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UNIVERSITY OF CALIFORNIA, SAN DIEGO

Chemistry and Chemical Ecology of Marine Sponges
of the Order Dendroceratida

A dissertation submitted in partial satisfaction of the
requirements for the degree Doctor of Philosophy
in Oceanography

by

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ABSTRACT OF THE DISSERTATION

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This thesis describes the chemical investigation of several species of marine sponges of the taxonomic order Dendroceratida. Secondary metabolites which are presumably derived from the spongian diterpene skeleton 26 were isolated from all of the species investigated, while one species also possessed secondary metabolites of other structural classes. Whenever possible, experiments were conducted to determine whether these secondary metabolites serve an ecologically relevant function for the sponge.

The sponge *Aplysilla polyrhaphis* was found to possess the novel spongian diterpenes polyrhaphin A (40), -B (41), -C (7), and -D (42), along with five known

spongian diterpenes. Chemical investigation of the dorid nudibranch *Chromodoris norrisi*, which was collected in the same locality as *A. polyrhaphis*, resulted in the isolation of four of the nine diterpenes found in *A. polyrhaphis*, which is the presumed dietary source. Polyrhaphin C (7), shahamin C (9), and the γ -lactone 8 were shown to inhibit feeding by the wrasse *Thallasoma lucasanum* in a laboratory assay. Some of these diterpenes also exhibited antimicrobial, cytotoxic, antiviral, and anti-inflammatory properties.

A reinvestigation of the sponge *Dendrilla* sp. collected in Palau led to the isolation of four of the five diterpenes previously reported, along with the minor metabolites dendrillolide D (58), dendrillolide E (59), 12-desacetoxypolyrhaphin A (60), and 12-desacetoxysahamin C (61). The structure of dendrillolide A was reassigned from 55 to 93 by the extensive use of two-dimensional NMR techniques. The structure previously reported for dendrillolide B (56) was determined to be incorrect, but a new structure could not be proposed. The novel indole alkaloids dendrillin A (94) and dendrillin B (95) were isolated from the more polar components of *Dendrilla* sp. Dendrillin A exhibited moderate anti-inflammatory activity.

Chelonaphysilla sp. collected in Pohnpei was found to possess three new spongian diterpenes, chelonaplysins A-C (103-105), along with six known diterpene metabolites. This unidentified species of *Chelonaphysilla* is proposed to be identical with the unidentified species of *Dendrilla* collected in Palau. The chemical composition of these two samples, and the sample previously reported in the literature, is compared.

Several diterpene metabolites and sterol endoperoxides were isolated from collections of *Aphysilla glacialis* obtained from French Wells, Crooked Island, Bahamas. Cholesterol endoperoxide (111) was also isolated from the mucus exuded by *A. glacialis*, indicating a defensive role for this secondary metabolite. Manoöl (110), cholesterol endoperoxide (111), and the dichloromethane soluble portion of the crude methanol

extract of *A. glacialis* deterred feeding by a natural assemblage of fish predators in an *in situ* assay. Cholesterol endoperoxide and the crude hexane, dichloromethane, ethyl acetate, and methanol extracts of a freeze-dried sample of *A. glacialis* deterred feeding by the wrasse *Thallasoma lunare* in a laboratory assay. Manoöl and cholesterol endoperoxide were determined to enhance the rate of fouling of surfaces in an *in situ* assay. 1-methyladenine (116) was isolated as an antimicrobial component of *A. glacialis* which showed activity against bacterial isolates obtained from seawater samples collected at French Wells.

