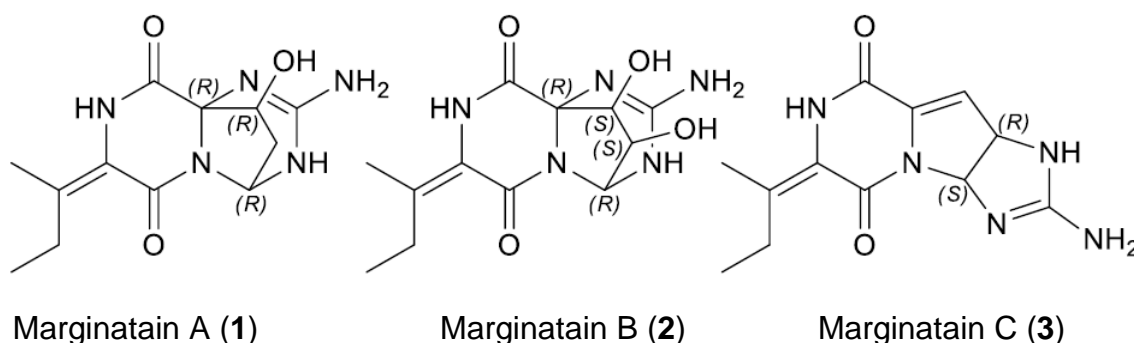


Structure Elucidation, Biosynthesis and Chemical Ecology of Unprecedented Diketopiperazine Alkaloids from Fruiting Bodies of *Mycena aurantiomarginata*

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The golden-edge bonnet (*Mycena aurantiomarginata* (Fr.) Quél., German name: Feueriger Helmling) is a small mushroom with a orange-brown, bell-shaped cap that is characterised by its strikingly orange coloured gills. Some years ago, we identified the coloured principle to be a new polyene that we named mycenaaurin A [1]. In the course of our search for new secondary metabolites in this species, we recognised that the methanolic extract of the fruiting bodies also contains so far unknown diketopiperazine alkaloids. Two of the new alkaloids that we named marginatain A (**1**) and marginatain B (**2**) contain an unique bicyclo[3,2,1]triazacyclooctane core structure. The structures of the new alkaloids **1** – **3** were mainly elucidated by NMR spectroscopy and mass spectrometry and their stereochemistry was assigned by a comparison of measured CD spectra of the isolated natural products with those obtained by quantum chemical calculations.



Marginatain A (**1**) shows nematocidal activity against *C. elegans* at concentrations of 12.5 µg/mL and might play a role in the chemical defence of *M. aurantiomarginata*. By structure elucidation of several potential biosynthetic intermediates occurring in traces in the fruiting bodies we were able to make a detailed proposal for the biosynthesis of the marginatains commencing from L-arginine and L-isoleucine.

[1] R. J. R. Jaeger, P. Spiteller, *J. Nat. Prod.* **2010**, *73*, 1350–1354.