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Titel des Beitrags: Isolation, structure determination, synthesis, and sensory activity of N-phenylpropenoyl-L-amino acids from cocoa (Theobroma cacao)

Abstract: Application of chromatographic separation and taste dilution analyses recently revealed besides procyanidins a series of N-phenylpropenoyl amino acids as the key contributors to the astringent taste of nonfermented cocoa beans as well as roasted cocoa nibs. Because these amides have as yet not been reported as key taste compounds, this paper presents the isolation, structure determination, and sensory activity of these amino acid amides. Besides the previously reported (-)-N-[3',4'-dihydroxy-(E)-cinnamoyl]-3-hydroxy-L-tyrosine (clovamide), (-)-N-[4'-hydroxy-(E)-cinnamoyl]-L-tyrosine (deoxyclovamide), and (-)-N-[3',4'-dihydroxy-(E)-cinnamoyl]-L-tyrosine, seven additional amides, namely, (+)-N-[3',4'-dihydroxy-(E)-cinnamoyl]-L-aspartic acid, (+)-N-[4'-hydroxy-(E)-cinnamoyl]-L-aspartic acid, (-)-N-[3',4'-dihydroxy-(E)-cinnamoyl]-L-glutamic acid, (-)-N-[4'-hydroxy-(E)-cinnamoyl]-L-glutamic acid, (-)-N-[4'-hydroxy-(E)-cinnamoyl]-3-hydroxy-L-tyrosine, (+)-N-[4'-hydroxy-3’-methoxy-(E)-cinnamoyl]-L-aspartic acid, and (+)-N-[(E)-cinnamoyl]-L-aspartic acid, were identified for the first time in cocoa products by means of LC-MS/MS, 1D/2D-NMR, UV-vis, CD spectroscopy, and polarimetry, as well as independent enantiopure synthesis. Using the recently developed half-tongue test, human recognition thresholds for the astringent and mouth-drying oral sensation were determined to be between 26 and 220 micromol/L.
(water) depending on the amino acid moiety. In addition, exposure to light rapidly converted these [E]-configured N-phenylpropenoyl amino acids into the corresponding [Z]-isomers, thus indicating that analysis of these compounds in food and plant materials needs to be performed very carefully in the absence of light to prevent artifact formation.