The hop is both a unique and a versatile plant. It is unique, in that the hop is relatively isolated within the botanical classification scheme, and it produces valuable secondary metabolites that have not yet been found in other plant species. The versatility of the hop is demonstrated in this article which shows that hop products can be used profitably for a number of food and non-food uses.

Hops are classified botanically within the Cannabaceae family (the hemp or Cannabis family) that contains two commercially important genera: *Cannabis* and *Humulus*. The genus *Humulus* contains the common or brewing hop *Humulus lupulus*, together with another species *Humulus japonicus*.[1] Hops have long been grown for brewing beer, and the major roles of the hop are to impart bitterness and flavour to the brew, and to act as a natural preservative. The hop is a perennial plant that grows as a climbing vine. Hops are dioecious, but only the female flowers (known as "cones") are used for brewing purposes, as they contain the lupulin glands that produce the important, hop-specific secondary metabolites. Since the hop is a short-day plant, it requires a significant change in day length during the growing season, and so the hop can be successfully cultivated between latitudes of 35^{o} and 55^{o}, in either the Northern or Southern hemisphere.[2]

Bittering products for brewing

The lupulin glands, or trichomes, of the female hop cones contain a number of interesting and unique molecules, including the so-called α-acids, or humulones, and the β-acids, or lupulones. The structures of these compounds are shown in Figure 1. The α-acids are the precursors of the bitterness of beer. In fact, the α-acids themselves are not particularly bitter tasting, but they are very readily isomerized during the wort boiling part of the brewing process to iso-α-acids (or isohumulones), which are intensely bitter tasting compounds. The amount of iso-α-acid in the finished brew is directly related to the bitterness of the beer.

Iso-α-acids are highly reactive in the presence of a thiol donor and UV light, and produce the compound 2-methyl-3-butene thiol (MBT) that has a descriptive common name of “skunky thiol”! As can be imagined, this does not have a positive effect on flavour, and it is responsible for the so-called “light-struck” flavour of beer. This is why certain beers are sold in brown bottles, to limit the damaging effect of UV light.

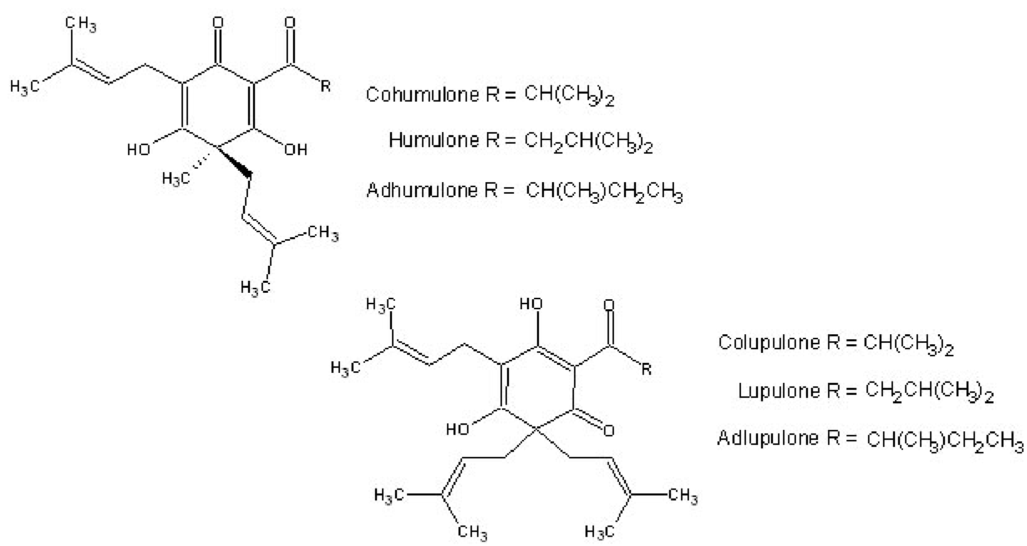

Figure 1 Chemical structures of the hop α-acids (humulones) and β-acids (lupulones).

A couple of elegant chemical solutions exist to solve the lightstruck flavour problems. The reactive side chain of the iso-α-acids that gives rise to MBT can be either reduced or catalytically hydrogenated, giving rise to light-stable bittering products. These are shown in Figure 2. Catalytic hydrogenation has the added advantage of producing a product with enhanced foam stability. A combination of the above two approaches can also be used to produce hexahydro-iso-α-acids.[3]

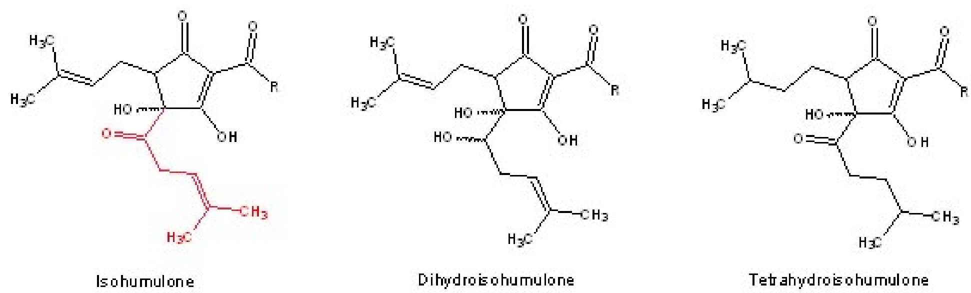

Figure 2 Light stable derivatives of iso-α-acids. The reactive side chain of isohumulone (shown in red) can be reduced to produce dihydroisohumulone, or hydrogenated to produce tetrahydroisohumulone.

Foam stability and anti-foam products for brewing

Foam stability is an important aspect of beer quality – in general consumers appreciate a stable head of foam, and rapidly collapsing foam will be perceived as poor quality. Surface-active proteins within the beer (mainly derived from the malted barley) are thought to be the main agents for stabilising the foam structure. Iso-α-acids, which possess both hydrophillic groups and hydrophobic side chains (see Figure 2 above) can further promote foam stability by acting to bridge the proteins that make up the foam structure. Tetrahydro-iso-α-acids are particularly effective in stabilising foams, and this is probably due to the greater hydrophobic character of the side chains (see Figure 2).[4]

Anti-foam products

Hops not only provide the raw materials for foam stabilising products, but certain components of hops can also act as natural anti-foam products. Liquid and supercritical CO_2 can be used to extract lipid and wax compounds from hops. The proteins and iso-α-acid products mentioned above as foam stabilisers have both hydrophobic and hydrophillic groups, and can thus can act as surface-active compounds in aqueous solutions. In contrast, the hop lipids and waxes are entirely hydrophobic and act to decrease foaming. Products such as Lipohop F® and Lipohop K® are used currently in brewing and other food applications, as natural alternatives to silicones.[5]

Aroma products

The female hop cones are a source of hop essential oil, that contains numerous terpenoid compounds giving a characteristic aroma that is important for beer. Hop oils can be extracted from hop cones under mild conditions with liquid CO_2, and the resulting oil can be further fractionated using techniques such as molecular distillation. Research and development at Botanix has led to the production of a large number of Pure Hop Aromas, and further technical information can be found via the Botanix website.[6] Fractionation of the hop oils means that concentrated products can be obtained to faithfully reproduce either the aroma of a particular hop variety (for instance Goldings or Cascade), or a distinctive sensory characteristic, such as a citrussy, floral, herbal or spicy note. This is an important development both for ensuring consistent aroma quality in brewed products, or to develop new and exciting aromas in beer and beer-related drinks.

Anti-microbial products

The α– and β-acids of hops display anti-bacterial properties. A detailed explanation of their mode of action is given in an excellent paper by Simpson (1993).[7] Simpson studied the effects of α-acids (humulones), β-acids (lupulones), iso-α-acids (isohumulones) and humulinic acid on Gram positive lactic acid bacteria. Each of these compounds was found to inhibit the growth of the bacteria at low levels – minimum inhibitory concentrations (MICs) were at low μM levels if solutions of the hop products were held at a low pH (*ca*. 4). However, these hop compounds are weak acids, and their effectiveness depends upon whether they are present in the undissociated form (active) or the ionised form (inactive). Increasing the pH from 4 to 7 markedly decreased the effectiveness of the α-acids, iso-α-acids and humilinic acid, as shown by steeply increasing MIC values. On the other hand, Simpson showed that the effectiveness of β-acids remained relatively constant over the pH range 4 – 7, because beta acids have a pK_a value of *ca*. 6 and remain undissociated at higher pH than α-acids and iso-α-acids.

β-Acids have therefore been developed commercially as natural anti-microbial products, and are currently used as process aids in the production of sugar and bio-ethanol. Technical information on beta acid products (Betastab ® 10A) can be found on the Botanix website hop products page.[7]

Pharmaceutical applications

Recently there has been much interest in the prenylated flavonoids found in hops, believed to be unique to this species. The hop cones contain xanthohumol, at levels of up to *ca*. 1% w/w in dried hop cones, and desmethylxanthohumol at approximately 10-fold lower levels. Xanthohumol is a valuable molecule that it is being tested as a novel anti-cancer agent, and it also shows anti-inflammatory properties. Desmethylxanthohumol is readily isomerized to two compounds, 6-prenylnaringenin

(6-PN) and 8-prenylnaringenin (8-PN). 8-PN is a powerful phytoestrogen – its activity is much greater than the soy isoflavones daidzein and genistein.[8]

Other potentially beneficial hop products include isoxanthohumol and the iso-α-acids. Xanthohumol is readily isomerized to form isoxanthohumol, and a recent article by Biendl (2007) indicates that isoxanthohumol may alleviate the problems of osteoporosis. Iso-α-acids appear to reduce the intestinal absorption of fat in mice, and so may be helpful in preventing diet-induced obesity.[9]

In all cases where exciting pharmaceutical applications are suggested for natural products, care must be taken to properly consider whether significant effects are demonstrated reproducibly in clinical trials. However, there is a wealth of scientific evidence showing promising effects of the hop compounds, and these unique natural products warrant further investigation.

Pectins and fibres

A study of CO_2-extracted hops of the variety 'Target' showed that a pectin yield of 2% was obtained, with the extracted material containing 59% polysaccharides. Although the study showed that the hop pectins had a similar viscosity to commercially available apple and citrus pectins, the molecular make-up of the hop pectins suggested that they would have limited use as gelling agents.[10] However, commercial use for hop pectins as foam stabilizers is indicated by a US patent.[11] Pectins isolated from either hop bines or hop cones could be used to stabilise beer foams and replace non-hop-derived polysaccharides that are otherwise used commercially. This is important if the beer requires only hop-derived components.

The fibre and residual resins in spent hops can also be used to make fibre boards. A US patent describes how the resins in spent hops can act as a natural binder.[12] Dried hop waste can be compacted by hot-pressing with no further additions, although addition of a catalyst doubled the cross-breaking strength of the hop fibre board.

Conclusions

The hop is a truly versatile plant and the examples described in this paper show how hop-derived components can be used in sensory, technical, structural and pharmaceutical applications. Part of the appeal of hop products is their uniqueness, such as the bittering products and xanthohumol, as well as the possibility of obtaining natural replacements for commercial anti-foams, anti-microbials and foam stabilisers. Fractionation of the hop products and an understanding of the chemistry of the hop components is key to developing and refining a wide variety of commercial uses.

Dr Yannick Ford, Research Coordinator, June 2007.

References

[1] Classification information obtained from the United States Department of Agriculture Plants Database http://www.plants.usda.gov/index.html

[2] Botanical and cultivation information obtained from T.R. Roberts and R.J.H. Wilson (2006) Hops, in: *Handbook of Brewing*, 2nd edition, F.G. Priest and G.G. Stewart (eds.), CRC Press, Boca Raton, pp. 177-279.

[3] Information on prevention of lightstruck flavour production obtained from (i) T.R. Roberts and R.J.H. Wilson (2006) Hops, in: *Handbook of Brewing*, 2nd edition, F.G. Priest and G.G. Stewart (eds.), CRC Press, Boca Raton, pp. 177-279, and from (ii) D. de Keukeliere (2000) Fundamentals of beer and hop chemistry. *Quimica Nova* **23**: 108-112.

[4] Information on foam stability obtained from (i) D. de Keukeliere (2000) Fundamentals of beer and hop chemistry. *Quimica Nova* **23**: 108-112, (ii) G.G. Stewart (2004) The chemistry of beer instability. *Journal of Chemical Education* **81**: 963-968 and (iii) D.S. Ryder and J. Power (2006) Miscellaneous ingredients in aid of the process, in: *Handbook of Brewing*, 2nd edition, F.G. Priest and G.G. Stewart (eds.), CRC Press, Boca Raton, pp. 333-381.

[5] See technical specifications for Lipohop F® and Lipohop K® at http://www.botanix.co.uk/html/hopprods.html

[6] Technical information on Pure Hop Aromas can be found on the Botanix website at http://www.botanix.co.uk/html/hopprods.html, following the link to the Barth-Haas group pages.

[7] Information on anti-bacterial effects of hop compounds obtained from W.J. Simpson (1993) Studies on the sensitivity of lactic acid bacteria to hop bitter acids. *Journal of the Institute of Brewing* **99**: 405-411. Technical specifications for Betastab ® 10A are found at http://www.botanix.co.uk/html/hopprods.html

[8] Information on phytoestrogen properties of hop compounds obtained from S. Milligan et al. (2002) Oestrogenic activity of the hop phyto-oestrogen, 8-prenylnaringenin. *Reproduction* **123**: 235-242.

[9] Information on the potential beneficial effects of isoxanthohumol and iso-alpha acids obtained from M. Biendl (2007) Beer – bitter and healthy. *Brauwelt International* **25**: 23-25.

[10] See A. Oosterveld et al. (2002) Characterization of hop pectins shows the presence of an arabinogalactan-protein. *Carbohydrate Polymers* **49**: 407-413.

[11] See US patent 6910663 Pectins as foam stabilizers for beverages having a foam head.

[12] See US patent 4354879 Utilization of fibrous waste.