Which hop variety for a better flavour and colloidal stability of dry-hopped beers: evidence of the key-role of minor flavan-3-ols

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Introduction

In dry-hopped beers, hop can be responsible for more than 30 % of beer polyphenols. Flavan-3-ols can affect beer bitterness and astringency[1]. Among them, its oxidized oligomers with the epicatechin in the upper position, which comes exclusively from hops, are suspected to be involved in colloidal instability while monomer quinones are responsible of colour[2] and polyfunctional thiol scavenging[3]. The aim of the present work was to investigate flavan-3-ols in hops and in Belgian dry-hopped beers (A–U), before and after aging.

Colour instability

Monomers

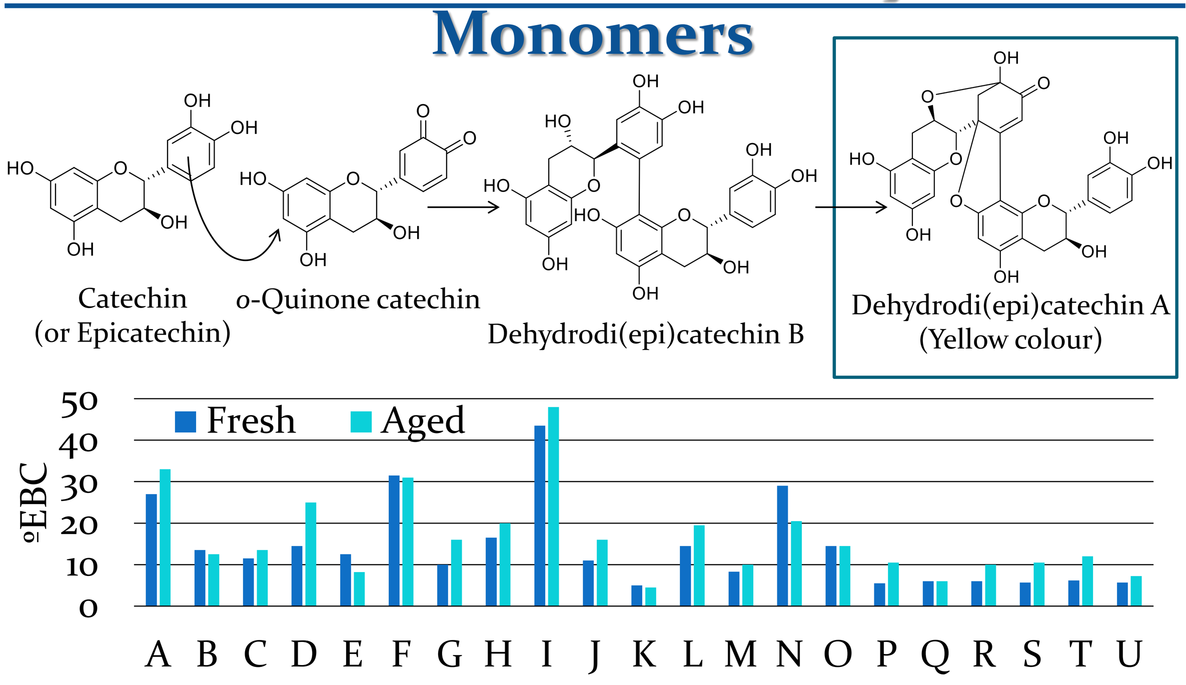

Figure 1. Colour of Belgian dry-hopped beers before and after two years of storage at 20 ºC, and mechanism of dehydrodi(epi)catechin A production from o-quinone catechin[4].

Thiol instability

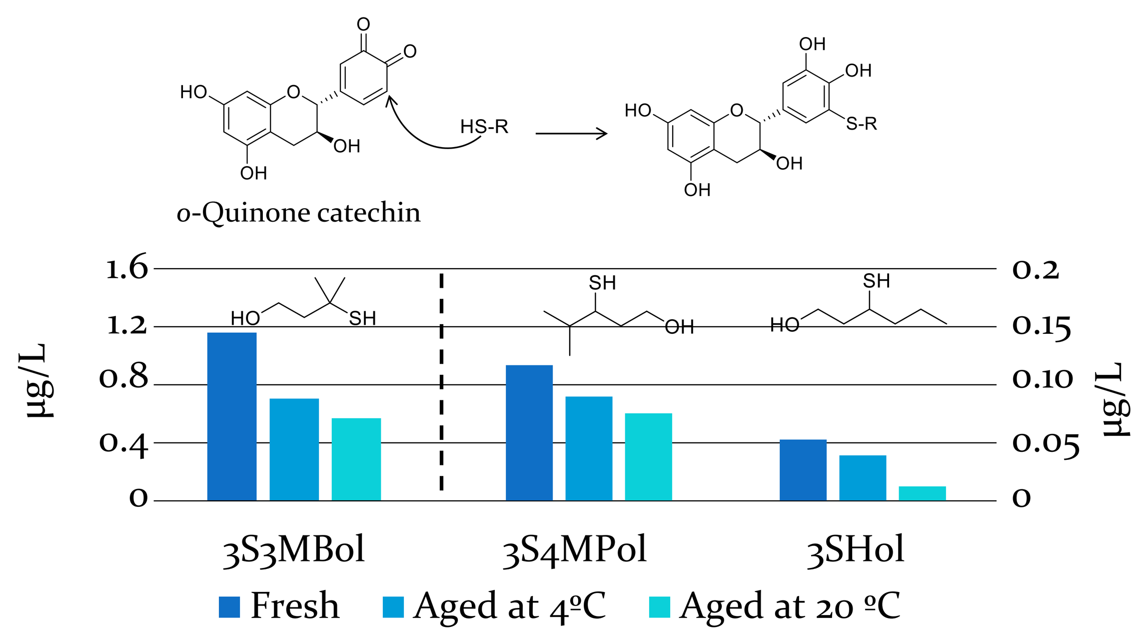

Figure 2. Hop polyfunctional thiols in beer D before and after 4 months of storage at 4 or 20 ºC. 3S3MBol (left axis), 3S4MPol and 3SHol (right axis).

Colloidal instability

Dimers and trimers with epicatechin

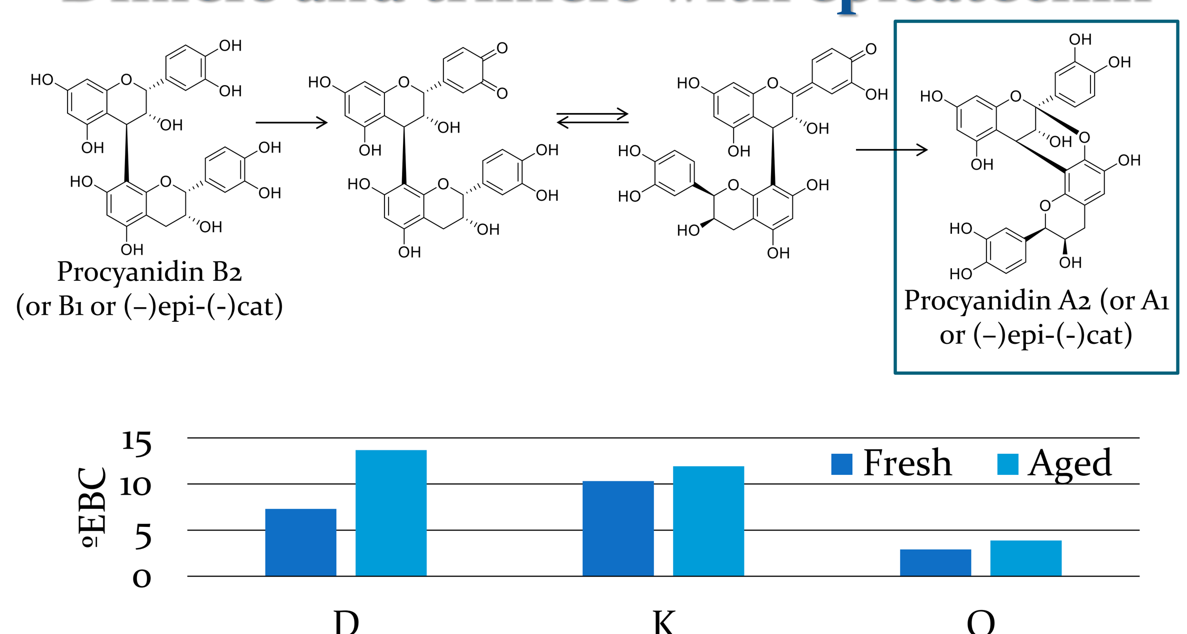

Figure 3. Haze (4 ºC) of dry-hopped beers before and after 4 months of storage at 20 ºC, and mechanism of Procyanidin A2 production from Procyanidin B2[5].

Polyphenol analysis: which methods?

Total polyphenols and total flavanoids of twenty-one Belgian dry-hopped beers (A–U) were investigated before and after two years of storage at 20 ºC (EBC methods 9.11 and 9.12, respectively). Total polyphenols concentrations remained stable while a loss of total flavanoids was observed in all beers (Figure 4). Such analyses are not sufficiently focused on the sub-fractions of interest.

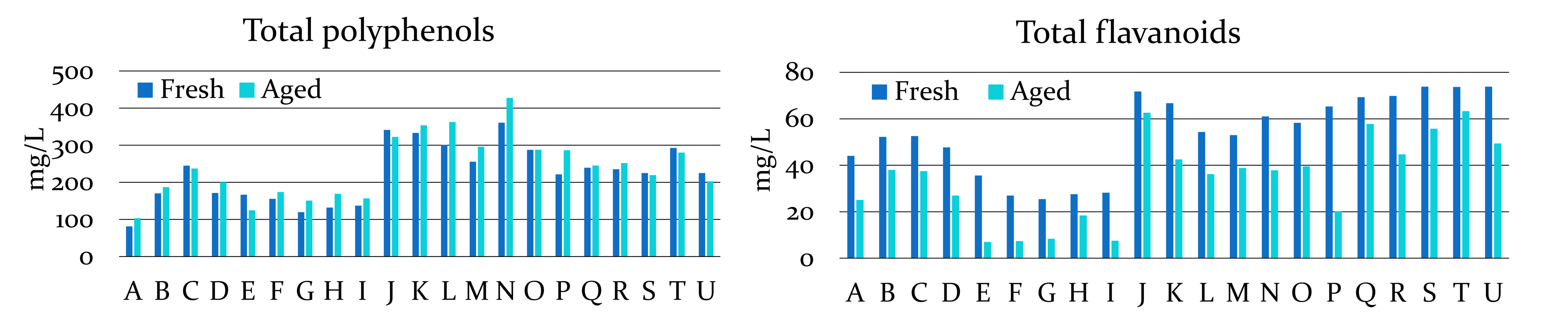

Figure 4. Total polyphenols (left) and total flavanoids (right) in Belgian dry-hopped beers before and after two years of storage at 20 ºC.

Flavan-3-ols were isolated[6] from hop, beer and wort. Hop delipidation was required prior to Sephadex LH-20 extraction. Beer/wort were directly loaded into the resin (Figure 5).

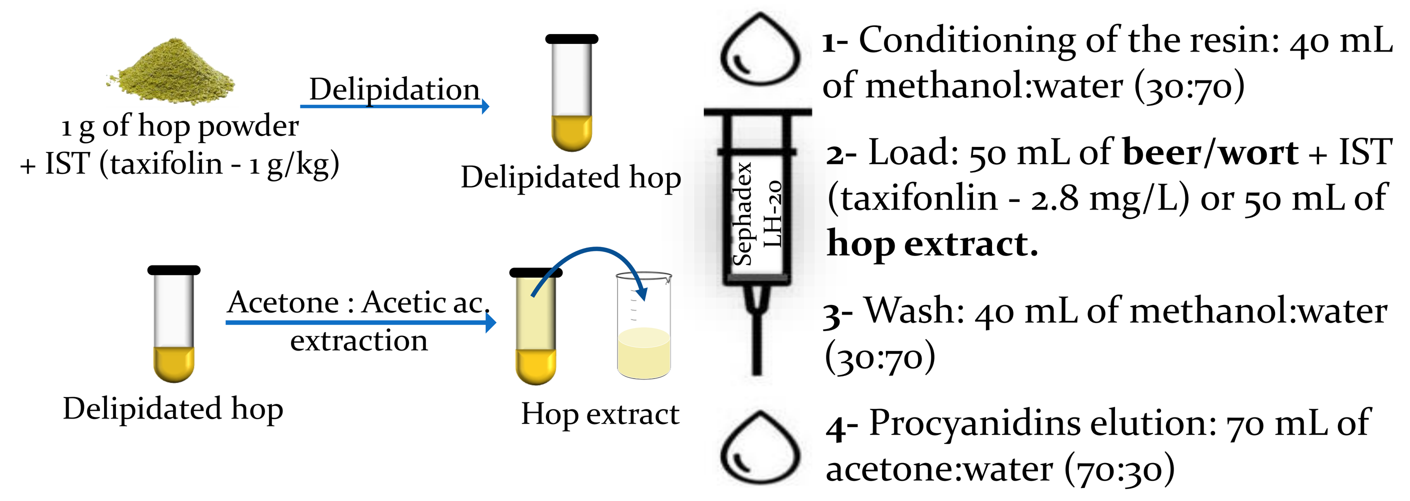

Figure 5. Selective extraction method for hop, beer and wort flavan-3-ols using the Sephadex-LH20 resin.

Flavan-3-ols in hop and in fresh dry-hopped beers

Monomers and derived compounds

Hops / Dry-hopped beers

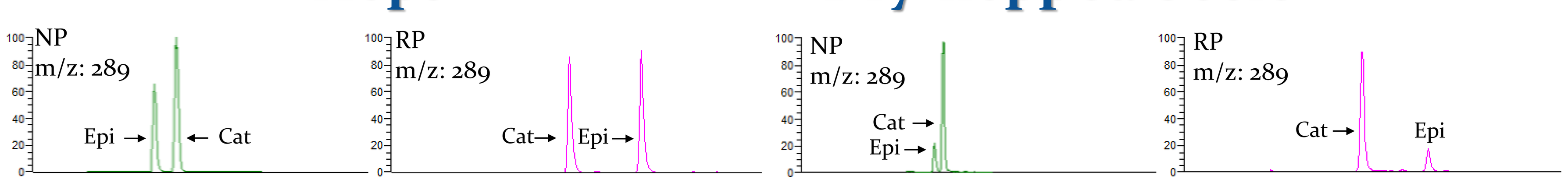

Figure 6. RP- and NP- HPLC-ESI(-)-MS/MS chromatograms of catechin (Cat) and epicatechin (Epi) in the Eureka hop (left) and beer Q (right).

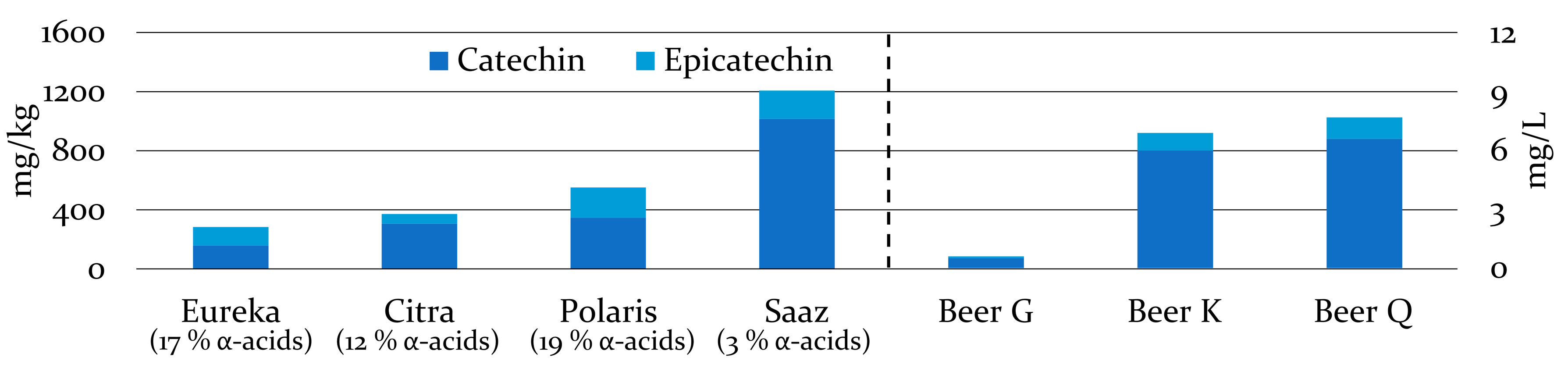

Figure 7. Catechin and epicatechin levels in Eureka, Citra, Polaris and Saaz hop varieties (left axis) and in the dry-hopped beers G, K and Q (right axis).

Some dual hop varieties revealed high levels of monomers despite their high level of α-acids. Eureka gives here the highest epicatechin/catechin ratio. Coming from malt, catechin is in all cases the major monomer in dry-hopped beer. The amount of flavan-3-ol monomers in fresh beer is not directly related to colour instability. → Key-factor = risk of oxidation.

Dimers and trimers

Hops / Dry-hopped beers

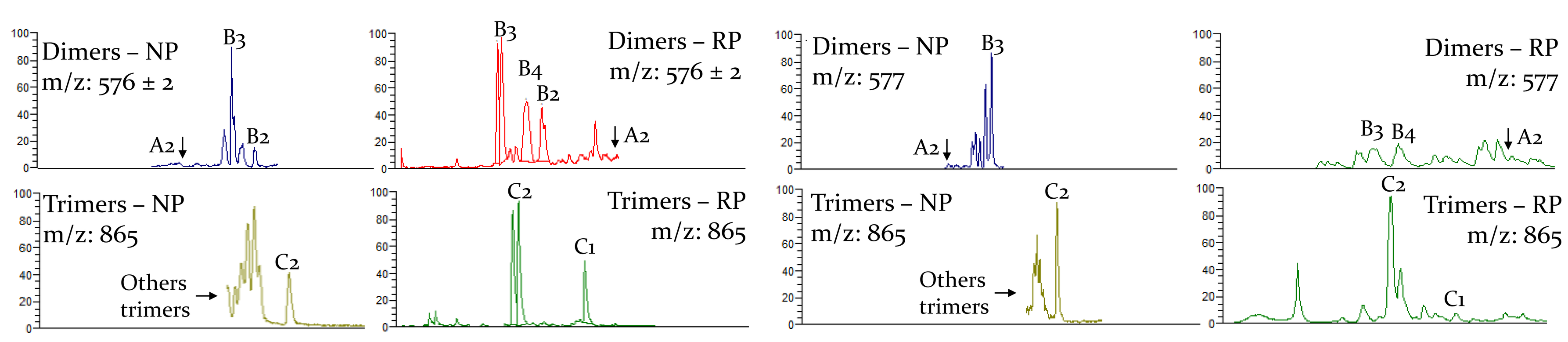

Figure 8. RP- and NP- HPLC-ESI(-)-MS/MS chromatograms of flavan-3-ol dimers and trimers in the Eureka hop (left) and beer Q (right).

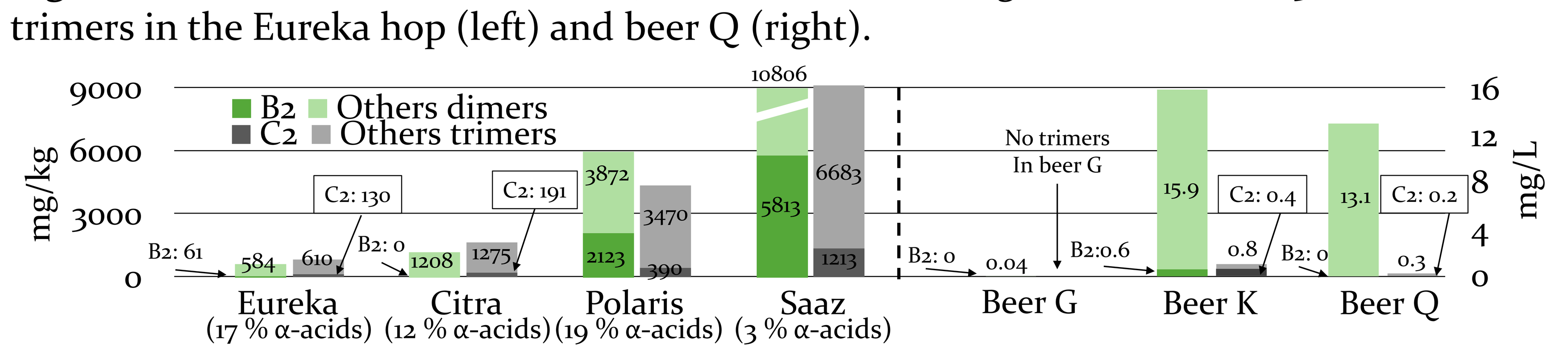

Figure 9. Dimers and trimers levels in Eureka, Citra, Polaris and Saaz hop varieties (left axis) and in the dry-hopped beers G, K and Q (right axis).

Again, high α-acid dual hops can contain high oligomer levels, but much lower compared to the Saaz. B2 is minor in dual hops and dry-hopped beers. A2 is absent in fresh hops and dry-hopped beers. → Key-factor = risk of oxidation.

Fate of flavan-3-ols throughout beer production

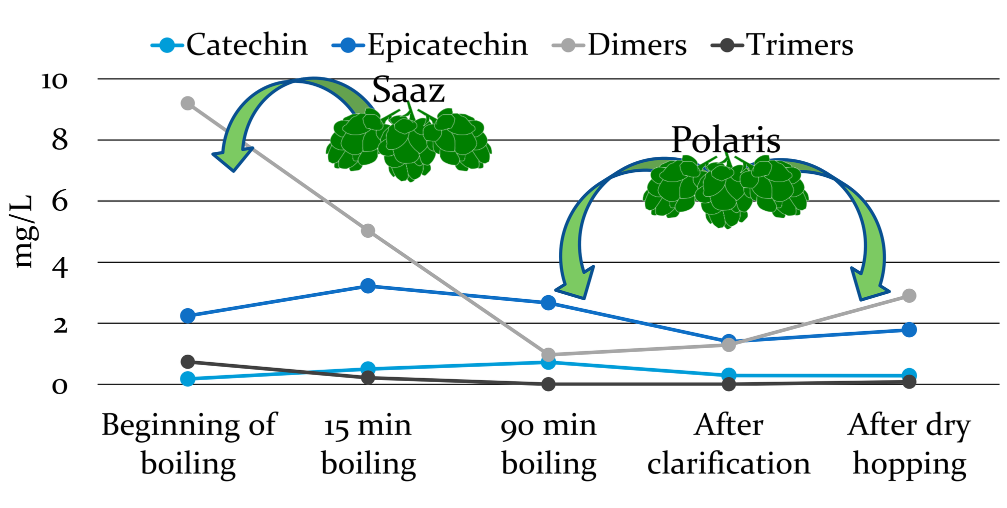

Figure 10. Concentrations of catechin, epicatechin, dimers and trimers throughout a beer production.

Flavan-3-ols were analyzed throughout a pilot beer production (50 L) using Saaz (2 min of boiling) and Polaris (end of the boiling and dry hopping) (Figure 10). Flavan-3-ols were mostly depleted after clarification. Yet, dry hopping with Polaris significantly increased the catechin and procyanidin dimers concentrations.

Conclusions

Catechin and epicatechin concentration increase after dry hopping, especially when no post-dry hopping treatment is done, leading to colour increase through storage. B2, responsible for haze formation in beers, was evidenced in hop and in dry-hopped beers (no A2 in fresh beers). Although the hop variety can also be of prime importance, the key factor for colour, polyfunctional thiols and colloidal instability is beer oxidation.

Acknowledgements

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