Monitoring the thermal induced degradation of selected coumarin derivatives using AMD-HPTLC

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Introduction

Coumarins are a sub-class of the phenolic compounds, the largest group of the so called secondary plant metabolites. There is growing recognition that especially phenolic secondary metabolites present in foodstuffs may possibly exert beneficial effects on human health[1]. The coumarins have long been recognized to possess anti-inflammatory, antiallergic, hepatoprotective, antithrombotic, antiviral, and even anticarcinogenic activities. However, these physiological and pharmacological properties are still discussed very controversial, because some of the 1500 coumarin derivatives showed cytotoxicity in cell culture and liver toxic effects[2/3].

Further, health promoting effects are mostly determined in model experiments on the basis of isolated (pure) substances. Such approaches do not consider any changes of phenolic compounds, although these alterations cannot be excluded in harvesting, storage, and in particular during thermal food processing.

The objective of the present study was to investigate the influence of a thermal treatment on the degradation of selected coumarin derivatives.

Material and Methods

Selected coumarins were roasted under varying reaction parameters (temperature; oxidative conditions). AMD-HPTLC was used to follow the changes during the roasting. Besides UV-detection, staining with Naturstoff reagent was performed. Antioxidative activity was determined using DPPH as a colouring reagent.

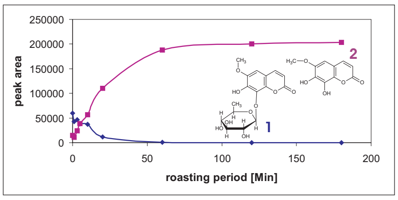

Fig. 4. Degradation of fraxin [1] and the forming of ist aglycon - fraxetin [2].

Results and Discussion

As it was shown recently for flavonoids, a thermal induced degradation may lead either to smaller substances or even to polymers[4-6]. Here, HPTLC is an exquisite technique to follow all the fractions formed, because polymeric fractions might be discriminated during HPLC analysis.

A strong degradation of the model substances, especially of those possessing a glycosidic substituent, was observed. The major reaction product is the corresponding aglykon (aesculin: Figure 1 and 2; fraxin: Figure 3 and 4).

More pronounced effects were found by oxidative conditions and higher temperatures (Results not shown). The antioxidative activity of the samples changed during the thermal treatment (Figure 5).

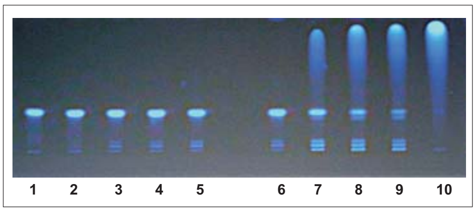

Fig. 1. HPTLC of the aesculin degradation (366 nm); 1) aesculin, 2-9) roasting of aesculin: 2) 3min, 3) 5min, 4) 10min, 5) 20min, 6) 30min, 7) 60min, 8) 120min, 9) 180min, 10) aesculetin.

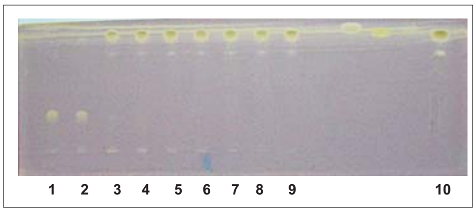

Fig. 5. HPTLC - Antioxidative activity of the aesculin degradation (coloured with DPPH) 1) aesculin, 2-9) roasting of aesculin:2) 3min, 3) 5min, 4) 10min, 5) 20min, 6) 30min, 7) 60min, 8) 120min, 9) 180min, 10) aesculetin.

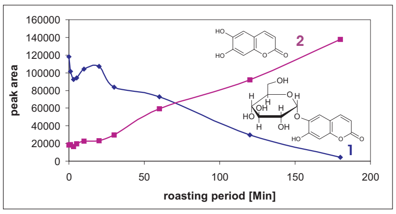

Fig. 2. Degradation of aesculin [1] and the forming of ist aglycon - aesculetin [2].

Although, the antioxidative activity is increasing resulting from thermal treatment, it has to be considered, that the antioxidative activity of coumarins is not high compared to other phenolic compounds (especially flavonols) (Figure 6).

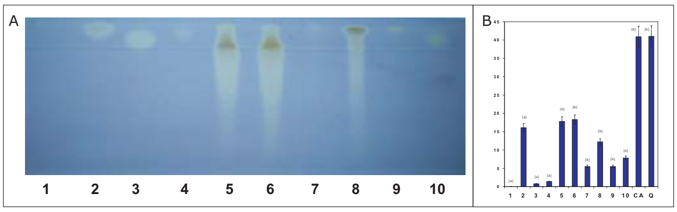

Fig. 6. A) Antioxidative activity of selected coumarins - HPTLC (coloured with DPPH)
B) Antioxidative activity of selected coumarins - Electron spin resonance spectrometry
1) coumarin, 2) 3-hydroxycoumarin, 3) 4-hydroxycoumarin, 4) 7-hydroxycoumarin, 5) methylaesculetin, 6) aesculetin, 7) aesculin, 8) fraxetin, 9) fraxin, 10) scopoletin, CA) caffeic acid, Q) quercetin, (a) 10 mM, (b) 0.5 mM

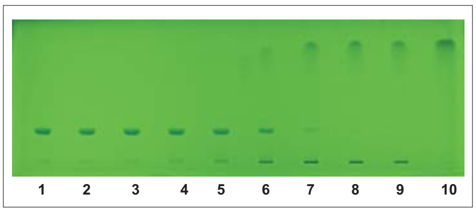

Fig. 3. HPTLC of the fraxin degradation (254 nm); 1) fraxin, 2-9) roasting of fraxin: 2) 3min, 3) 5min, 4) 10min, 5) 20min, 6) 30min, 7) 60min, 8) 120min, 9) 180min, 10) fraxetin.

Conclusions

These results are significant with regard to further experiments planned, involving food, which is rich in coumarin derivatives and is heated during food processing (e.g. drying of spices and herbs).

[1] Parr and Bolwell, *J. Sci. Food Agric.* **2000**; *80*: 985-1012, [2] Finn et al., *Melanoma Res.* **2001**; *11*: 461-467, [3] Zhuo et al., *J. Pharmacol. Exp. Ther.* **1999**; *288*: 463-471, [4] Buchner et al. *Rapid Commun.Mass Spectrom.* **2006**; *20*: 3229-3235, [5] Rohn et al., *Proc. Germ. Nutr. Soc.* **2005**; *7*: 84. [6] Rohn et al., **2006**; *submitted*