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3-AMINO-1-(2-AMINOIMIDAZOLYL)-PROP-1-ENE FROM THE
MARINE SPONGES *TEICHAXINELLA MORCHELLA*
AND *PTILOCAULIS WALPERSI*

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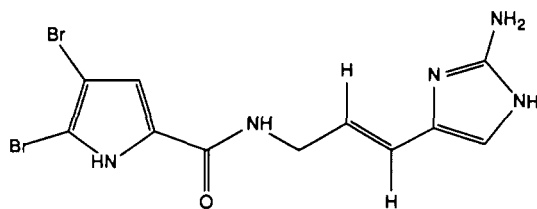
ABSTRACT.—The compound 3-amino-1-(2-aminoimidazolyl)-prop-1-ene (**3**), a possible biosynthetic precursor to the oroidin class of metabolites, has been isolated from the marine sponges *Teichaxinella morchella* and *Ptilocaulis walpersi*. Its isolation and structure elucidation are reported.

Sponges of the genera *Agelas*, *Hymeniacidon*, and *Phakellia* have been the source of a number of compounds which have been proposed to be derived from oroidin [**1**] (1–4) or its keto (5) or dihydro (6) analogues. Oroidin and related metabolites could arise from condensation between pyrrole **2** and 3-amino-1-(2-aminoimidazolyl)-prop-1-ene (**3**). A similar condensation was used in the structure proof of oroidin (2). Bromopyrrole **2** has been reported to co-occur with oroidin or related metabolites in a number of *Agelasidae* and *Axinellidae* sponges (1,7), whereas the isolation of compound **3** has not yet been reported. In this paper, we report the isolation and structure elucidation of **3** from the *Axinellidae* sponges *Teichaxinella morchella* Wiedenmayer, 1977 (8) and *Ptilo-*

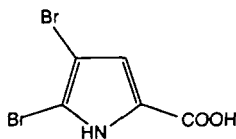
caulis walpersi Duchassaing and Micholotti, 1864 (9).

T. morchella and *P. walpersi* are common shallow water *Axinellid* sponges found in reef habitats throughout the Caribbean and southern Atlantic near Florida. Samples for this study were collected throughout the Bahamas and at Los Roques, Venezuela. All samples analyzed to date contain compound **3**. MeOH extracts of the sponges were partitioned between *n*-BuOH and H₂O. The aqueous phase was further purified on Biorex-70 cation exchange resin to yield pure **3**.

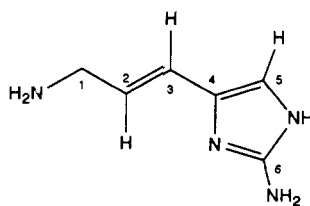
Positive ion fab/MS suggested a molecular formula of C₆H₁₀N₄ for **3**. This formula requires four sites of unsaturation, three of which can be attributed to two olefins (¹³C δ 115.3 d, 119.1 d, 125.4



1



2



3

d, 128.9 s) and one guanidine functionality (^{13}C δ 151.4 s). No further unsaturation was indicated by the nmr spectrum, which suggested that **3** contains one ring. The presence of a 1,3-disubstituted propene unit was indicated by the proton resonances observed at δ 6.51 (d, $J = 15.8$ Hz, H-3), 6.01 (dt, $J = 15.8$, 6.9 Hz, H-2), and 3.63 (2H, d, $J = 6.9$ Hz, $\text{H}_{\text{a}-1}$ and $\text{H}_{\text{b}-1}$). Homonuclear proton decoupling experiments confirmed this assignment. The olefin was assigned *trans* geometry based upon the large coupling constant observed between H-2 and H-3 (15.8 Hz). Carbon-hydrogen assignments were made based upon interpretation of a 2D carbon-hydrogen correlation experiment (XHCORR) optimized for 140 Hz (10). The methylene protons observed at 3.63 ppm $\text{H}_{\text{a,b}-1}$ were attached to the carbon observed at 42.4 ppm, which is consistent with amino substitution at this position. The presence of a 2-amino-imidazole moiety in **3** was suggested by the following ^{13}C -nmr resonances: δ 128.8 s (C-4), 115.3 d (C-5), and 151.4 s (C-6), which are similar to those reported for this functionality in oroidin (11), hymenidin (12), and stevensine (4). The propene and 2-amino-imidazole portions of the molecule were connected based upon a 2D carbon-hydrogen correlation experiment optimized for 10 Hz couplings, yielding structure **3**. The observed couplings are shown in Figure 1.

Compound **3** may be a biosynthetic precursor to oroidin and related metabolites. The major organic metabolite pres-

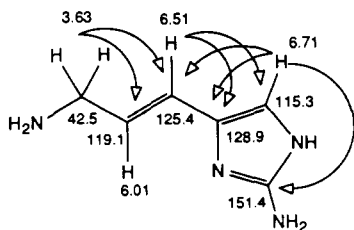
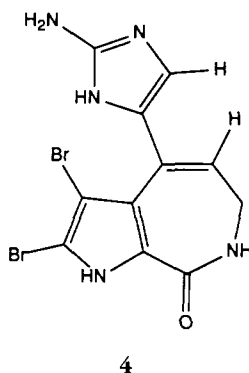


FIGURE 1. Long-range ^{13}C - ^1H nmr correlations observed for **3** by XHCORR optimized for 10 Hz.

ent in all of the sponges examined was found to be stevensine [4], a compound presumably derived from oroidin (4). Alternatively, **3** may be a degradation product of stevensine and/or oroidin. The sponges *T. morchella* and *P. walpersi* are very closely related morphologically and are indistinguishable chemically. They may at some future date be separated from other *Teichaxinella* species and found to be synonymous with each other. (S. Pomponi, personal communication).



EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Spectral data were measured on the following instruments: uv/visible, Perkin-Elmer Lamda 3B; nmr, Bruker AM360 with the Aspect 3000 computer; and hr fabs on a Kratos MS-80RFA (Chemical Instrumentation Center, Yale University). ^1H -nmr chemical shifts are reported as δ values in ppm relative to $\text{MeOH}-d_4$ (3.31 ppm). ^{13}C -nmr chemical shifts are reported as δ values in ppm relative to $\text{MeOH}-d_4$ (49.0 ppm). ^{13}C multiplicities were measured using the DEPT sequence. One bond ^{13}C - ^1H correlations were detected using the XHCORR experiment optimized for 140 MHz. Multiple bond ^{13}C - ^1H correlations were detected using the XHCORR experiment optimized for 10 Hz.

COLLECTION AND ISOLATION.—*T. morchella* was collected by scuba at Joulter's Cay, Bahamas (100 feet, 9-VI-86-1-018). *P. walpersi* was collected at Dos Mosquises, Los Roques, Venezuela (100 feet, 30-V-88-4-007, 140 feet, 28-V-88-2-012) and Cayo de Agua, Los Roques, Venezuela (80 feet, 30-V-88-3-012). Taxonomic reference samples are deposited in the Harbor Branch Oceanographic Museum with catalog numbers 003:00066, 003:00063, 003:00064, and

003:00065, respectively. The organisms were frozen at -20° until workup. Each sponge was extracted exhaustively with MeOH, and the extract was filtered and concentrated by distillation under reduced pressure. The MeOH extract was partitioned between *n*-BuOH and H₂O to separate stevensine (the major organic compound present in the extract) from compound **3**. The H₂O phase was concentrated by distillation under reduced pressure and chromatographed on Bio-Rex-70 weak cation exchange resin. Elution of the column with 0.2 N HOAc yielded pure **3** as a light brown oil. The average yield of **3** was 0.0001% of wet wt of sponge. Compound **3**: uv (MeOH) λ max 276 nm (ϵ 8785); ¹H nmr (MeOH-*d*₄) δ 6.71 (s), 6.51 (d, *J* = 15.8 Hz), 6.01 (dt, *J* = 15.8 and 6.9 Hz), 3.76 (d, 2H, *J* = 6.9 Hz); ¹³C nmr (MeOH-*d*₄) see Figure 1.

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