40 years of total resin extract – useful information from A to X (Part 1)

HOP EXTRACTION | Along with pellets and CO_2 extracts, total resin extract (formerly referred to as ethanol extract) has proven itself to be a valuable hop product in the production of beer for decades. In this two-part series, the properties of total resin extract are presented in alphabetical order and the latest research findings are included where applicable.

100 YEARS BEFORE hop pellets were on the market, the first hop extracts were already being produced in the middle of the 19th century (refer to the timeline in the info box). However, the techniques employed in the early days, such as the application of steam, give the impression that the quality of the extracts obtained back then would leave much to be desired and would be a far cry from the quality available today.

The goal of sustainable hop extraction is the quantitative, yet gentle, recovery of the bitter substances in addition to the essential oils from the plant material. For a long time, methylene chloride (dichloromethane) was the preferred solvent. Due to its selective nature, all of the other hop constituents remain in the residue after extraction. Another advantage is its low boiling point (40 °C); the resultant low energy costs made the extraction process economical. In addition, there is no danger of combustion or explosion with methylene chloride. In response to increasing concerns regarding its toxicity, it was replaced over a very short period of time in the early 1980s by two natural solvents that are already present in beer: alcohol (ethanol) and carbon dioxide (CO_2).

While gaseous CO_2 has to be compressed in a technically complex manner when used as an extraction agent in the liquid (or supercritical) phase, alcohol posed different challenges for its application in this process: its polarity (i.e., good miscibility in water) and its relatively high boiling point (78 °C). Solutions were found for both issues, and consequently total resin extract has been available for over 40 years on the market. These key aspects of this product, from A (as in alcohol) to X (as in xanthohumol), are described in greater detail in this article series.

Alcohol

In the production of total resin extract, alcohol (ethanol) is used as a solvent. The extraction process is outlined briefly in fig. 1: Whole hops (dried hop cones) serve as the raw material for this process. The extraction is continuous and is carried out in a countercurrent manner with a mixture of alcohol and water (in a ratio of 90 to 10 by volume) using a percolation process.

The solvent is then evaporated under a vacuum. This lowers the high boiling point of the alcohol. The extracted substances can be completely separated into two phases using a centrifuge after the alcohol has been removed.

The by-product of the extraction is the "tannin extract" (the polar phase containing the water and all water-soluble hop constituents) while the main product is the "total resin extract" (non-polar phase containing the bitter compounds and essential oil from the hops). This fraction, also known as pure resin extract, is quite similar to the

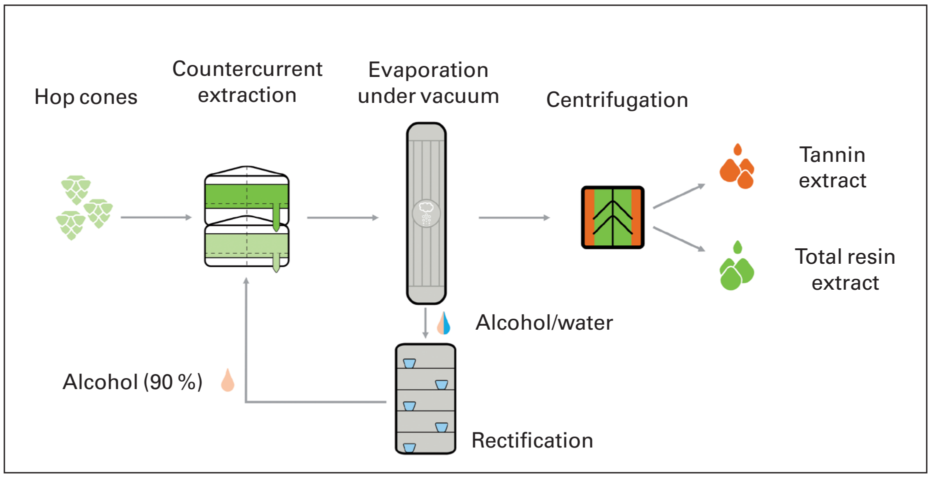

Fig. 1 Schematic diagram for the production of total resin extract

Author: Dr. Martin Biendl, Head of Research & Development/Analytics, HHV Hallertauer Hopfenveredelungsgesellschaft m.b.H., Mainburg, Germany

extracts obtained in the past with methylene chloride or to modern-day extracts produced using CO_2.

However, the pure resin extract obtained with alcohol is now called total resin extract. This change is due to the recent scientific discovery regarding the positive contribution of hard resins to beer bitterness, which are only present in this extract and not in the extract produced using CO_2 [1].

The alcohol used for extraction originates from fermentation processes. After extraction and evaporation are complete, the solvent is recovered through condensation and then re-enters the extraction cycle. Since even dried whole hops still contain around ten percent water, dilution of the solvent takes place during the production process, making a prior rectification necessary.

Bitter substances: yield

The primary objective of all hop extraction processes is to transfer the alpha acids from the hops to the extract at an overall yield of 95 percent. This is also achieved in the production of total resin extract. Moreover, compared to other hop extracts on the market today, the fact that the complete spectrum of bitter substances is present in total resin extract is a unique selling point.

Chlorophyll

A characteristic feature of total resin extract is its dark green appearance. This is due to the extraction of the chlorophyll, a pigment found in the hop leaves. By contrast, this green pigment is either not extracted or only partially extracted with CO_2. Therefore, its appearance is dependent upon the extraction parameters. Extracts prepared with liquid CO_2 are yellow in color, with darker colors resulting from higher temperatures and pressures due to the co-extraction of a portion of the leaf pigments.

Differences compared to CO_2 extract

In addition to the difference in color, there are other differences between total resin extract and CO_2 extract. The proportions of all of the fractions in the whole hops relevant for beer production compared with various hop products are illustrated in fig. 2:

In the production of type 90 pellets (hop powder milled and then pressed into granules), 100 percent of the tannins and all of the bitter substances are transferred to the product. There are only minor losses of highly volatile compounds (mainly myrcene) from the hop oil, which may occur during the subsequent drying of the hops in preparation for processing or later during pelletizing.

On the other hand, more tannins are lost with enriched pellets (type 45), because part of the hop leaf fraction is separated from the lupulin glands of the hops. These losses depend upon the degree of enrichment, i.e., on the achieved and targeted ratio of the lupulin to the leaf fractions.

In total resin extract, the tannins have been completely eliminated, but all of the resin fractions (bitter substances) are retained. The volatile compounds found in the essential oils are lost to a certain degree during the evaporation of the solvent.

Finally, CO_2 extraction removes not only the tannins but also the hard resins (even under very high pressure, only slight traces are extracted, while at low pressure, portions of the unspecific soft resins are not dissolved). Since pelletization takes place prior to extraction with CO_2, the balance of essential oils from the original hop material compared to the final product is not completely recovered.

The primary difference between total resin extract and CO_2 extract is the composition of the bitter compounds, or more precisely, of the hard resins.

Extraction parameters

As mentioned above, whole hops do not need to be pelletized prior to their extraction with alcohol but may serve directly as the raw material. Hop extraction with alcohol proceeds continuously for 60–80 minutes at approximately 55 °C (CO_2 extraction is a batch process lasting several hours with extraction occurring in a semi-continuous manner in multiple extraction vessels). The subsequent removal of the solvent by means of falling film evaporation takes only a short time and is carried out under a vacuum in order to reduce the boiling point of the alcohol (78 °C). At the end of the process, the

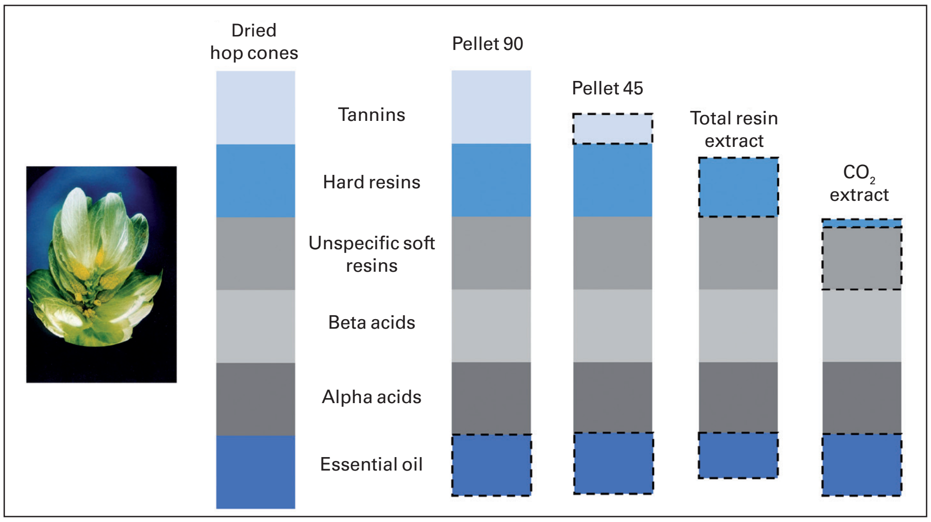

Fig. 2 The composition of hop products compared to dried whole hops

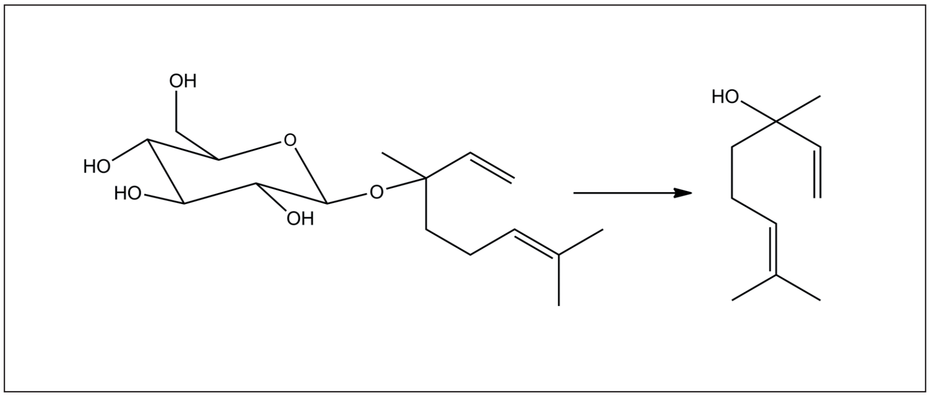

Fig. 3 Structural formulas of linalool bound to glucose and linalool after its release

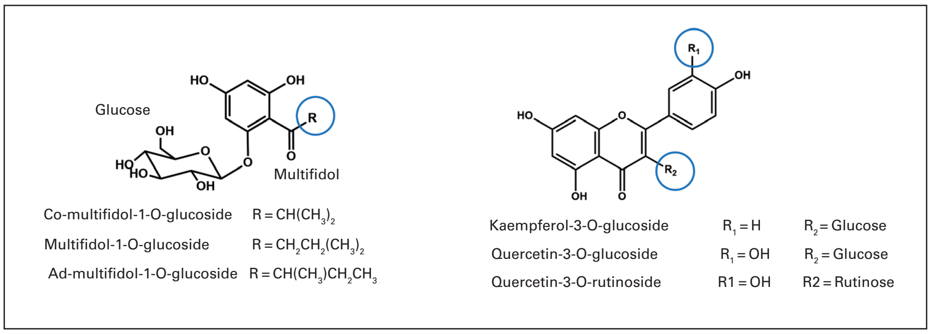

Fig. 4 Structural formulas of important glycosidically bound polyphenols (constituents of the hard resin)

alcohol content in the total resin extract is significantly below 0.5 percent.

Filling station for hop extracts

After extraction, the hop extract is collected in large tanks fitted with agitators. After homogenization at 40–50 °C, the extract is filled into cans of various sizes (0.5–4 kg), drums (maximum 200 kg) or containers (up to 1000 kg), depending upon customers' specifications. Filling in cans is done on the basis of kilograms of extract by weight or by kilograms of alpha acids (in this case, the alpha acid content of a homogenized batch of hop extract is determined by laboratory analysis prior to filling).

Glycosides

Many aroma compounds and polyphenols are found in hops, not only in their unbound form but also as glycosides, i.e. bound to a sugar molecule (e.g. glucose); refer to figures 3 and 4.

Terpene alcohols, such as the well-known key aroma compound linalool, are also introduced into the brewing process as glycosides when the hops are added. Enzymatic or chemical reactions occurring later, during the fermentation or lagering processes, can result in the cleavage of these compounds from the sugar molecules, allowing the free forms of the compounds to make a contribution to beer aroma. The transfer of linalool glucosides and other glycosidically-bound hop aroma compounds occurs only in pellets and total resin extracts but not in CO_2 hop extract [2].

Furthermore, flavonols, such as quercetin and kaempferol are present in hops, both in their free forms and as glycosides, while multifidols, as they are known, have to date only been detected bound to glucose. The importance of these polyphenol glycosides for beer production will be discussed in more detail in the next section.

Hard resins

By definition, hard resins are more polar than soft resins (which consist largely of alpha and beta acids). In the Wöllmer fractionation method, hard resins only dissolve in methanol but not in hexane, while soft resins are soluble in both.

Until just a few years ago, the hard resins fraction was viewed in a rather negative light, or at least it was not considered particularly important for beer production. Since their content increases as hops age during storage, without studying the individual chemical structures in more detail, it was assumed that they were mainly oxidative degradation products of the alpha and beta acids.

In the meantime, however, it has been proven without a doubt that a distinction must be made between the native hard resins originally present in fresh hops and the hard resin compounds that form in the period during which hops are stored under exposure to air. It was confirmed that oxidation of the soft resins also occurs during this time. Nevertheless, these transformation reactions first tend to take place on a larger scale only under drastic conditions (increased temperature, long storage period) and do not occur in hop products packaged under an inert gas atmosphere [3].

By contrast, the native hard resin fraction does not consist of oxidation products but of the plant's own polyphenol compounds, which can generally be divided into the following two groups:

- polyphenols with prenyl side chains, which are known as prenyl flavonoids (approximately 30 substances);
- phenolic acids (esters) and polyphenols bound to sugars as described above (approximately 10 compounds).

From a quantitative perspective, xanthohumol is the primary constituent in the hard resin of each hop variety. Xanthohumol is converted to isoxanthohumol during wort boiling in the brewery. In addition, numerous other prenyl flavonoids with similar molecular structures have been identified in hops.

A positive contribution to beer bitterness has since been attributed to the native hard resins, both quantitatively and qualitatively, as shown by extensive trials during research performed at the Chair for Food Chemistry and Molecular Sensory Science at the TU München under the direction of Prof. Hofmann [4, 5]:

Nearly 40 individual polyphenol compounds with a bitter flavor were identified in the hard resin and their occurrence was confirmed in 75 different hop varieties from all over the world.

These compounds are introduced with the hop addition either directly in the

Timeline for the development of hop products

- 1860–1870: the first patents were issued for hop extraction (with steam or alcohol mixtures)
- 1960–1970: the first patents were issued for the compression of milled hop powder into pellets
- 1965: first industrial production of a liquid isomerized hop extract
- until 1980: methylene chloride was the preferred solvent for hop extraction in Germany
- 1979: the first industrial hop extraction was performed with liquid CO_2 (5–15 °C, 60–65 bar) in England
- 1980: the first industrial hop extraction was performed with supercritical CO_2 (40–60 °C, 200–250 bar) in Germany
- 1981: a patent application was submitted in Germany for the production of total resin extract using an alcohol/water mixture
- 2020: the first industrial hop extraction was carried out with supercritical CO_2 at 500 bar in Germany

brewhouse or can be detected subsequently after transformations have occurred at some point in the brewing process. In some cases, they are only present in very low concentrations and usually below the sensory perception threshold. Nevertheless, the hard resin fraction can influence the bitterness of beer through its additive effects, which stems from this multitude of compounds, since they interact with the same human receptors for the perception of bitterness.

By conducting a recombination experiment, it was finally possible to prove that after the stepwise addition of individual substances to a non-hopped base beer serving as control, it was only possible to achieve the characteristic intensity of the bitterness in a pilsner as well as the "authentic perception of bitterness" through the combination of iso-alpha acids and all of the individual constituents in the hard resin fraction.

It was also observed that both the prenyl flavonoids as well the polyphenols bound to sugars in the hard resins are not only transferred to pellets during hop processing but also to the total resin extract. By contrast, commercial CO_2 extracts do not contain any substances from the hard resin fraction.

Research focusing on the important individual constituents of hard resins has served to expand and deepen the knowledge about these substances and their role in beer. Dry hopped beers have been analyzed together with numerous international hop varieties from several crop years and in the form of various hop products [6, 7]. It has been confirmed that hard resins are not extracted by CO_2. This was the case until just recently, when pressures up to a maximum of 300 bar were prevalent in the large-scale extraction of hops. Now, however, there is an extraction plant capable of hop extraction at much higher pressures, up to 500 bar. This was first reported in 2020 [8]. The following statements were made in that publication:

- Substances can be extracted with CO_2 at 500 bar which are insoluble at 300 bar.
- Besides containing more chlorophyll – the extract is "greener" –, the extracts are slightly richer in xanthohumol and contain more positive auxiliary bitter substances from the hops.
- The extract yield based on the quantity of pellets is almost 1 % higher at 500 bar than at 300 bar.

Thus, although compounds found in the hard resin fraction are only present in small quantities, this new CO_2 process now produces extracts which are somewhat closer in composition to total resin extract.

The second part of this article will be published in BRAUWELT International issue 2, 2022. ■

References

1. Biendl, M.; Cocuzza, S.: "Hard resins – New findings about a familiar hop fraction", Hopfenrundschau International 2016/2017, pp. 59–68.
2. Kollmannsberger, H.; Biendl, M; Nitz, S.: "Occurence of glycosidically bound flavour compounds in hops, hop products and beer", Monatsschrift für Brauwissenschaft 2006, pp. 83–89.
3. Taniguchi, Y.; Matsukura, Y.; Ozaki. H.; Nishimura, K.; Shindo, K.: "Identification and quantification of the oxidation products derived from α acids and α acids during storage of hops (Humulus lupulus L.)", J. Agric. Food Chem. 2013, pp. 3121–3130.
4. Dresel, M.; Dunkel, A.; Hofmann, T.: "Sensomics analysis of key bitter compounds in the hard resin of hops (*Humulus Lupulus L.*) and their contribution to the bitter profile of Pilsener-type beer", J. Agric. Food Chem. 2015, pp. 3402–3418.
5. Dresel, M.; Vogt, C.; Dunkel, A.; Hofmann, T.: "The bitter chemodiversity of hops (*Humulus lupulus L.*)", J. Agric. Food Chem. 2016, pp. 7789–7799.
6. Schmidt, C., Biendl, M.: "On the trail of hard resin components", BRAUWELT International no. 3, 2021, pp. 162–165.
7. Biendl, M.; Schmidt, C.: "Contents of glycosidically bound polyphenols in different hop varieties and their recoveries in hop extracts", oral presentation, Virtual World Brewing Congress 2020.
8. Forster, A.; Schuell, F.; Gahr, A.: "Advances in hop extraction with supercritical carbon dioxide", BRAUWELT International no.5, 2020, pp. 324–330.