Depth-Related Alkaloid Variation in Mediterranean *Aplysina* Sponges

Annika Putz[a], Anne Kloeppel[b], Martin Pfannkuchen[b], Franz Brümmer[b], and Peter Proksch[a,*]

[a] Institut für Pharmazeutische Biologie und Biotechnologie, Heinrich-Heine-Universität Düsseldorf, Universitätsstrasse 1, Geb. 26.23, D-40225, Düsseldorf, Germany. Fax: ++49–2 11–8 11 19 23. E-mail: proksch@uni-duesseldorf.de

[b] Biologisches Institut, Abteilung Zoologie, Universität Stuttgart, Pfaffenwaldring 57, D-70569 Stuttgart, Germany

* Author for correspondence and reprint requests

Z. Naturforsch. **64c**, 279–287 (2009); received November 10/December 15, 2008

Total amounts and patterns of bromoisoxazoline alkaloids of *Aplysina* sponges from Croatia (Mediterranean Sea) were analyzed along an underwater slope ranging from 1.8 to 38.5 m. Total amounts of alkaloids varied from sample to sample and showed no correlation with depth. In contrast, striking differences of alkaloid patterns were found between sponges from shallow sites (1.8–11.8 m) and those collected from deeper sites (11.8–38.5 m). Sponges from shallow depths consistently exhibited alkaloid patterns typical for *Aplysina aerophoba* with aerophobin-2 (**2**) and isofistularin-3 (**3**) as main constituents. Sponges from deeper sites (below 11.8 m) resembled *Aplysina cavernicola* with aerothionin (**4**) and aplysinamisin-1 (**1**) as major compounds. The typical *A. cavernicola* pigment 3,4-dihydroxyquinoline-2-carboxylic acid (**6**), however, could not be detected in *A. aerophoba* sponges but was replaced by the *A. aerophoba* pigment uranidine (**5**) which appeared to be present in all sponge samples analyzed. During transplantation experiments sponges from sites below 30 m featuring the *A. cavernicola* chemotype of bromoisoxazoline alkaloids were translocated to shallower habitats (10 m). The alkaloid patterns in transplanted sponges were found to be stable over a period of 12 months and unaffected by this change in depth. In a further experiment, clones of *Aplysina* sponges from shallow depths of 5–6 m resembling the *A. aerophoba* chemotype were either kept *in situ* under natural light conditions or artificially shaded by excluding photosynthetically active radiation (PAR). Neither **4** nor **1** were detected in artificially shaded sponges over an observation period of 12 months. In summary, two chemically distinct types of *Aplysina* sponges were discovered in this study that proved to be remarkably stable with regard to the bromoisoxazoline patterns and unaffected either by changing the light conditions or depth. It is not clear presently whether the *Aplysina* sponges collected from depths < 11.8 m represent a new chemotype of *A. cavernicola* lacking the pigment **6** or whether we have incidentally come across a so far undescribed species of the genus *Aplysina*.

Key words: Aplysina Sponges, Bromoisoxazoline Alkaloids, Depth Profile, Chemical Variation