Effect of brewing process on phenolic compounds and their corresponding antioxidant activities

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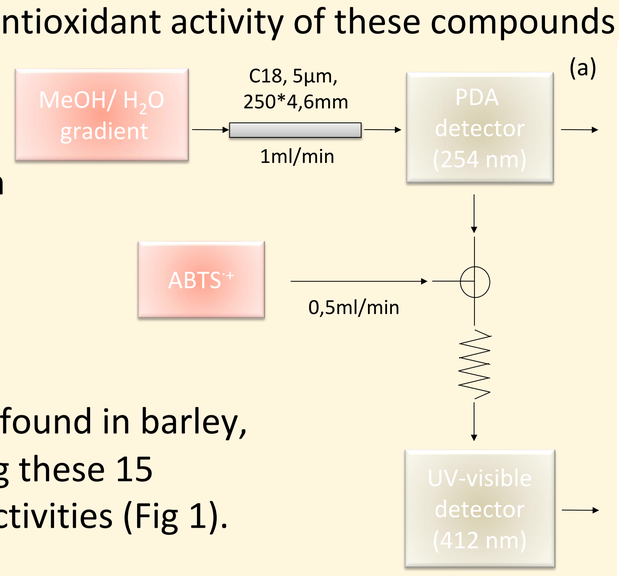
Introduction : The phenolic contents of beer extracts and their corresponding antioxidant activities at different stages of processing were investigated using liquid chromatography with online detection of antioxidant compounds.

Material and methods : Ethyl acetate extracts of barley, malt, wort, boiled wort and beer were separated using reverse phase HPLC with a linear MeOH/H_2O gradient (Fig 1a).
Compounds eluting from the column were submitted to two UV-visible detections :

- one for the identification of phenolic compounds (Fig 1b)
- the other for the monitoring of the antioxidant activity of these compounds (Fig 1c).

The presence of antioxidants, acting as radical scavengers, resulted in a reaction with $ABTS^{\cdot+}$ and a subsequent decrease in absorption detected as a negative peak at 412 nm.



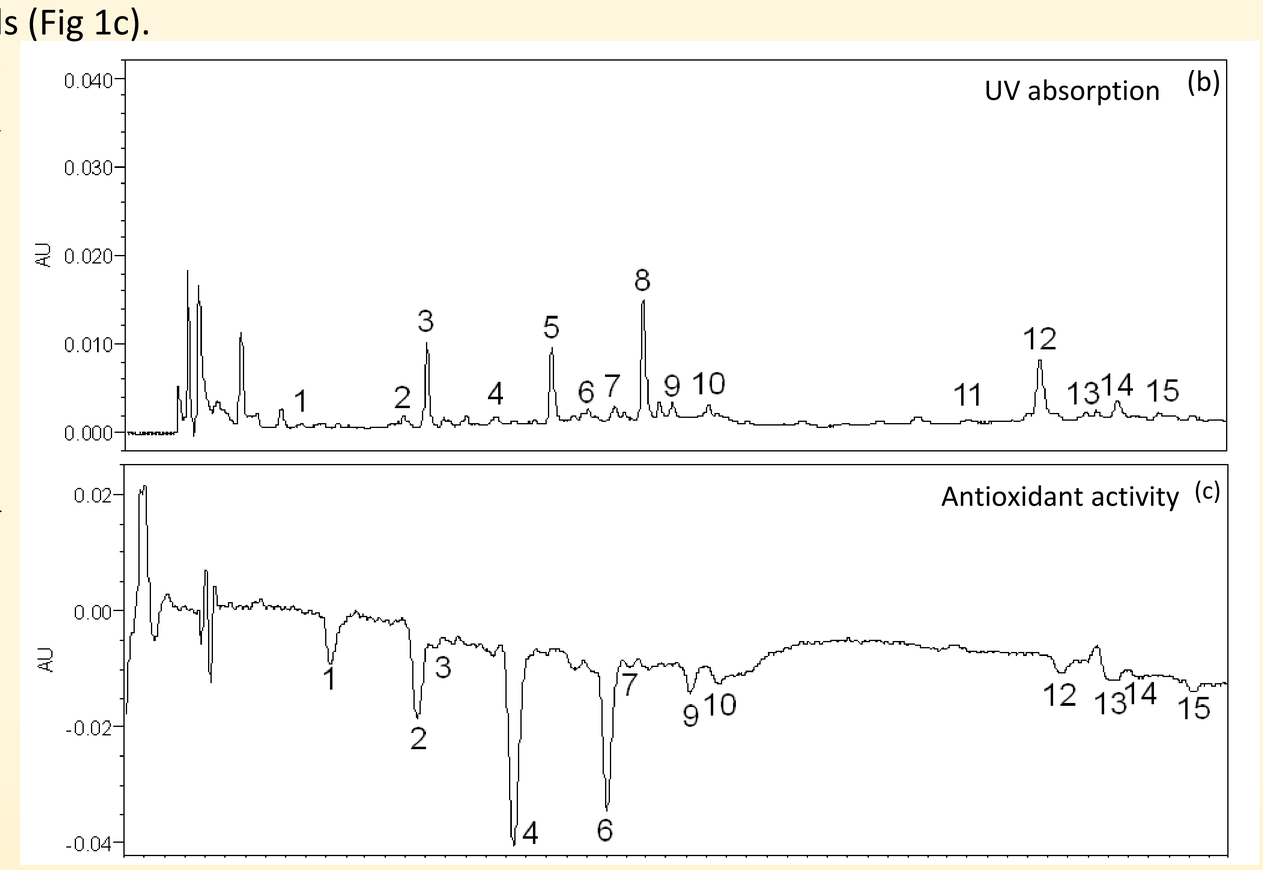


Figure 1: Chromatographic detection of antioxidant compounds of barley extract : (a) Experimental chart; (b) separation of barley polyphenols : 1, unknown compound; 2, prodelphinidin B3; 3, protocatechuic acid; 4, procyanidin B3; 5, p-hydroxybenzoic acid; 6, catechin; 7, chlorogenic acid; 8, vanillic acid; 9, caffeic acid; 10, epicatechin; 11, p-coumaric acid; 12, ferulic acid; 13, sinapic acid; 14, unknowm compound; 15, unknown compound; (c) their corresponding antioxidant activity.

Results : 15 phenolic compounds were found in barley, malt, wort, boiled wort and beer. Among these 15 compounds, 12 presented antioxidant activities (Fig 1).

Barley and malt : The largest antioxidant contribution came from catechin, procyanidin B3 and prodelphinidin B3 (Fig 1)[1].
Malting had a dramatic impact resulting in a decrease in the amounts of these compounds and their associated antioxidant activities (Fig 2). Such a decrease has already been reported for proanthocyanidins and catechins, and has been attributed to glycosylation reactions during malting[2].

Wort, boiled wort and beer : The contents of catechin, procyanidin B3 and prodelphinidin B3 increased during the brewing step, then slightly decreased during hopping and fermentation (Fig 2)[3]. The malting process would therefore not result in a degradation of these compounds.

Their presence in wort could be due to the brewing step. Glycosylation of compounds during malting increases their solubility in water and this solubility increases with rising temperatures. The enzymes activated at different temperature levels would allow deglycosylation of compounds which could be then detected in wort.

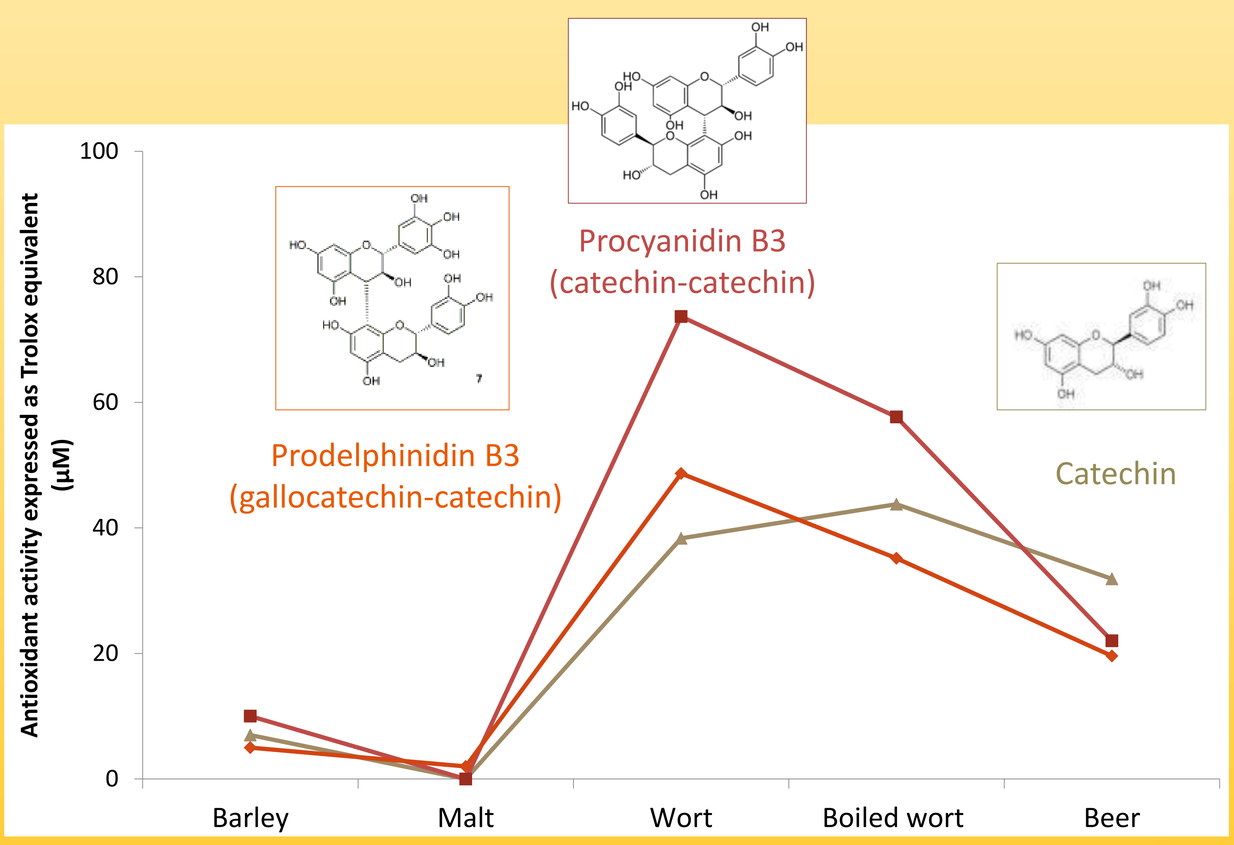


Figure 2: Antioxidant activity of prodelphinidin B3, procyanidin B3 and catechin during normal process at different steps of beer processing (n=9, 40% < SE < 80%).

Total antioxidant activity : The total antioxidant activities, expressed as Trolox equivalent (µM), follow a similar trend since they were six-fold higher in wort than in malt, mainly due to catechin, procyanidin B3 and prodelphinidin B3 presence in wort (Fig 3).
Hopping and fermentation on the other hand did not seem to affect these activities ($p > 0,05$). The decrease in the antioxidant contributions of compounds like catechin, procyanidin B3 and prodelphinidin B3 in boiled wort and beer was balanced by the increase in that of epicatechin and compound 1.

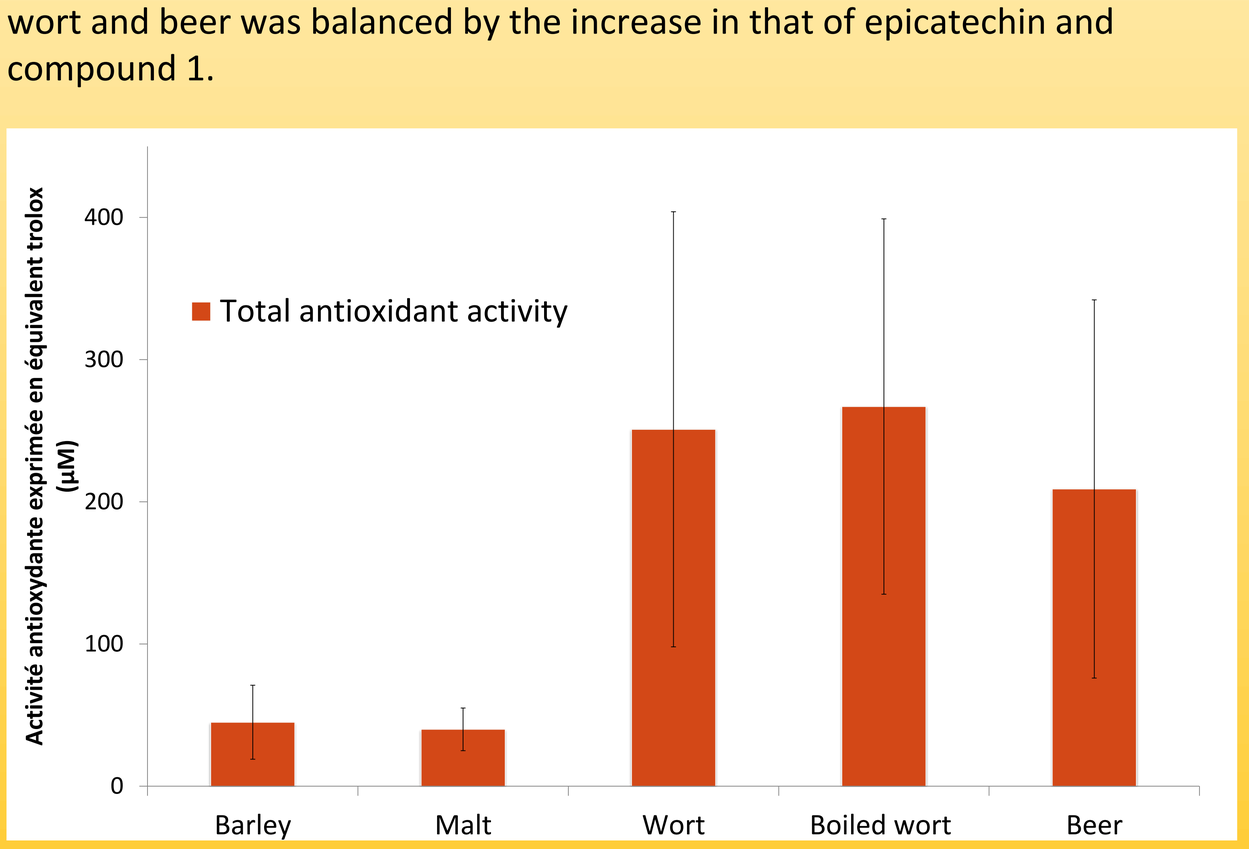


Figure 3: Total antioxidant activity at different steps of beer processing.

Conclusion : This study allowed the comparison of the phenolic contents and the corresponding antioxidant profiles of barley, malt, wort and beer. Prodelphinidin B3, procyanidin B3 and catechin were identified as the three major contributors in the antioxidant activity at the various stages of beer processing.

[1]Leitao, C. et al., 2012. Fate of polyphenols and antioxidant activity of barley throughout malting and brewing. Journal of Cereal Science 55, 318-322.
[2]Friedrich, W., Galensa, R., 2002. Identification of a new flavanol glucoside from barley (Hordeum vulgare L.) and malt. European Food Research and Technology 214, 388-393.
[3]Leitao, C. et al., 2012. Effect of processing steps on the phenolic content and antioxidant activity of beer. Journal of Agricultural and Food Chemistry 59, 1249-1255.