

ABOUT HOP CONES FOR A GOLDEN BREW

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Common hop¹ or hops (*Humulus lupulus* L., Fig. 1, ref.²), is a perennial dioecious right-handed liana in the hemp family Cannabaceae. It has been grown since time immemorial and it can be seen that in the old days it has been used as a herb of much use, such as hair dyeing (hop-pickers can prove it with a view of its hands), “blood cleansing”, such as cattle feed, ropes, fabric and paper, packaging of fragile objects and repelling demons at night³.

As for the use of hops in human medicine, already Dioscorides⁴ advises its mixing with ointments made for suppositories, with other ointments for the astringent quality in it, for the preparation of perfumes, and is put into medicines called acopi to remove fatigue, the use of hops for hot or cold in decoctions made for all those disorders requiring bathing around the vulva⁴; the last recommends also Matthioli⁵, e.g. against the “swelling and hardness of the womb”. Spring salad from shoots is considered to be



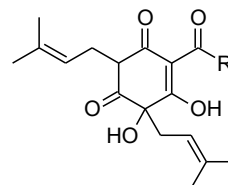
Fig. 1. Hops (*Humulus lupulus* L., ref.²)

a good means to “open congestion liver” (probably a means of the release of bile); otherwise, hops heal jaundice, leprosy, and French disease. Then “drinking the decoction of hops tops makes the body nice”, which can still be seen on beer drinkers. Also internally to alleviate sexual instinct (anaphrodisiac)⁶, surprisingly, even in homeopathic products (even against “painful erections”⁷). In folk medicine, it is also used as a sedative and

a means of stimulating appetite. Helps against insomnia, and diuretic effects and is used in muscle cramps⁸. It is used in menopause problems to improve the mental condition. It has a positive effect on blood cholesterol. The European Drug Reference Encyclopedia presents⁹ many applications and effects, including as a medicinal drug with estrogen activity. The drug is used to alleviate weaker symptoms of psychological stress and induce sleep.

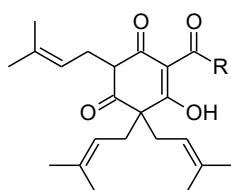
Hops are not well known in our country as food, but it is one of the oldest and most traditional uses of the plant¹⁰, it is consumed in spring, similar to asparagus when young hop shoots are collected. These are then fragile vegetables and are used, wild and grown, either as a salad or as cooked (similar to asparagus) or as pickled. After cooking, young shoots have low-fat content, energy value (104 kJ/100 g) and are a good source of fibre. They contain vitamin C and folic acid, but also oxalic acid. The shoots have short durability, so they should be consumed shortly after harvest¹¹. Today it is one of the most expensive vegetables of its type, one shoot up to 10 cm is about 1 gram. Older parts of the plant are no longer edible, but they will serve to decorate its aroma.

The most in use is the healing drug itself: hop strobiles (egg-shaped seed cones of female inflorescence; light green seed cones), *Lupuli flos* (dried, usually whole female inflorescence *Humulus lupulus* L.), *Flores lupuli* (hop flowers), *Fructus lupuli* (hop fruit), *Strobuli lupuli* (hop cones), consisting of up to 2 cm long scales with golden-yellow lupulin glands (*Glandulae lupuli* or *Lupulinum* (lupulin)). Hop strobiles are used mainly for beer production¹². The drug contains floriglucanols (up to 20 %): humulone type (= α -acids, up to ~17 %) – humulone, cohumulone, prehumulone, posthumulone, adhumulone (Fig. 2), and lupulone type (= β -acids, up to ~10 %) – lupulone, colupulone, prelupulone, postlupulone and adlupulone (Fig. 3). Essential oil (0.5–3 %) – containing β -myrcene (monoterpene), β -caryophyllene, humulene (sesquiterpenes), forming 57–82 % of oil, flavonoids



humulone	R = CH ₂ CH(CH ₃) ₂
kohumulone	R = CH(CH ₃) ₂
adhumulone	R = CH(CH ₃)CH ₂ CH ₃
prehumulone	R = CH ₂ CH ₂ CH(CH ₃) ₂
posthumulone	R = C ₂ H ₅

Fig. 2. Hops α -bitter acids



lupulone	R = CH ₂ CH(CH ₃) ₂
colupulone	R = CH(CH ₃) ₂
adlupulone	R = CH(CH ₃)CH ₂ CH ₃
prelupulone	R = CH ₂ CH ₂ CH(CH ₃) ₂

Fig. 3. Hops β -bitter acids

(0.5–1.5 %) – prenylated flavanones 6-prenylnaringenin, 8-prenylnaringenin, isoxanthohumol), chalcones – xanthohumol, desmethylxanthohumol. The drug contains also polysaccharides (50–60 %), 2–6 % tannins and nitrogen compounds⁶, choline and adenine. From the hops there have been so far isolated and have been characterized more than 1000 compounds⁹. As far as aromatic substances are concerned, from cones can be obtained by extraction or distillation with water steam an oil, which has been produced since the early 19th century.

A mixture of volatile ingredients (essentials) and resins of hops (oleoresins) 3–20 % consists⁹ of various prenylated derivatives of phloroglucinol called “bitter acid”. They are classified either as “ α -acids” or “ β -acids”, which are distinguished by the fact that the first ones are precipitated from the rough extract by adding lead acetate. β -Acids should remain in a solution by definition. α -Acids are humulons (2–12 % of dried cones), while β -acids are called lupulones (1–10 % of dried cones). α -Acids are considered to be the most important components in determining the quality of the hops. They contribute to the stability of the beer head and also to antibacterial properties. Although they are considered the main “bitter acids” of hops, paradoxically they do not have a bitter taste, even at concentrations as 100 $\mu\text{g ml}^{-1}$.

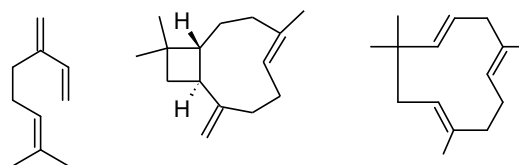
Hop α -acids (humulones) isomerize to the corresponding “iso- α -acids” under various reaction conditions, e.g. at higher pH values. These bitter iso- α -acids are artefacts and make up more than 80 % of hops compounds that occur in typical beers. They can also be oxidized for humulinones and 4'-hydroxyallohumulinones. Under the same circumstances, β -acids (lupulones) are transformed into so-called hulupons.

For these reasons, the drug is relatively unstable and loses its quality after a certain period (depending on the method of storage). The fresh drug has a sharp aromatic hops aroma, and a drug in which oxidation products were formed has a distinctive cheese smell; these decomposition products reduce biological activity. According to older pharmacopoeias, the drug could have been used for a maximum of 1 year after its preparation, but at present, the Czech pharmacopoeia does not contain this requirement.

The essential oil (0.5–1.5 %) consists mainly of sim-

ple oxidized alkanes, monoterpenes and sesquiterpenes. The primary volatile components in all hop cultivars are monoterpene myrcene and sesquiterpenes β -caryophyllene and humulene (57–82 % essential oil), Fig. 4. Regarding traditional economic value, essential oils and bitter acids represent the most important components of hops.

Humulone and lupulone of bitter acids, their degradation product 2-methyl-3-buten-2-ol and 7-methyl-3-methylene-1,6-octadiene (myrcene) are mentioned as components with sedative activity. Both last ones are known as insect pheromones¹³. However, the alcohol is present only in trace amounts in freshly harvested hops, but increases after two years up to 20 % of the content of volatile substances due to the degradation of bitter acids.

Fig. 4. Myrcene, β -caryophyllene and humulene

The third group of compounds consists of flavonoids (0.5–1.5 %) including quercetin (Fig. 5) and glycosides of kaempferol and about 30 prenylated, oxidized and/or cyclic chalcones. The most abundant chalcones are xanthohumol (up to 1 % of dry cones and 80–90 % of total flavonoids, Fig. 6) and desmethylxanthohumol. These chalcones are easily isomerized to corresponding flavanones i.e. isoxanthohumol and a mixture (approx. 3:2) 6-prenylnaringenin and 8-prenylnaringenin (25–60 mg/kg), Fig. 7.

The European Drug Reference Encyclopedia lists⁹ in hops substances many different activities, such as sedative, estrogenic, antimicrobial, antidiabetic (and associated positive effects on hypertriacylglycemia, including reduced risk of related diseases such as atherosclerosis), antiosteoporotic, antiinflammatory, antiproliferation, antiangiogenic, anticancer.

It is worthwhile that the preparation, as we would say today cereal-hops smoothie, which has already been brewed by Odin himself in Walhalla, and whose brewing is regulated by the first Code of our world, published by King Chammurapi, was by the rulers understood as an extremely important and many laws and the lists of rights

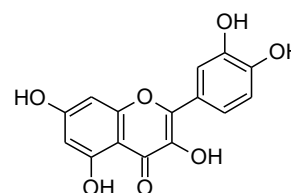


Fig. 5. Quercetin

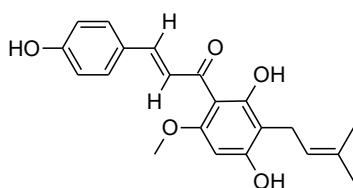
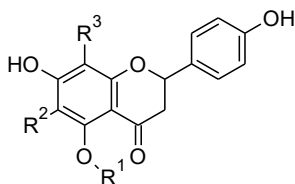


Fig. 6. Xanthohumol



isoxanthohumol $R^1 = \text{CH}_3$, $R^2 = \text{H}$, $R^3 = \text{prenyl-}$
 6-prenylnaringenine $R^1 = R^3 = \text{H}$, $R^2 = \text{prenyl-}$
 8-prenylnaringenine $R^1 = R^2 = \text{H}$, $R^3 = \text{prenyl-}$

Fig. 7. Flavanones

regulates it. In the Czech environment, it has always been said that when a government allows the price of beer to be increased, it will fall within a year (but this could be related to period dreams in the time of building a “better future”). However, if that were true, we would probably have to have a new government several times a year. Let us pay the tribute to the medicinal herb that gave rise to our “liquid daily bread”.

We bring this article as a teaching text describing various interesting aspects of the chemistry of natural substances^{14–16}, and because we want to respond to the number of fictions, half-truths and nonsense that are spread around natural compounds today. It is clear that the exploration of natural substances as renewable substances is one of the ways to contribute to general benefit^{17,18}. If it is done with a natural product, which has been popular with the gods and the kings, and which is used by mankind for thousands of years is only good.

REFERENCES

1. Neve R. A.: *Hops*. Springer Dordrecht 1991.
2. Thomé O. W.: *Flora von Deutschland, Österreich und der Schweiz*. Gera 1885.
3. Korpelainen H., Pietiläinen M.: *Econ. Bot.* 75, 302 (2021).
4. Dioscorides P.: *De materia medica* (Διοσκουρίδης Π.: Περὶ ὕλης ἰατρικῆς), Kilkis between years 50 to 75

A.D. English commented translation: Osbaldeston T. A., Ibis Press, Johannesburg South Africa 2000; https://ia802907.us.archive.org/16/items/de-materia-medica/scribd-download.com_dioscorides-de-materia-medica.pdf, downloaded 5. 4. 2022.

5. Mathioli P. O.: *Commentarii in sex libros Pedacii Dioscoridis*, Praha 1562; Czech translation „*Herbář neboli Bylinář*“, p. 411, Levné knihy Praha 2003.
6. Vydržel A.: *Codex Agrol*. Codex Agrol-Vydržel Olomouc 1935.
7. https://www.webhomeopath.com/homeopathy/homeopathic-remedies/homeopathy-remedy-Lupulus_humulus.html, downloaded 11. 7. 2022.
8. Krejča J., Kresánek J.: *Atlas léčivých rostlin a lesných plodov*. Osveta, n.p., Martin 1982.
9. EMEA: Humulus (Lupuli flos) - Herbal medicines for human use - European Drugs Reference Encyclopedia Community Herbal Monograph on Humulus lupulus L., flos, 2008; <https://theodora.com/drugs/eu/index.html>, downloaded 29. 5. 2022.
10. Ruggeri R., Loreti P., Rossini F.: *Eur. J. Agron.* 93, 11 (2018).
11. Rossini F., Virga G., Loreti P., Provenzano M. E., Danieli P. P., Ruggeri R.: *Agronomy* 10, 1547 (2020).
12. Rybáček V. et al.: *Hop Production* (Chmelářství), SZN Prague 1980.
13. <https://www.pherobase.com/>, downloaded 1. 6. 2022.
14. Bejček J., Spiwok W., Kmoníčková E., Ruml T., Rimpelová S.: *Chem. Listy* 115, 4 (2021).
15. Jurášek M., Opletal L., Kmoníčková E., Drašar P.: *Chem. Listy* 115, 363 (2021).
16. Jurášek M., Opletal L., Drašar P.: *Chem. Listy* 115, 458 (2021).
17. Kaczorova D., Beres T., Zeljkovic S. C., Bjelkova M., Kuchar M., Tarkowski A. P.: *Chem. Listy* 114, 277 (2020).
18. Rádl S.: *Chem. Listy* 115, 246 (2021).

Abstract

As a component of drinks, food, cosmetics, and spice, hops yields a plethora of biologically active compounds. This plant, which was valued by gods and kings through the history, may serve as a basis for pharmaceutical exploitation: not only as a healthy folk medicine but also in a search for the effective sedative, estrogenic, antimicrobial, antidiabetic, and cancerostatic compounds.

● Jurášek M., Rybka A., Opletal L., Drašar P.: *Chem. Listy* 116, 668–671 (2022).

● <https://doi.org/10.54779/chl20220668>