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Beer phenols issued from malt and hop 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, while oxidized flavonoids strongly influence astringency, haze, and color. The instability of stilbenes, prenylchalcones, and derived flavanones could also modify their health potential.

Keywords: Aging - beer - brewing process - colloidal stability - flavor - polyphenols
Polyphenols and Beer Quality

S. Collin, V. Jerkovic, M. Bröhan, and D. Callemien

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Abstract
Beer phenols issued from malt and hop 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, while oxidized

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flavonoids strongly influence astringency, haze, and color. The instability of stilbenes, prenylchalcones, and derived flavanones could also modify their health potential.

**Keywords**
Aging • beer • brewing process • colloidal stability • flavor • polyphenols

**Abbreviations**
- AEDA: Aroma extract dilution analysis
- APCI: Atmospheric-pressure chemical ionization
- C: Catechin
- E: Epicatechin
- EGC and GC: Epigallocatechin and gallocatechin
- ESI: Electrospray ionization
- FD: Dilution factor
- HPLC or LC: High-performance liquid chromatography
- MS: Mass spectroscopy
- MS/MS: Tandem mass spectroscopy
- 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 hop can contribute directly to several characteristics of beer, mainly color, flavor, astringency, and haze. 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 chapter, all phenolic structures that have been found in beer will be described.

2 **Catechins and Proanthocyanidins**
Even compared to grapes, hop emerges as an exceptional source of catechins and proanthocyanidins. Therefore, although added in 100 times lesser quantity than malt, it can account for 30% of total beer polyphenols. Among hop cultivars, the lower the bitterness, the higher the flavonoid level (up to 1% “total flavanoids” in Saaz pellets, as expressed in terminal unit weight [1]). During mashing, malt
flavonoids 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. 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 flavonoids will be brought into the wort in the boiling kettle [2]

In hop dried cones or pellets, (+)-catechin and (-)-epicatechin monomers can reach up to 2,821 and 1,483 ppm, respectively [3–7]. Malt contains only 10–100 ppm (+)-catechin (and no epicatechin at all) [3, 5, 8–10]. The main monomeric unit identified in beer is (+)-catechin (0.5 to 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 78.1) [8, 11–21].

Hop is also an excellent source of flavonoid oligomers (proanthocyanidins, known as anthocyanogens in the brewing field). For instance, B3 and B4 procyanidin dimers have been detected at levels up to 0.1% [3, 5–7]. Malt contains two B3 dimers (prodelphinidin and procyanidin) at lower levels than in hop, but with higher amounts of galloallocatechin units [3, 5, 10, 22]. Many trimers have also been detected in malt (catechin and galloallocatechin units) and hop (catechin, epicatechin, and galloallocatechin units, but always a catechin unit at the terminal position). Thiolytic hyphenated to RP-HPLC-ESI(-)-MS/MS was recently optimized by our group to investigate beer polyphenolic oligomers [17]. Thiolytic indicated that most beer dimers are procyanidins B3 (two catechin units), while most trimers are prodelphinidins (catechin in terminal units and galloallocatechins 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 [16]. Four dimers were identified: three procyanidins (B1, B3, and B4) and one prodelphinidin (B3) (Table 78.1). Previously detected in hop or malt, three trimers (the procyanidin C-4α-8-C-4α-8-C and two prodelphinidins, GC-4α-8-C-4α-8-C and GC-4α-8-GC-4α-8-C), were distinguished for the first time in beer. As expected, according to previous thioacidolysis data, most beer proanthocyanidins carry a catechin as terminal unit.

2.1 Colloidal Instability

Colloidal instability due to interactions between polyphenols and proteins limits the shelf life of beer. A lag phase is usually observed in lager beers before chill-haze development [23–25]. 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. [25] for different batches, the longer the lag phase, the better the colloidal stability. Chill haze (or reversible haze), defined
### Table 78.1 Flavan-3-ol monomers, polymers, and range of concentrations in beer [8, 11, 13, 14, 16, 19–21, 31, 62, 70, 124–126]

<table>
<thead>
<tr>
<th>Compounds</th>
<th>R1</th>
<th>R2</th>
<th>R3</th>
<th>R4</th>
<th>Concentrations in beer (mg.L(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(+)-Catechin</td>
<td>H</td>
<td>OH</td>
<td>H</td>
<td>OH</td>
<td>0.28–6.9</td>
</tr>
<tr>
<td>(-)-Epicatechin</td>
<td>OH</td>
<td>H</td>
<td>H</td>
<td>OH</td>
<td>&lt;0.10–1.9</td>
</tr>
<tr>
<td>(-)-Catechin gallate</td>
<td>H</td>
<td>Gallate</td>
<td>H</td>
<td>OH</td>
<td>5–20</td>
</tr>
<tr>
<td>(-)-Epicatechin gallate</td>
<td>Gallate</td>
<td>H</td>
<td>H</td>
<td>OH</td>
<td>5–20</td>
</tr>
<tr>
<td>3-O-methylcatechin</td>
<td>H</td>
<td>OCH(_3)</td>
<td>H</td>
<td>OH</td>
<td>Detected</td>
</tr>
<tr>
<td>Catechin-7-O-β-D-glucopyranoside</td>
<td>H</td>
<td>OH</td>
<td>OH</td>
<td></td>
<td>Detected</td>
</tr>
<tr>
<td>Catechin-7-O-β(6&quot;-O-nicotinoyl)-β-D-glucopyranoside</td>
<td>H</td>
<td>OH</td>
<td>OH</td>
<td></td>
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## Dimers

### Procyanidins B

<table>
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<th>Formula</th>
<th>Detection</th>
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</thead>
<tbody>
<tr>
<td>B1</td>
<td>(-)-Epicatechin-(4β-8)-(+) catechin</td>
<td>Detected</td>
</tr>
<tr>
<td>B3</td>
<td>(+)-Catechin-(4α-8)-(+) catechin</td>
<td>Traces-3.1</td>
</tr>
<tr>
<td>B4</td>
<td>(+)-Catechin-(4α-8)-(-) epicatechin</td>
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<th>Structures</th>
<th>Compounds</th>
<th>R1</th>
<th>R2</th>
<th>R3</th>
<th>R4</th>
<th>Concentrations in beer (mg.L(^{-1}))</th>
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<tr>
<td>t1.14</td>
<td>Table 78.1 (continued)</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>t1.15</td>
<td><strong>Prodelphinidins B</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>t1.16</td>
<td></td>
<td>B3 (−)-Gallocatechin-(4α-8)-(++)-catechin</td>
<td>H</td>
<td>OH</td>
<td>H</td>
<td>OH</td>
<td>Traces–3.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B9 (−)-Galloepicatechin-(4β-8)-(++)-catechin</td>
<td>OH</td>
<td>H</td>
<td>H</td>
<td>OH</td>
<td>Detected</td>
</tr>
</tbody>
</table>
Prodelphinidins A

t检测

(+)-catechin

(-)-Epigallocatechin

(-)-Epigallocatechin (4x, 8x, 2x-O-7)-78 Polyphenols and Beer Quality
Table 78.1 (continued)

<table>
<thead>
<tr>
<th>Structures</th>
<th>Concentrations in beer (mg L⁻¹)</th>
<th>Detected</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-)-Epigallocatechin (4x6, 2x-O-7)- (+)-catechin</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-)-epicatechin</td>
<td></td>
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</table>
Trimers

**Procyanidins C**

<table>
<thead>
<tr>
<th>C2</th>
<th>H</th>
<th>OH</th>
<th>and</th>
<th>and</th>
<th>Detected</th>
</tr>
</thead>
<tbody>
<tr>
<td>(+)-Catechin-(4z-8)-(+)catechin - (4z-8)-(+)catechin</td>
<td>R5 = H</td>
<td>R6 = OH</td>
<td></td>
<td></td>
<td></td>
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</table>

Detected (continued)
<table>
<thead>
<tr>
<th>Structures</th>
<th>Compounds</th>
<th>Concentrations in beer (mg.L(^{-1}))</th>
<th>Detected</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(-)-Gallocatechin-(4(\alpha)-8)-(+)-gallocatechin-</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-)-Gallocatechin-(4(\alpha)-8)-(+)-gallocatechin-</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-)-Gallocatechin-(4(\alpha)-8)-(+)-catechin-</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-)-Gallocatechin-(4(\alpha)-8)-(+)-catechin-</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>S. Collin et al.</td>
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</table>
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. Upon storage, however, it does.
Likewise, colloidal instability caused by dimers and trimers is enhanced after
oxidation (not true for tetramers and pentamers) [26–28]. Free radicals are known
to enhance haze [29]. Tannoids have been defined by Chapon [30] as intermediates
in the oxidation of simple flavanoids to tannins, forming complexes with proteins.
On the other hand, according to O’Rourke et al. [28], oxidized flavanols cause
chill haze, but only subsequent polymerization leads to tannoids and permanent
haze [28, 31].

Leemans et al. [25] have proposed a model in which aldehydes and oxygen play
key roles in tanning polyphenol formation [25, 31]. Not only dissolved oxygen but
also shaking, higher temperature, polyphenol-rich raw materials, light, and heavy
metals will significantly increase colloidal instability [25, 31].

Beer contains less haze-active polyphenols than haze-active proteins. Derived
from barley hordeins, haze-active proteins (10–30 kDa) are acidic hydrophilic
polypeptides, rich in both proline and glutamic acid [26] and glycosylated [32].
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, while strong
haze is observed at higher concentrations [33].

To preserve beer colloidal stability, brewers usually remove haze-active mate-
rials [34]. To get rid of haze-active proteins, precipitation with tannic acid,
hydrolysis with papain and adsorption to bentonite [35] or silica gel [36, 37] are
very effective, but unfortunately in some cases, such procedures also remove
foam proteins. To remove haze-active polyphenols, the most usual way is adsorp-
tion to polyvinylpolypyrrolidone-PVPP. Because of the structural analogy
between these compounds and proline [38], pyrrolidone rings bind polymerized
flavanoids through hydrogen and ionic bonds.

New combined absorbents are now proposed to brewers, such as PVPP mixed
with silica xerogel, PVP bound onto silica, and tannin linked to silica [23, 39].
Another innovative way is the use of flavan-3-ol and proanthocyanidin-free malt
which allows affording an excellent colloidal stability [40].

2.2 Astringency

In beer, flavanoids could be also responsible for astringency [41, 42]. Catechin and
epicatechin thresholds lie between 1 and 20 ppm [41, 42], with higher values for the
beer matrix (20 ppm). Astringency is intensified at low pH, especially near 4.0–4.2
[43], but a higher astringency has been measured by François et al. [44] 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. 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
[45]. 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) [44]. 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 [44, 45].

2.3 Color

Beer color increases through storage, especially in the presence of oxygen and at higher temperature. At pH 3, colorless catechin-derived products are formed after enzymatic oxidation, whereas at pH 6 after chemical degradation, yellow products including dehydrodicatechin A dimers differing by their interflavan linkages can be detected in model media (Fig. 78.1) [46, 47]. Recently, Callemien and Collin [15] detected dehydrodicatechin A in a beer spiked with catechin after storage.

2.4 Health Properties

Flavan-3-ols induce cardioprotective effects, including antioxidant effects (protection against LDL oxidation) and inhibition of platelet activity and vasodilatation [48, 49]. Flavonoids might reduce the risk of cancer, although some procarcinogenic activities have also been reported [48, 50]. Flavonoids alter the synthesis of eicosanoids (mediators of inflammation). They decrease the leukotriene/prostacyclin ratio by modifying lipoxygenase activity [51, 52]. Immune regulation has also been observed [53]. Hop proanthocyanidins can help prevent nitric oxide-related disorders such as Alzheimer’s and Parkinson’s diseases [7].

3 Prenylchalcones and Derived Flavanones

More than twenty prenylchalcones and derived flavanones, studied mainly for their biological effects, have been identified in hop [54]. Concentrations higher than 0.6%, with a predominance of xanthohumol and desmethylxanthohumol, are usually found (Fig. 78.2) [55]. Levels of 80 and 90 ppm have been reported for the corresponding flavanones, isoxanthohumol and hopein. The higher the α-acid content (bitter acids in hop), the higher the xanthohumol level [56].

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 [57]. Only 15–50% hop xanthohumol remains in the final beer [58, 59], leading to concentrations often below 1 mg.L⁻¹ [18, 55, 60, 61]. Stout- and Porter-style beers are characterized by slightly higher levels because dark malts contain compounds inhibiting xanthohumol isomerization [57]. The use of xanthohumol-enriched hop products (obtained by ethanol-CO₂ extraction) combined with late hopping makes it possible to increase significantly the xanthohumol and isoxanthohumol potential of beer (close to 10 mg.L⁻¹).
Fig. 78.1 Proposed degradation schemes of (−)-catechin to form colorless compounds with Mw = 578 and yellow compounds with Mw = 576 \[15, 46\]
3.1 Health Properties

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 [18, 61–64].

Prenylflavanones have mainly been studied for their estrogenic activity. Hopein is a very potent phytoestrogen. The authors recommend its application in prevention or treatment of (post)menopausal symptoms and osteoporosis [61, 63, 65]. Weak estrogenic activity has been observed for close analogs like 6-prenylnaringenin, 8-geranylneringin, 6,8-diprenylneringin, and isoxanthohumol. Prenylchalcones like xanthohumol and xanthogalenol also show lower activity [66].
4  Flavonols

Sixteen flavonol glycosides (mainly mono-, di-, and triglycosides of quercetin and kaempferol) have been detected in hop [31]. Although boiling can extract 91% of the kaempferol and 88% of the quercetin glycosides, only a few ppms of flavonols are found in the final beer (Fig. 78.3) [8, 11, 13, 67, 68].

4.1  Bitterness

In beer, flavonols could be responsible for bitterness but do not participate in beer haze formation [31].

4.2  Health Properties

Flavonols induce cardioprotective effects, including antioxidant effects (protection against LDL oxidation) and inhibition of platelet activity and vasodilatation [48, 69], while very little information is available on their potential anticancer effects.

5  Hydroxybenzoic Acids, Hydroxycinnamic Acids, and Derived Compounds

Malt and hop contain various hydroxybenzoic acids, which are retained at least partially up to the final beer (Fig. 78.4). Total hydroxybenzoic acids – mainly p-hydroxybenzoic, vanillic, and gallic acids – usually reach a few ppms in beer. They have also been found as glycosides or other bound forms [8, 11–14, 70–74].

Hydroxycinnamic acids are partially recovered in beer (Fig. 78.4). Most of them are in combined forms in the raw materials, either with quinic acid, glucose, or cell-wall constituents [8, 11–14, 70–78]. In malt, p-coumaric and ferulic acids are esterified with arabinoxylans [79]. They can be both water extracted and enzymatically solubilized by cinnamoyl esterases [80]. After mashing, an additional release of ferulic acid may occur during fermentation due to yeast cinnamoyl esterases [81].

Three coumarins issued from orthohydroxycinnamic acid cyclization have also been found in beer (Fig. 78.5) [8, 73].

5.1  Flavor

Hydroxybenzoic and hydroxycinnamic acids are characterized by relatively high flavor thresholds (> ppm, mainly bitter taste and astringency) [82]. On the other hand, their decarboxylated derivatives (Fig. 78.5) can impart very strong phenolic/clove/smoked flavors to beer because of their low threshold values (ppb order).
Decarboxylation can occur either by thermal degradation [83] during malt kilning and in the boiling kettle [77, 84], 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) [85, 86] and in some contaminating microorganisms like *Brettanomyces/Dekkera* spp. [87] or *Enterobacteriaceae* [88]. In this way, 4-vinylguaiacol is issued from ferulic acid, while 4-vinylphenol derives from *p*-coumaric acid. 4-Vinylguaiacol has been also found in hop [89].

In Belgian white beer production, enzymatic decarboxylation of ferulic acid occurs linearly through fermentation at a rate close to 140 ppb/day (Fig. 78.6). The rate decreases strongly during secondary fermentation, down to 20 ppb/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 ppm) [31]. Concentrations up to 6.2 ppm in 4-vinylguaiacol and up to 3.2 ppm in 4-vinylphenol have been reported in wheat beers [8, 77–79, 81, 90–97]. For instance, 4-vinylguaiacol contributes to the specificity of Belgian white beers.
(made with unmalted wheat) and German rauch and weizen beers (made with malted wheat) [92, 94, 97, 98]. According to its concentration, 4-vinylguaiacol can lead either to strong pharmaceutical off-flavor defects [91] or to pleasant clove flavors [79], while 4-vinylphenol is always considered to be an off-flavor [79]. These vinyl compounds can be further oxidized or reduced into smaller molecules like vanillin, 4-ethylguaiacol, guaiacol, and 4-ethylphenol through chemical reactions [99] or through the activity of wild yeasts like *Brettanomyces*/Dekkera spp. [87].

Degradation of 4-vinylguaiacol through natural aging (25% after 20 days) or at 40°C (50% after 20 days) has been reported [77, 94, 100]. This compound could be partially transformed to 4-ethylguaiacol, vanillin, and guaiacol [79, 101].

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 of the cardboard off-flavor in aged beer) [102, 103]. 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.

**Fig. 78.4** Hydroxybenzoic acids and hydroxycinnamic acids and range of concentrations in beer (Adapted from [31])
5.2 Color

Phenolic acids do not participate in beer haze formation [27, 104], but vinylphenol and cinnamic acid have been described as potential pigments [105–108].

6 Stilbenes

Our group recently discovered three stilbenes in hop: trans-resveratrol, trans-piceid, and cis-piceid [4, 109]. Concentrations ranging from 0.7 to 11 ppm trans-piceid and from 0.03 to 2.3 ppm trans-resveratrol have been reported in hop cones [110]. 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 \cite{110}. Even during hop storage, a significant loss occurs, especially in highly oxygen-sensitive varieties, leading to new analogs like cis-resveratrol and dimers \cite{111}. Likewise, hop pelletization induces strong degradation \cite{111,112}. trans-Resveratrol and glycosides are absent from malt \cite{113}, so one should not be surprised to find only traces of stilbenes in beer (Fig. 78.7). Up to 5 µg.L\(^{-1}\) trans-resveratrol was detected by our group in Belgian commercial beers \cite{114}.

Taking into account a concentration of 1–10 ppm stilbenes in hop and hopping close to 200 g.L\(^{-1}\) in wort, a maximum of 2–20 µg.L\(^{-1}\) stilbenes 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. 78.8a). 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 mg.L$^{-1}$ before fermentation – Fig. 78.8b). 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 [114]. 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).

6.1 Health Properties

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) \[115\]. Although less potent, cis-resveratrol, trans-, and cis-piceid also improve the antioxidant activity \[116, 117\]. Piceid absorption is enhanced by the presence of its sugar \[118\].

trans-Resveratrol inhibits the initiation and growth of tumors. It inhibits cyclooxygenase, ornithine decarboxylase, and angiogenesis \[119, 120\]. trans-Piceid is a weaker inhibitor of ROS production \[121\]. As flavonoids, trans-resveratrol alters the synthesis of eicosanoids (mediators of inflammation) and decreases the leukotriene/prostacyclin ratio by modifying lipoxygenase activity \[120–122\]. Estrogenic activity has recently been reported for some stilbenes, especially trans-resveratrol. cis-Resveratrol appears less potent \[120, 123\].

7 Conclusion

The aim of the present chapter 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 chapter, it is very difficult to advice brewers as to which phenols should be kept in the final beer and at what levels.

Beer phenols issued from malt and hop 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.

References


85. Clausen M, Lamb CI, Megnet R, Doerner PW (1994) PAD1 encodes phenylacrylic acid decarboxylase which conlers resistance to cinnamic acid in *Saccharomyces cerevisiae*. Gene 142:107–112


   carboxylic acid and phenols in the raw material and beer preparation. Brauwelt 122:618–20,
   622, 624, 626.
   Brauerei 31:52–55
   compounds in the preparation of Bavarian wheat beers. Monatschrift fuer Brauwissenschaft
   37(9–18):55
93. Madigan D, McMurrough I (1994) Rapid determination of 4-vinyl guaiacol and ferulic acid in
94. Schieberle P (1991) Primary odorants of pale lager beer – differences to other beers and
95. Tressl R, Renner R, Apetz M (1976) Volatile phenolic components in beer, smoked beer and
   sherry. Zeitschrift fuer Lebensmittel-Untersuchung und -Forschung 162:115–122
   Brew Chem 44:114–117
98. Narziss L, Miedaner H, Nitzsche F (1990) The formation of 4-vinylguaiacol during the
   manufacture of Bavarian wheat beers (Weizenbier). Monatschrift fuer Brauwissenschaft
   43:96–100
   Monatschrift fuer Brauerei 27:98–102
100. Schieberle P, Komarek D (2003) Changes in key aroma compounds during natural beer
    aging. In: Freshness and shelf life of foods. ACS symposium series. ACS, Washington DC,
    pp 70–79
    damascenone and dimethyl trisulfide production through beer aging. J Agric Food Chem
    50:5612–5616
    temperatures. Affinity of proanthocyanidins and their oxidation products for haze-forming
    nolic compounds with xanthylum skeletons formed through reaction between (+)-catechin
106. Es-Safi NE, Fulcrand H, Cheynier V, Moutounet M (1999) Studies on the acetalddehyde-
    induced condensation of (−)-epicatechin and malvidin 3-O-glucoside in a model solution
    and furfural derivatives in the presence or absence of anthocyanins and their implication in
    formation involved in wine colour changes. Int J Food Sci Technol 35:63–74
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