

Instrumental Analysis and Sensory Studies on the Role of Melanoidins in the Aroma Staling of Coffee Brew

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SUMMARY

In order to investigate the chemical mechanisms involved in the rapid aroma staling during warm-keeping of coffee brews, melanoidins isolated from coffee brew were added to a model solution containing 25 aroma compounds in their “natural” concentrations mimicking the aroma of a coffee brew. Sensory analyses revealed that, in particular, the intensity of the roasty-sulfury aroma quality was reduced when melanoidins were present. Comparative aroma dilution analysis on the headspace of aqueous solutions containing the total volatile fraction isolated from coffee brew, alone, or in mixture with melanoidins visualized that the losses of the odorous thiols 2-furfurylthiol (FFT), 3-methyl-2-butenthiol (MBT), 3-mercapto-3-methylbutyl formate (MMBF), 2-methyl-3-furanthiol, and methane thiol are responsible for the aroma change. Quantification by means of stable isotope dilution assays confirmed that these thiols are rapidly degraded with increasing time during warm-keeping of coffee brews in a thermos flask. Quantitative model studies and labelling experiments with [$^2\text{H}_2$]-2-furfurylthiol, followed by ^2H -NMR and LC/MS spectroscopic detection gave strong evidence that these thiols are covalently bound to pyrazinium ions, the oxidation products of 1,4-bis-(5-amino-5-carboxy-1-pentyl)pyrazinium radical cations, which were recently identified in coffee as key intermediates in roasting-induced melanoidin genesis. Based on model experiments, these pyrazinium compounds were shown to rapidly react with thiols, such as, 2-furfurylthiol, thus giving rise to 2-(2-furyl)methylthio-1,4-dihydropyrazines, bis[2-(2-furyl)methylthio]-1,4-dihydropyrazines and 2-(2-furyl)methylthio-hydroxy-1,4-dihydropyrazines as the primary reaction products. The data suggest that the thiol-binding activity of pyrazinium derivatives in melanoidins undoubtedly contribute to the decrease of the sulfury-roasty odour quality shortly after preparation of the coffee brew.