INTRODUCTION

Several N-heterocyclic compounds, such as 2-acetylthiazole (AT), 2-acetyl-2-thiazoline (ATn), 2-acetylpyrazine and 2-acetyl-1-pyrroline having a typical pleasant roasty and popcorn like odour character are formed during roasting of coffee by Maillard-type reactions [1]. The concentrations of these odorants in coffee samples are in the magnitude above their detection thresholds, and hence, an impact on the aroma profile can be expected. Cysteamine, the Strecker degradation product of cysteine, and methylyglyoxal were evidenced as intermediates leading to ATn [2], a potent compound with a 10 times lower odour threshold in water than AT. Dry-heating of different sugar/cysteamine mixes resulted in significant higher amounts of ATn as compared to aqueous conditions [3]. Kinetic studies under mild aqueous conditions revealed that ATn easily undergoes an oxidation step to form AT [4].

Objective and Approach

Our study aimed at understanding the role of precursors in coffee in the formation of o-acyl-N-heterocycles, as well as at the elucidation of the intrinsic formation pathways.

A combination of biomimetic in-bean experiments and spiking of green coffee with unlabelled and stable isotope labeled precursors was implemented [5].

RESULTS & CONCLUSIONS

New Coffee Beans Experiments

Incorporation of labelled precursors

Impact of Amino acids (AA):
• As expected, spiking with cysteine (Fig. 6) resulted in highly increased amounts of Thiazolines and Thiazoles
• Enhanced quantities of Thiazolines and Thiazoles in water-extracted beans (WEB), indicating their formation from water non-extractable precursors (Fig. 6)
• Absence of free amino acids (Fig. 5) in the coffee bean did not significantly influence their formation

Impact of Sugars:
• Contrary behaviour in the formation of Thiazolines and Thiazoles as function of sugar composition;
  - Surprisingly, omission of sugars (Fig. 5) resulted in highly increased concentrations of Thiazolines; a result that was not observed for the assessed Thiazoles
  - Whereas spiking of green beans with sucrose (Fig. 4) had a suppressing effect only for Thiazolines
• ADHT was formed from same precursors as o-acetyl-thiazolines, since similar formation characteristics were shown (Fig. 5 & 6)

Conclusions

✓ Results from labelling studies indicate a direct relationship in the formation of AT from ATn, whereas omission and spiking experiments revealed rather the opposite.
✓ The role of C$_2$H$_2$S and C$_2$H$_2$O sugar fragments as key intermediates in the formation of assessed acyl-N-heterocycles has been confirmed in the coffee bean.
✓ The key precursor role of cysteine in the formation of many character impact compounds indicates options for the modulation of coffee flavour.
✓ The in-bean experiments represent a promising avenue to understand the mechanisms leading to various types of coffee aroma.