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Review

# Chemical transformations of characteristic hop secondary metabolites in relation to beer properties and the brewing process: A review

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ABSTRACT

The annual production of hops (*Humulus lupulus* L.) exceeds 100,000 mt and is almost exclusively consumed by the brewing industry. The value of hops is attributed to their characteristic secondary metabolites; these metabolites are precursors which are transformed during the brewing process into important bittering, aromatising and preservative components with rather low efficiency. By selectively transforming these components off-line, both their utilisation efficiency and functionality can be significantly improved. Therefore, the chemical transformations of these secondary metabolites will be considered with special attention to recent advances in the field. The considered components are the hop alpha-acids, hop beta-acids and xanthohumol, which are components unique to hops, and alpha-humulene and beta-caryophyllene, sesquiterpenes which are highly characteristic of hops.


**Contents**



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## 1. Introduction

The beneficial properties of hops (*Humulus lupulus* L.) are well known, and the first accounts of the use of hops for medicinal purposes date back to the 9th century (Moir, 2000). Later, the principal use of hops became that of a combined bittering, aromatising and preservative agent in the brewing industry. Currently, the global hop production – 101,000 mt of hops were grown in 2011 – is almost exclusively consumed by the brewing industry (Barth & Meier, 2012).

The relevance of the hop plant for the brewing industry is mainly attributed to the secondary metabolites present in the lupulin glands of the female inflorescences. According to their physicochemical properties, these secondary metabolites are often categorised into three fractions: the hop resins, the hop oil and hop polyphenols. The hop resins are characterised by their solubility in cold methanol and diethyl ether and are further classified, depending on their solubility in hexane. The soft resins are soluble in hexane and mainly contain prenylated phloroglucinol derivatives such as the hop alpha-acids and hop beta-acids. The hard resins are characterised by their insolubility in hexane and they primarily consist of prenylated chalcones and flavanones, with xanthohumol being the major constituent of the hard resins. The hop (essential) oil is, by definition, the fraction of hops that can be isolated by steam distillation. The monoterpene myrcene and the sesquiterpenes, alpha-humulene and beta-caryophyllene, make up the bulk of the essential oil, but O- and S-containing components are present as well. Next to the hop resins and the hop oil, a complex mixture of polyphenols, consisting of aromatic carboxylic acids and non-prenylated flavonoids, including proanthocyanidins and flavonol glycosides, is present in the hop cones.

During the wort-boiling step of the brewing process, these secondary metabolites are transformed into desired components with bittering, aromatising, preservative and even anticarcinogenic function. However, these precursors can be evaporated and/or precipitated during the brewing process, whereas the desired products may be degraded. Consequently, the efficiency of hop use in the traditional brewing process is quite low. Through off-line chemical processing of these hop components prior to their application in the brewing process, the overall efficiency of the hop usage and the stability of the desired hop products can be increased significantly.

The goal of this work is to summarise the key aspects and recent advances of the chemical transformation of these hop components. The isomerisation/degradation, photochemical, oxidation and reduction reactions of the hop acids, xanthohumol, alpha-humulene and beta-caryophyllene will be addressed with attention to the reaction mechanisms, the impact on the beer and the brewing processes, and the role of catalysis in the transformation processes.

## 2. Alpha-acids

### 2.1. Structure and chemical properties of alpha-acids

The alpha-acids are direct precursors of the main bittering principles of beer, the iso-alpha-acids. Alpha-acids can be added in the brewing process in the form of dried hop cones, pellets or extracts. Alpha-acid contract prices varied in 2012 between 5 and 15 € $kg^{-1}$, depending on variety (Barth & Meier, 2012). The fact that hop prices are expressed as a function of alpha-acid content is illustrative of the importance of this class of compounds. The alpha-acids are part of the soft resins and consist of diprenylated phloroglucinol derivatives with variable acyl side chains. Alpha-acid content is highly cultivar-dependent but hops contain, on average, 9–10 wt% of alpha-acids (Yakima Chief, 2013). Recently developed hop cultivars can contain up to 19 wt% of alpha-acids (Yakima Chief, 2013). The alpha-acids can be isolated from a hop extract, on lab scale, by precipitation with $Pb(OAc)_2$ or, on a larger scale, through acid–base extraction (Verzele & De Keukeleire, 1991). Hop alpha-acids are primarily used as precursors of the bitter-tasting iso-alpha-acids in the brewing industry. While *n*-humulone (**1a**) and co-humulone (**1b**) are the major alpha-acids in all hop cultivars, up to seven different alpha-acids have been identified (see Scheme 1) (Briggs, Boulton, Brookes, & Stevens, 2000).

Individual alpha-acids can be isolated from a crude supercritical (sc) $CO_2$ hop extract by centrifugal partition chromatography, using the two-phase liquid system, toluene – 0.1 M triethanolamine HCl (pH 8) (Hermans-Lokkerbol, Hoek, & Verpoorte, 1997; Hermans-Lokkerbol & Verpoorte, 1994). Next to chromatography, crystallisation and complexation can be used to isolate particular hop acid derivatives. **1a** can be isolated from a total alpha-acid mixture by recrystallisation after complexation with 1,2-diaminobenzene. Due to the relative ease with which **1a** is isolated, it is often used as a model substrate. The different alpha-acid analogues all possess comparable intrinsic chemical reactivities. The structure of **1a** was tentatively identified in 1969 as (−)-(6*R*)-2-(3-methylbutanoyl)-4,6-bis-(3-methyl-2-butenyl)-3,5,6-trihydroxycyclohexa-2,4-dien-1-one and this claim remained unchallenged for more than 40 years (De Keukeleire & Verzele, 1970). Recently, however, using XRD analysis of the crystallised complex of **1a** with (1*R*,2*R*)-(−)-diaminocyclohexane, the C6-atom was demonstrated to possess a *S*-stereoconfiguration, resulting in the definitive structure for **1a** as depicted in Scheme 1 (Tyrrell et al., 2010; Urban, Dahlberg, Carroll, & Kaminsky, 2013). The conjugated beta-tricarbonyl motif is responsible for the main physicochemical properties of the hop alpha-acids, relevant for further processing. It serves as chromophore, metal-chelating group and (weak) acid site. The UV absorption maxima of **1a**, are situated at 320, 277 and 234 nm. Hop alpha-acids possess weak acid behaviour, due to the stabilizing effect of the conjugated system on the enolate, with reported