



Polyphenols in Conventional Beers, Dry-Hopped Beers and NABLAs

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Abstract

Beer phenols issued from malt and hops can contribute directly to several characteristics of beer, mainly flavor, astringency, haze, body, and fullness. Some phenolic structures can also impart very interesting health properties. Yet phenolic structures also evolve through storage. Low-molecular-weight phenols like 4-vinylsyringol can impart off-flavors in aged beer, whilst oxidized flavonoids strongly influence astringency, haze, and color, especially in dry-hopped beers. The instability of stilbenes, prenylchalcones, and derived flavanones could also modify their health potential.

Keywords

Beer · Polyphenols · Dry-hopping · Colloidal stability · Low-alcohol beer · Aging

Abbreviations

AEDA	Aroma extract dilution analysis
APCI	Atmospheric pressure chemical ionization
C	Catechin
E	Epicatechin
EGC and GC	Epigallocatechin and gallic acid
ESI	Electrospray ionization
FD	Dilution factor
HPLC or LC	High performance liquid chromatography
MS	Mass spectroscopy
MS/MS	Tandem mass spectroscopy
NABLABs	Non- or low-alcoholic beers
NP	Normal phase
P1 to P10	Procyanidins from monomers to decamers
PVP	Polyvinylpyrrolidone
PVPP	Polyvinylpolypyrrolidone
RP	Reversed phase
UV	Ultraviolet

1 Introduction

Beer phenols issued from malt and hops can contribute directly to several characteristics of beer, mainly color, flavor, astringency, and haze [1, 2]. As antioxidants, they can also protect raw materials from oxidative degradation throughout the process, minimizing, therefore, off-flavors such as *trans*-2-nonenal.

In this review, all phenolic structures that have been found in beer will be described. Special attention will be dedicated to the comparison between conventional beers, dry-hopped beers, and non- or low-alcoholic beers (NABLABs) in terms of color and colloidal stability.

2 Flavan-3-ol Monomers

2.1 Beer Catechins

The main monomeric flavan-3-ol unit identified in beer is (+)-catechin (0.5–6.9 mg.L⁻¹), but(–)-epicatechin (0.8–1.9 mg.L⁻¹), (–)-catechin gallate, (–)-epicatechin gallate, and two glycosides have also been detected (Table 1) [3–10, 17–20].

2.2 Malt Catechins

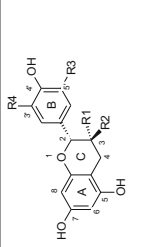
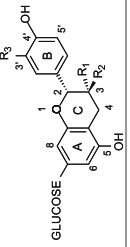
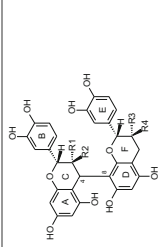
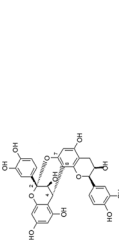
Malt contains only 10–100 mg.kg⁻¹ (+)-catechin (and no epicatechin at all) [3, 21–23]. During mashing, malt flavanoids are progressively dissolved in the wort (monomers dissolve much faster than oligomers). From mash filtration to boiling, a great proportion of them will be lost through oxidation, adsorption to spent grains, linkage to coagulated proteins, etc.

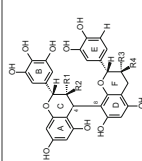
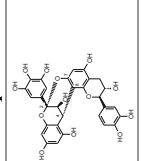
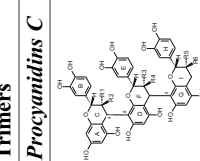
2.3 Hop Catechins

Even compared to grapes, hops emerges as an exceptional source of flavan-3-ols. Therefore, although added in one-hundred-times lesser quantity than malt, it can account for 30% of total beer polyphenols. According to the type of hop conditioning used (CO₂ extracts are much poorer in polyphenols than pellets and cones) and the stage of addition, more or less flavanoids will be brought into the wort in the boiling kettle [24]. With the extra addition of hops into dry-hopped beers (during primary fermentation or even later), their contribution increases, and this often leads to unwanted color modification and colloidal haze during aging.

In hop cones or pellets, the total monomer content can reach up to 4500 mg.kg⁻¹ [21, 22, 25–27]. The iconic Saaz aromatic variety always appears as the most abundant. Among traditional hop cultivars, the lower the bitterness, the higher the flavanoid level (up to 1% “total flavanoids” in Saaz, as expressed in terminal unit weight [28]). Yet, recent studies show that no inverse correlation can be found between total flavanoids and the α -acid content when dual-purpose (abundant in both essential oils and α -acids) varieties are considered [29]. The most attractive feature of these novel varieties (including Amarillo, Citra, CTZ, Eureka!, Mandarina Bavaria, Mosaic, Polaris, Sabro, etc.) appeared to be their polyfunctional thiol profile, with both a wide variety of nice odorants and a huge amount of bound

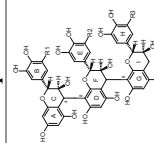
Table 1 Flavan-3-ol monomers, polymers, and range of concentrations in beer [3–16]

Structures	Compounds	R1	R2	R3	R4	Concentrations in beer (mg.L ⁻¹)
Monomers						
	(+)-Catechin	H	OH	H	OH	0.28–6.9
	(-)-Epicatechin	OH	H	H	OH	<0.10–1.9
	(-)-Catechin gallate	H	Gallate	H	OH	5–20
	(-)-Epicatechin gallate	Gallate	H	H	OH	5–20
	3-O-methylcatechin	H	OCH ₃	H	OH	Detected
	Catechin-7-O-β-D-glucopyranoside	H	OH	OH	OH	Detected
	Catechin-7-O-β-(6''-O-nicotinoyl)-β-D-glucopyranoside	H	OH	OH	OH	Detected
Dimers						
Procyanidins B						
	B1 (-)-Epicatechin-(4β-8)(+)-catechin	OH	H	H	OH	Detected
	B3 (+)-Catechin-(4α-8)(+)-catechin	H	OH	H	OH	Traces-3.1
	B4 (+)-Catechin-(4α-8)(-)-epicatechin	H	OH	OH	H	Detected
	Procyanidins A					
	A2 (-)-Epicatechin-(4β-8)(2α-O-7)(-)-epicatechin	OH	H	OH	H	Traces

Prodelpinidins B		H	OH	H	OH	H	OH	Traces-3.3
	B3 (-)-Gallicocatechin-(4 α -8)-(+)-catechin	H	OH	H	OH	H	OH	Traces-3.3
	B9 (-)-Galloepicatechin-(4 β -8)-(+)-catechin	OH	H	H	H	H	OH	Detected
Prodelpinidins A								
	<i>enl</i> -(-)-Epigallocatechin -(4 α -8, 2 α -O-7)-(+)-catechin							Detected
	<i>enl</i> -(-)-Epigallocatechin -(4 α -6, 2 α -O-7)-(+)-catechin							Detected
Trimers								
Procyanidins C								
	C2 (+)-Catechin-(4 α -8)-(+)-catechin -(4 α -8)-(+)-catechin	H	OH	and R5 = H	and R6 = OH			Detected

(continued)

Table 1 (continued)

Structures	Compounds	R1	R2	R3	R4	Concentrations in beer (mg.L ⁻¹)
	(-)-Gallocatechin-(4α-8)-(-)-gallocatechin-(4α-8)-(+)-catechin	OH	OH	H	/	Detected
	(-)-Gallocatechin-(4α-8)-(+)-catechin-(4α-8)-(+)-catechin	OH	H	H	/	Detected

glutathionylated and cysteinylated forms [30–32]. Among them, a rather unexpected data point was obtained with the CTZ dual-purpose hop variety, which emerged as the second richest sample in monomers (up to 2581 mg.kg⁻¹), despite its 15–17% α -acids. On the other hand, the high-bitter Polaris variety remains the less abundant in monomers (<800 mg.kg⁻¹) [29].

An atypical (+)-catechin/(–)-epicatechin ratio was also recently shown in a few hop cultivars (>3.7 only in Saaz and Citra, while <1.6 in all the others). A high level of (+)-catechin in a hop indicates a strong efficiency of leucoanthocyanidin reductase (LAR) to convert 3,4-flavandiol, while anthocyanidin reductase (ANR) is required to create (–)-epicatechin. Surprisingly, the (+)-catechin/(–)-epicatechin ratio proved stable within the same variety through two successive harvest years, contrary to individual amounts of both monomers (strongly influenced, as other phytoalexins, by climate conditions, region, and year). This suggests that whatever the (a)biotic stresses, the relative LAR/ANR enzymatic efficiency remains stable in a variety through successive harvest years [29].

2.4 Catechins and Color

Beer color increases through storage, especially in the presence of oxygen and at higher temperatures. At pH 3, colorless catechin-derived products are formed after enzymatic oxidation, whereas at pH 6, after chemical degradation, yellow products including dehydrodiccatechin appeared. Dimers differing by their interflavan linkages can be detected in model media (Fig. 1) [33, 34]. Callemien and Collin [18] detected the same dehydrodiccatechin A in an aged beer spiked with catechin before aging.

It has been confirmed that the increase in color intensity during aging (up to 6.4 °EBC after 2 years in dry-hopped beers) strongly correlates with the level of monomers in fresh beer [35, 36]. Both early hopping in the boiling kettle (with subsequent depolymerization of oligomers) and dry hopping can impart monomers, leading to unusually higher levels of flavan-3-ol monomers in dry-hopped beers (up to 7 mg.L⁻¹) [36].

3 Flavan-3-ol Procyanidins

3.1 Beer Procyanidins

Beer also contains flavanoid oligomers (proanthocyanidins), known as anthocyanogens in the brewing field. Thiolysis hyphenated to RP-HPLC-ESI(–)-MS/MS was optimized by our group to investigate beer polyphenolic oligomers [19]. Thiolysis indicated that most beer dimers are procyanidins B3 (two catechin units), whilst most trimers are prodelphinidins (catechin in terminal units and gallocatechins or catechins in extension units). Despite the absence of chromatographic peaks corresponding to oligomers above trimers, an apparent degree of polymerization (mDP) close to 6 was calculated in a total LH20 extract. Detailed structures were determined by RP-HPLC-ESI(–)-MS/MS

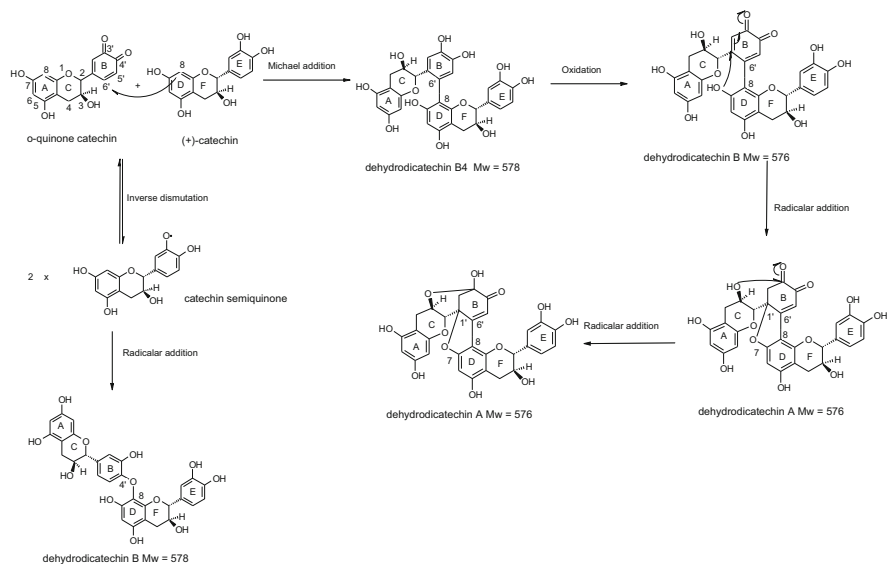


Fig. 1 Proposed degradation schemes of (+)-catechin to form colorless compounds with Mw = 578 and yellow compounds with Mw = 576 [18]. (Reprinted (adapted) with permission from Callemien and Collin, *J Agric Food Chem*, 2007, 55, 9066–9073. Copyright 2007 American Chemical Society)

[7]. Four dimers were identified: three procyanidins (B1, B3, and B4) and one prodelphinidin (B3) (Table 1). Previously detected in hops or malt, three trimers (the procyanidin C-4*α*-8-C-4*α*-8-C and two prodelphinidins, GC-4*α*-8-C-4*α*-8-C and GC-4*α*-8-GC-4*α*-8-C) were distinguished for the first time in beer. As expected, according to previous thioacidolysis data, most beer proanthocyanidins carry a catechin as a terminal unit.

3.2 Malt Procyanidins

Malt contains two B3 dimers (prodelphinidin and procyanidin), at lower levels than in hops, but with higher amounts of gallocatechin units [21–23, 37]. Many trimers have also been detected in malt (catechin and gallocatechin units).

3.3 Hop Procyanidins

Hop is an excellent source of flavan-3-ol dimers, B3 (the most representative one, often followed closely by B1 and B4) being detected at levels up to 0.1% [21, 22, 26, 27]. B2 is consistently found at the lowest amount. Again, Saaz and CTZ display the highest concentrations of dimers and Polaris the lowest. As with the (+)-catechin/(–)-epicatechin ratio, the Saaz and Citra B3/B2 ratios are notably high, above 3.8 (also the

case here for Polaris), resulting from much less inserted epicatechin [29]. Since oxidized procyanidins enriched in epicatechin have been identified in beer as significant contributors to haze (see hereunder), a better selection of hops could improve beer stability.

3.4 Procyanidins and Haze

Colloidal instability due to interactions between flavan-3-ols and proteins limits the shelf life of beer. A lag phase is usually observed in lager beers before chill-haze development [38–40]. The time needed to form critical amounts of tanning polyphenols leading to visible chill-haze particles corresponds to the lag phase. As described by Leemans et al. [40], for different batches, the longer the lag phase, the better the colloidal stability. Chill haze (or reversible haze), defined by non-covalent bonds between polyphenols and active proteins, can eventually turn into permanent haze that no longer dissolves as the beer warms. Catechin does not rapidly induce strong haze. Colloidal instability caused by dimers and trimers is strongly enhanced after oxidation (not true for tetramers and pentamers) [41–43]. Free radicals are known to enhance haze [44]. Tannoids have been defined by Chapon [45] as intermediates in the oxidation of simple flavanoids to tannins, forming complexes with proteins. Not only dissolved oxygen but also shaking, higher temperature, polyphenol-rich raw materials, light, and heavy metals will significantly increase colloidal instability [11, 40]. Leemans et al. [40] have proposed a model in which aldehydes and oxygen play key roles in tanning polyphenol formation [11, 40]. Now, we know that short A-type oligomers are the most tanning agents, both in cider [46] and in beer. Their synthesis during the lag phase requires the oxidation of A-type oligomers with at least an epicatechin in its extension units.

In dry-hopped beers, we recently evidenced a linear relationship between the oligomer loss through aging and chill haze increase [35]. The latter was also correlated with the oligomer concentration in the fresh beer. In the case of NABLABs, due to premature oxidation of flavanoids in the absence of ethanol, the oligomer concentration (dimer and trimer procyanidins) exhibited a strong correlation with chill haze before aging [36].

Beer contains less haze-active polyphenols than haze-active proteins. Derived from barley hordeins, haze-active proteins (10–30 kD) are acidic, hydrophilic polypeptides, rich in both proline and glutamic acid [41] and glycosylated [47]. Much more haze is produced near pH 4.0 than at pH 3.0 or above pH 4.2. At the beer pH, ethanol at low concentration causes a modest decline of haze, whilst strong haze is observed at higher concentrations [48].

To preserve beer colloidal stability, brewers usually remove haze-active materials [49]. To get rid of haze-active proteins, precipitation with tannic acid, hydrolysis with papain or other more selective enzymes, and adsorption to bentonite [50] or silica gel [51, 52] are very effective, but unfortunately in some cases, such procedures also remove foam proteins. To remove haze-active polyphenols, the most usual way is adsorption to polyvinylpyrrolidone

(PVPP). Because of the structural analogy between these compounds and proline [53], pyrrolidone rings bind polymerized flavanoids through hydrogen and ionic bonds. Combined adsorbents have been proposed to brewers, such as PVPP mixed with silica gel, PVP bound onto silica, and tannin linked to silica [38, 54]. Another way is the use of flavan-3-ol and proanthocyanidin-free malt, which allows affording an excellent colloidal stability [55].

3.5 Procyanidins and Astringency

Flavanoids are known to be responsible for astringency [56, 57]. Sensory analyses applied to top-fermented beers have shown that storage (20 °C or 40 °C with air in the headspace) decreases bitterness and post-bitterness but intensifies astringency [58]. On the other hand, no significant astringency-related deterioration was measured in lager beers aged for 5 days at 40 °C (with or without oxygen) [59]. In both cases, an increase in DP (global assay) and a decrease in total flavanoids were mentioned, especially at higher temperature or pH, in the presence of air [58, 59].

The levels of monomers found in beer are usually under the threshold reported for catechin and epicatechin (1 and 20 mg.L⁻¹ in water, but close to 20 mg.L⁻¹ in the beer matrix [56, 57]). Astringency is intensified at low pH, especially near 4.0–4.2 [60], but a higher astringency has been measured by François et al. [59] in beers with a pH close to 5. In this case it was suspected that the pH of the samples fell in the mouth before polyphenol/protein interactions occurred.

3.6 Procyanidins and Health Properties

Flavan-3-ols are known to induce cardioprotective effects, including antioxidant effects (protection against LDL oxidation) and inhibition of platelet activity and vasodilatation [61, 62]. Flavonoids might reduce the risk of cancer, although some procarcinogenic activities have also been reported [61, 63]. Flavonoids alter the synthesis of eicosanoids (mediators of inflammation). They decrease the leukotriene/prostacyclin ratio by modifying lipoxygenase activity [64, 65]. Immune regulation has also been observed [66]. Hop proanthocyanidins can help prevent nitric oxide-related disorders such as Alzheimer's and Parkinson's diseases [27].

4 Prenylchalcones and Derived Flavanones

4.1 Beer and Hop Prenylchalcones and Flavanones

More than twenty prenylchalcones and derived flavanones, studied mainly for their biological effects, have been identified in hops [67]. Concentrations higher than 0.6%, with a predominance of xanthohumol and desmethylxanthohumol, are usually found (Fig. 2) [68]. Levels of 80 and 90 mg.L⁻¹ have been reported for the

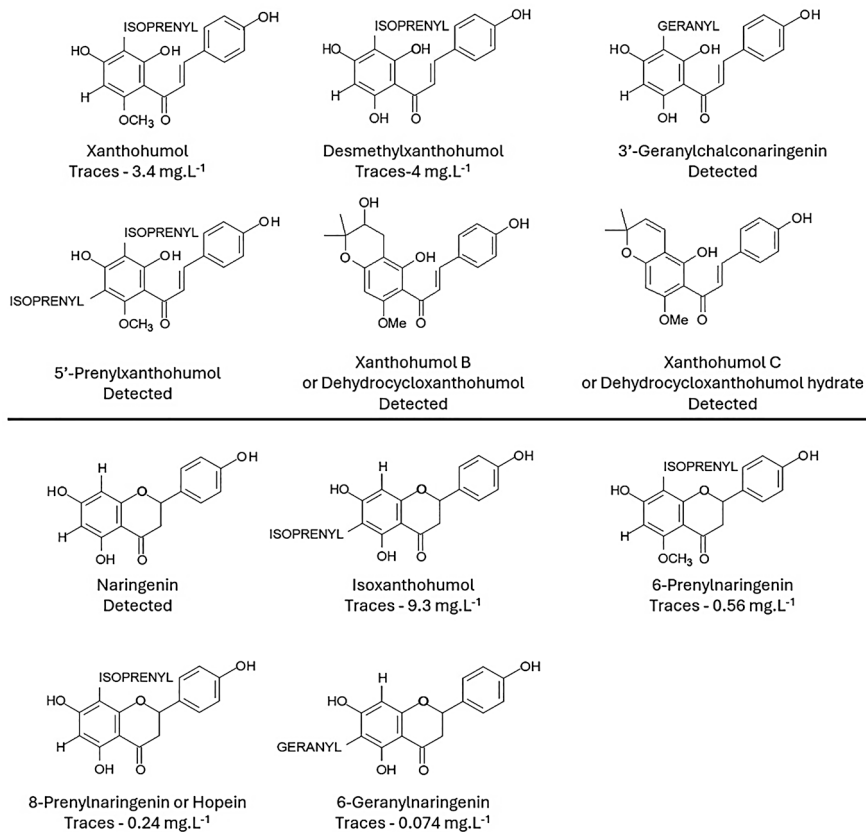


Fig. 2 Prenylchalcones, derived flavanones, and a range of concentrations in beer. (Adapted from [11])

corresponding flavanones, isoxanthohumol and hopein. The higher the α -acid content (bitter acids in hops), the higher the xanthohumol level [69].

Since hop is the only source of these compounds in beer, a relation can be established between their concentration and the rate of hopping. Xanthohumol isomerizes easily during the brewing process into isoxanthohumol [70]. Only 15–50% hop xanthohumol remains in the final beer [71, 72], leading to concentrations often below 1 mg.L⁻¹ [20, 68, 73, 74]. Stout- and porter-style beers are characterized by slightly higher levels because dark malts contain compounds inhibiting xanthohumol isomerization [70]. The use of xanthohumol-enriched hop products (obtained by ethanol-CO₂ extraction) combined with late hopping makes it possible to significantly increase the xanthohumol and isoxanthohumol potential of beer (close to 10 mg.L⁻¹).

4.2 Health Properties of Prenylchalcones and Flavanones

Xanthohumol is a “broad-spectrum” cancer chemopreventive agent acting on all three stages of carcinogenesis. Xanthohumol and isoxanthohumol are both active ROS scavengers, while only the former is active in superoxide scavenging assays. Isoxanthohumol, 8-prenylnaringenin, and xanthogalenol may also exert chemopreventive effects [12, 20, 74–76].

Prenylflavanones have mainly been studied for their estrogenic activity. Hopein is a very potent phytoestrogen. The authors recommend its application in the prevention or treatment of (post)menopausal symptoms and osteoporosis [74, 75, 77]. Weak estrogenic activity has been observed for close analogs like 6-prenylnaringenin, 8-geranylnaringenin, 6,8-diprenylnaringenin, and isoxanthohumol. Prenylchalcones like xanthohumol and xanthogalenol also show low activity [78].

5 Flavonols

5.1 Beer and Hop Flavonols

Sixteen flavonol glycosides (mainly mono-, di-, and triglycosides of quercetin and kaempferol) have been detected in hops [11]. Although boiling can extract 91% of the kaempferol and 88% of the quercetin glycosides, only a few mg per liter of flavonols are found in the final beer (Fig. 3) [3–5, 79, 80].

In beer, flavonols could be slightly responsible for bitterness but do not participate in beer haze formation [11].

5.2 Health Properties of Flavonols

Flavonols induce cardioprotective effects, including antioxidant effects (protection against LDL oxidation) and inhibition of platelet activity and vasodilatation [61, 81], while very little information is available on their potential anticancer effects.

6 Hydroxybenzoic Acids, Hydroxycinnamic Acids, and Derived Compounds

6.1 Beer, Malt, and Hop Hydroxybenzoic Acids

Malt and hops contain various hydroxybenzoic acids, which are retained at least partially up to the final beer (Fig. 4). Total hydroxybenzoic acids—mainly *p*-hydroxybenzoic, vanillic, and gallic acids—usually reach a few mg per liter in beer. They have also been found as glycosides or other bound forms [3–6, 13, 17, 82–85].

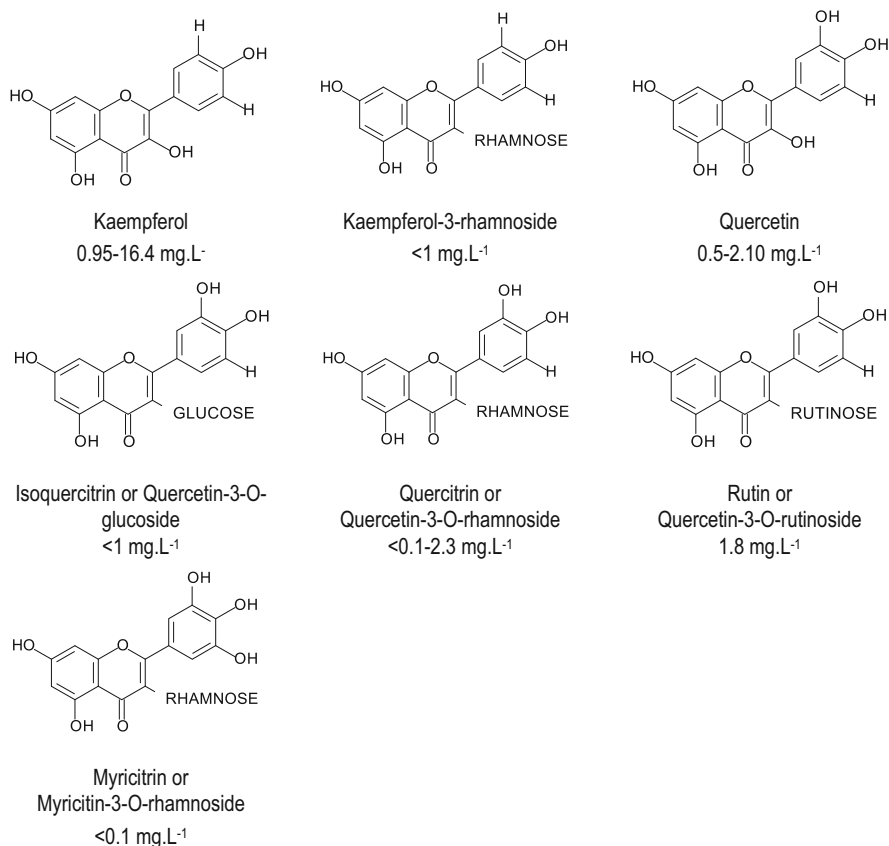


Fig. 3 Flavonols and range of concentrations in beer. (Adapted from [11])

6.2 Beer, Malt, and Hop Hydroxycinnamic Acids and Coumarins

Hydroxycinnamic acids are partially recovered in beer (Fig. 4). Most of them are in combined forms in the raw materials, either with quinic acid, glucose, or cell wall constituents [3–6, 13, 17, 82–89]. In malt, *p*-coumaric and ferulic acids are esterified with arabinoxylans [90]. They can be both water-extracted and enzymatically solubilized by cinnamoyl esterases [91]. After mashing, an additional release of ferulic acid may occur during fermentation due to yeast cinnamoyl esterases [92].

Three coumarins issued from orthohydroxycinnamic acid cyclization have also been found in beer (Fig. 5) [3, 84].

Hydroxybenzoic and hydroxycinnamic acids are characterized by relatively high flavor thresholds (>mg.L⁻¹, mainly bitter taste and astringency) [93]. On the other hand, their decarboxylated derivatives (Fig. 5) can impart very strong phenolic/clove/smoked flavors to beer because of their low threshold values (µg per liter order).

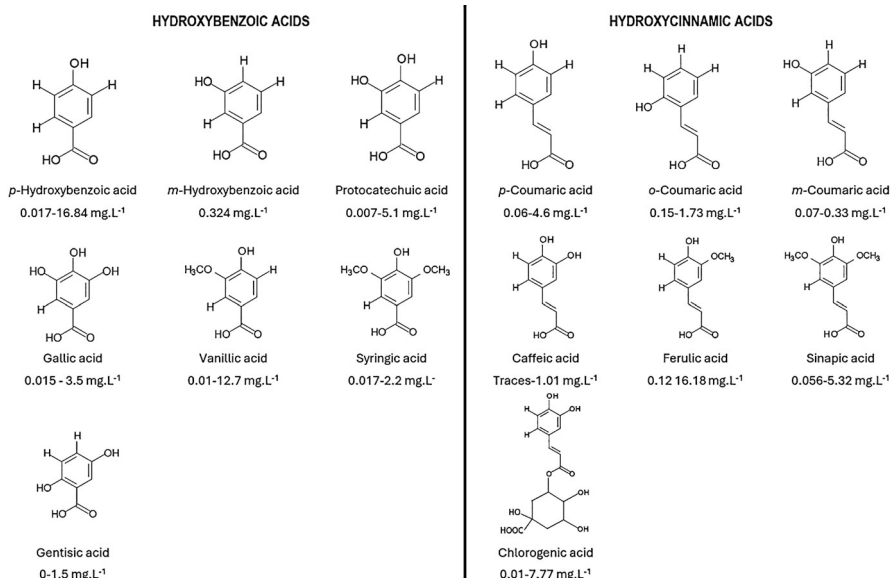


Fig. 4 Hydroxybenzoic acids and hydroxycinnamic acids and range of concentrations in beer. (Adapted from [11])

6.3 Beer Flavors Issued from Phenolic Acids

Decarboxylation of phenolic acids can occur either by thermal degradation [94] during malt kilning and in the boiling kettle [88, 95] or during fermentation. In this last case, decarboxylation is catalyzed by the phenylacrylic acid decarboxylase found in *Saccharomyces cerevisiae* strains displaying the Pof⁺ phenotype (Phenolic-Off-Flavor) [96, 97] and in some contaminating microorganisms like *Brettanomyces/Dekkera* spp. [98] or *Enterobacteriaceae* [99]. In this way, 4-vinylguaiaicol is issued from ferulic acid while 4-vinylphenol derives from *p*-coumaric acid. 4-Vinylguaiaicol has also been found in hops [100].

In Belgian white beer production, enzymatic decarboxylation of ferulic acid occurs linearly through fermentation at a rate close to 140 $\mu\text{g.L}^{-1}$ per day (Fig. 6). The rate decreases strongly during secondary fermentation, down to 20 $\mu\text{g.L}^{-1}$ per day. Compared to *p*-coumaric acid, ferulic acid is preferentially degraded by yeast (*p*-coumaric acid remains unmodified until the ferulic acid concentration reaches 2 mg.L⁻¹) [11]. Concentrations up to 6.2 mg.L⁻¹ in 4-vinylguaiaicol and up to 3.2 mg.L⁻¹ in 4-vinylphenol have been reported in wheat beers [3, 88–90, 92, 101–108]. For instance, 4-vinylguaiaicol contributes to the specificity of Belgian white beers (made with unmalted wheat) and German Rauch and Weizen beers (made with malted wheat) [103, 105, 108, 109]. According to its concentration, 4-vinylguaiaicol can lead either to strong pharmaceutical off-flavor defects [101] or to pleasant clove flavors [90], whilst 4-vinylphenol is always considered to be an off-flavor [90]. These vinyl compounds can

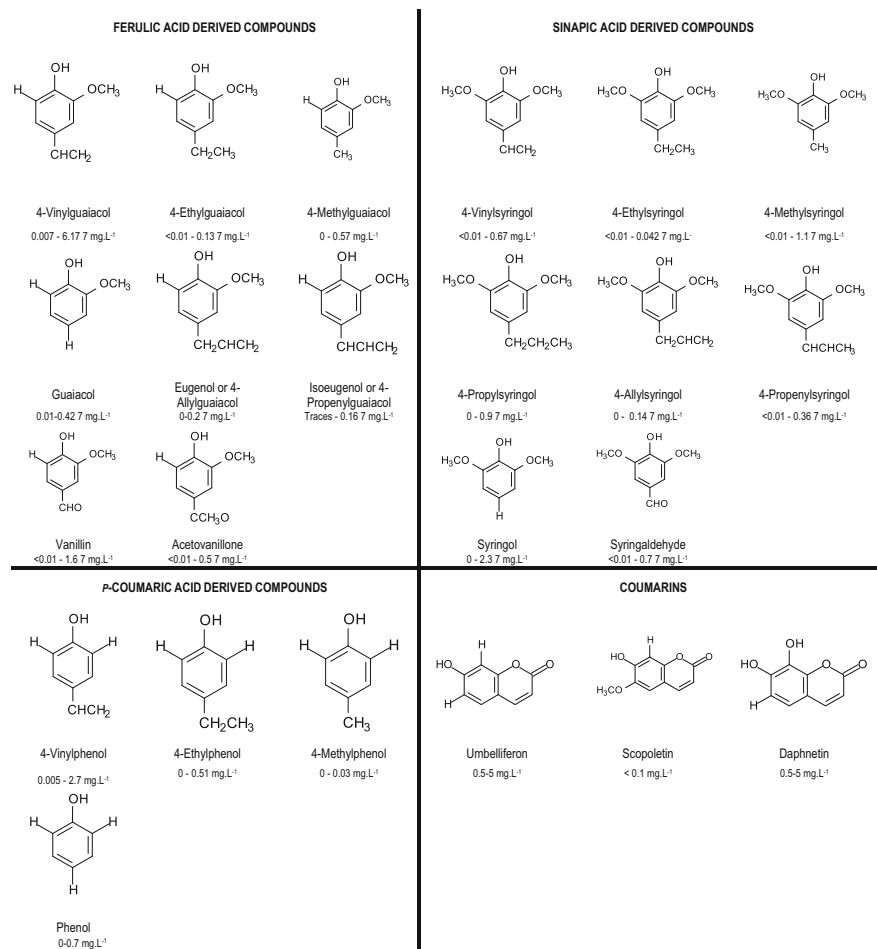


Fig. 5 Hydroxybenzoic and hydroxycinnamic acids-derived compounds and range of concentrations in beer. (Adapted from [11])

be further oxidized or reduced into smaller molecules like vanillin, 4-ethylguaiaicol, guaiacol, and 4-ethylphenol through chemical reactions [110] or through the activity of wild yeasts like *Brettanomyces/Dekkera* spp. [98].

As guaiacol and 4-methylphenol were found to be more concentrated in brown beers (>3.5 and >1.1 $\mu\text{g.L}^{-1}$, respectively), they have been proposed as specific markers of the utilization of dark malts [111]. Analysis of colored malts confirmed the high levels of guaiacol and 4-methylphenol (>180 and 7 $\mu\text{g.L}^{-1}$ in the corresponding wort, respectively) for chocolate and black malts only. Both compounds appeared even more concentrated in dark beers after aging, reaching levels not far from their sensory thresholds. This was explained by the occurrence of glucosides, recently evidenced in dark malt by HPLC-MS/MS.

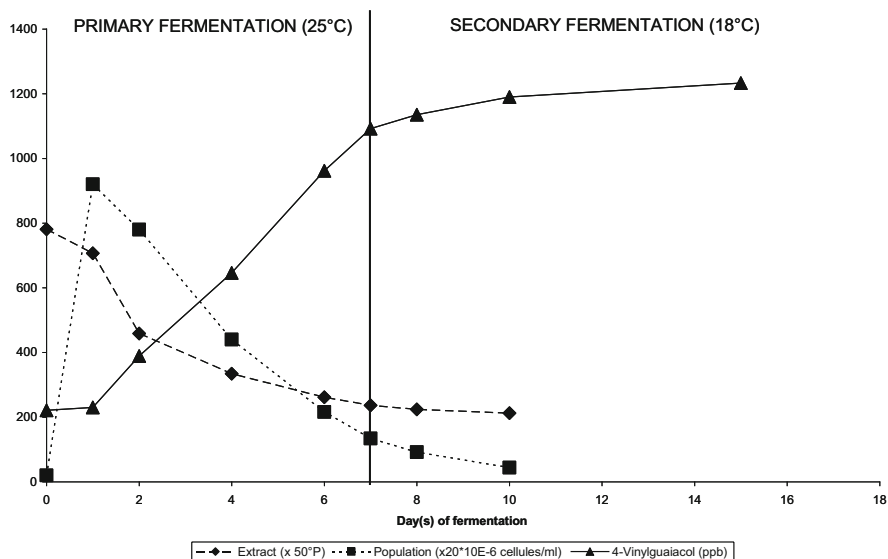


Fig. 6 Evolution of extract, cell population, and 4-vinylguaiacol concentration through fermentation of Belgian white beer

On the other hand, degradation of 4-vinylguaiacol through natural aging (25% after 20 days) or at 40 °C (50% after 20 days) has been reported [88, 105, 112]. This compound could be partially transformed to apocynol, guaiacol, and vanillin [90, 113].

By using the AEDA methodology on aged lager beers, 4-vinylsyringol was identified as a strong old-beer-like phenolic odorant (FD value as high as that of *trans*-2-nonenal, responsible for the cardboard off-flavor in aged beer) [114, 115]. Its release through aging should be due to acidic hydrolysis of a glycoside, since sinapic acid decarboxylation occurs much earlier in the process, either in the boiling kettle or during fermentation.

Phenolic acids do not participate in beer haze formation [42, 116], but vinylphenol and cinnamic acid have been described as potential pigments [117–120].

7 Stilbenes

7.1 Beer and Hop Stilbenes

Our group discovered three stilbenes in hops: *trans*-resveratrol, *trans*-piceid, and *cis*-piceid [25, 121]. Concentrations ranging from 0.7 to 11 mg.L⁻¹ *trans*-piceid and from 0.03 to 2.3 mg.L⁻¹ *trans*-resveratrol have been reported in hop cones [122]. A strong influence of geographic origin and harvest year has been shown, but American aromatic cultivars like Willamette and Cascade emerge in all cases as the best sources of stilbenes. Resveratrol is very sensitive to heat and light [122]. Even during hop storage, a significant loss occurs, especially in highly

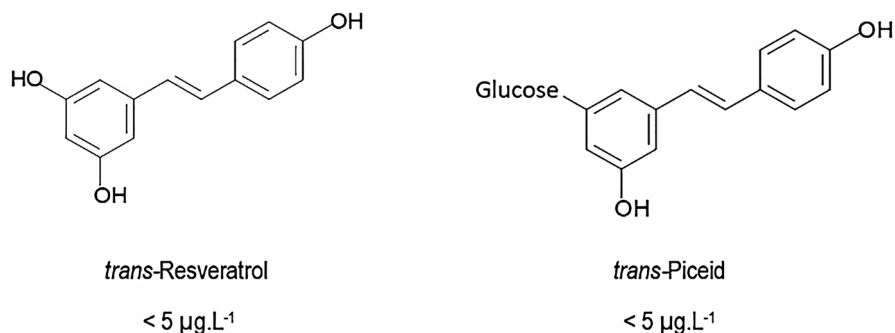


Fig. 7 Stilbenes and range of concentrations in beer [126]

oxygen-sensitive varieties, leading to new analogs like *cis*-resveratrol and dimers [123]. Likewise, hop pelletization induces strong degradation [123, 124]. *trans*-Resveratrol and glycosides are absent from malt [125], so one should not be surprised to find only traces of stilbenes in beer (Fig. 7). Up to $5 \mu\text{g}\cdot\text{L}^{-1}$ *trans*-resveratrol was detected by our group in Belgian commercial beers [126].

Taking into account a concentration of $1\text{--}10 \text{ mg}\cdot\text{L}^{-1}$ stilbene in hops and hopping close to $200 \text{ g}\cdot\text{hL}^{-1}$ in wort, a maximum of $2\text{--}20 \mu\text{g}\cdot\text{L}^{-1}$ stilbene could be expected in beer. Moreover, massive degradation of *trans*-resveratrol is known to occur in the boiling kettle (60% degradation after 7 min of boiling—Fig. 8a). *trans*-Piceid is much more stable during heat treatment, and it can be converted to free resveratrol through wort fermentation (only 60% recovered from a beer prepared by spiking an industrial wort at $10 \text{ mg}\cdot\text{L}^{-1}$ before fermentation—Fig. 8b). When the wort was not pitched, *trans*-piceid remained stable, suggesting that yeast enzymes catalyze this hydrolysis to free resveratrol, as previously described for wine [126]. On the other hand, the *trans*-resveratrol concentration decreased even in the absence of yeast (40% degradation), most likely because of reactions with wort components (apparent degradation of 17% in the presence of yeast, due to the equilibrium with piceid).

In order to increase the stilbene level, stilbene-enriched hop products and brewery process modifications are needed (e.g., adding a stilbene-enriched ethanolic hop extract after fermentation significantly increases the beer stilbene potential).

7.2 Health Properties of Stilbenes

trans-Resveratrol shows an impact on platelet aggregation and vasodilatation, and through its effect on the antioxidant status, regulates gene expression and decreases the total lipid concentration (cholesterol and triglycerides) [127]. Although less potent, *cis*-resveratrol, *trans*- and *cis*-piceid also improve the antioxidant activity [128, 129].

Piceid absorption is enhanced by the presence of its sugar [130].

trans-Resveratrol inhibits the initiation and growth of tumors. It inhibits cyclooxygenase, ornithine decarboxylase, and angiogenesis [131, 132]. *trans*-Piceid is a

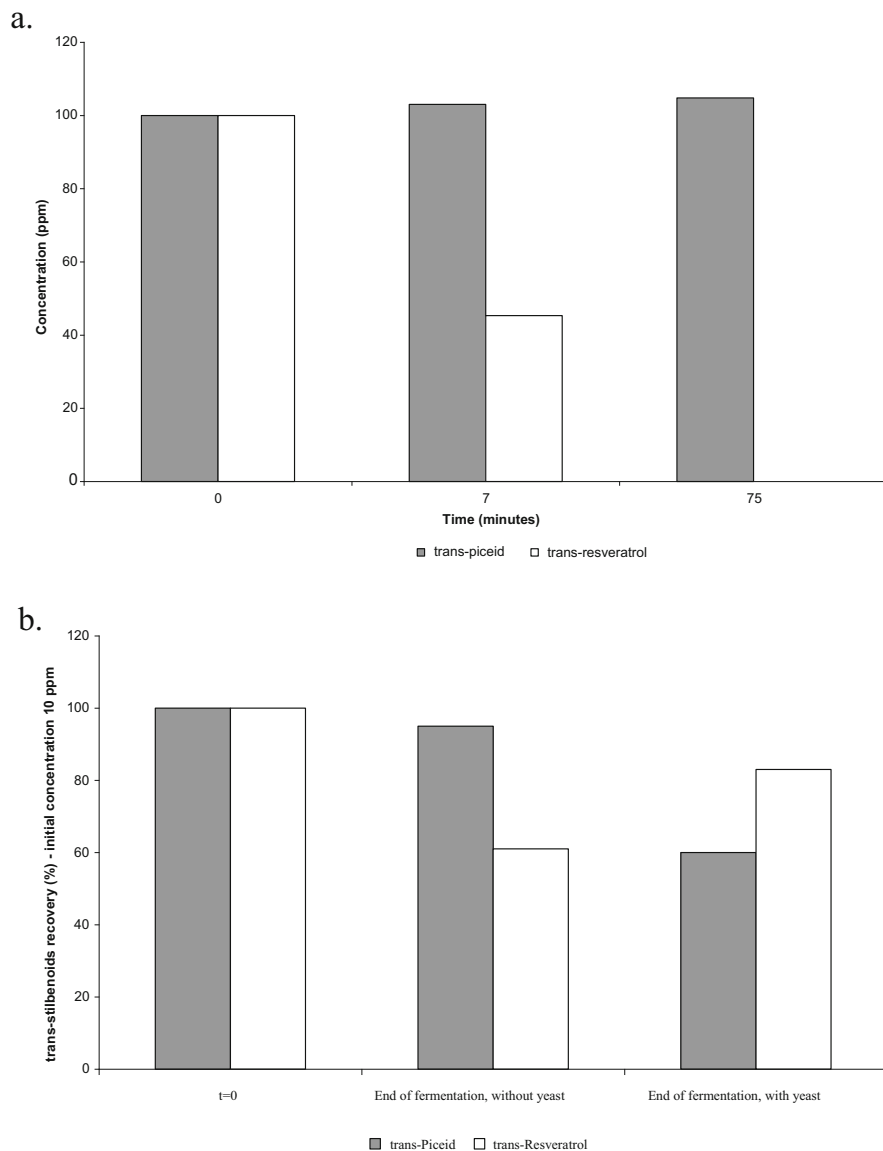


Fig. 8 Follow-up of the degradation of *trans*-resveratrol and *trans*-piceid (**a**) in an aqueous model medium previously flushed by nitrogen mimicking wort ebullition, (**b**) through wort fermentation [124, 126]. (Reprinted (adapted) with permission from Jerkovic et al., J Agric Food Chem, 2005, 53, 4202–4206. Copyright 2005 American Chemical Society. Reproduced with permission from the Journal of the Institute of Brewing)

weaker inhibitor of ROS production [133]. As flavonoids, *trans*-resveratrol alters the synthesis of eicosanoids (mediators of inflammation) and decreases the leukotriene/prostaglandin ratio by modifying lipoxygenase activity [132–134]. Estrogenic activity

has recently been reported for some stilbenes, especially *trans*-resveratrol. *cis*-Resveratrol appears less potent [132, 135].

8 Conclusion

The aim of the present paper was to review all phenolic structures that have been found in beer. Each family was discussed according to its properties and stability through storage. However, at the end of this paper, it is very difficult to advise brewers as to which phenols should be kept in the final beer and at what levels.

Beer phenols issued from malt and hops can contribute directly to several characteristics of beer, mainly flavor, astringency, haze, body, and fullness. Some phenolic structures also impart very interesting health properties. However, degradation of such compounds will inevitably lead to alteration of fresh beer. On the other hand, as antioxidants, these compounds can considerably protect raw materials from oxidative degradation throughout the process.

Competing Interest Declaration The author(s) has no competing interests to declare that are relevant to the content of this manuscript.

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