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TWO NEW PYRROLOQUINOLINE ALKALOIDS FROM THE SPONGE *DAMIRIA* SP.

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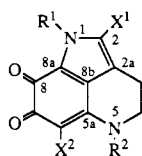
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ABSTRACT.—The structures of damirones A [**8**] and B [**9**], which are two new pyrroloquinoline pigments from the Palauan sponge *Damiria* sp., were determined by comparison of their spectral data with those of the batzellines.

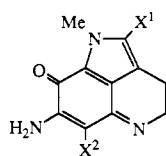
Alkaloids having the 1,3,4,5-tetrahydropyrrolo[4,3,2-*de*]quinoline skeleton are uncommon in nature. In the marine environment, they have only been reported from a deep water Caribbean sponge of the genus *Batzella*, which contained batzellines A [**1**], B [**2**], and C [**3**] (1) and isobatzellines A [**4**], B [**5**], C [**6**], and D [**7**] (2). This class of compounds is not unique to deep water sponges, for we have recently isolated similar compounds, damirones A [**8**] and B [**9**], from a shallow water Pacific sponge. The structural elucidations of damirones A [**8**] and B [**9**] are based on comparison of spectral data with those of quinone **10** that was prepared from batzelline A [**1**], the structure of which was determined by X-ray analysis.

The sponge *Damiria* sp. Keller (Order Poecilosclerida, Family Myxillidae) was collected by hand using scuba at Ngemelis drop-off (−20 m), Palau. The CH₂Cl₂-soluble material from an MeOH extract of the freeze-dried sponge was chromatographed on Sephadex LH20 CH₂Cl₂-MeOH (1:1) and then on Si gel to obtain damirone A [**8**] (0.04% dry wt) and damirone B [**9**] (0.04% dry wt) as purple solids.

The hreims of damirone A [**8**] established the molecular formula C₁₂H₁₂N₂O₂. The ¹³C-nmr spectrum contained two carbonyl signals at δ 179.3 (s) and 171.7 (s) and six olefinic signals at 153.8 (s), 127.1 (d), 124.9 (s), 124.7 (s), 115.6 (s), and 93.5 (d). Damirone A [**8**] was therefore tricyclic.



	R ¹	R ²	X ¹	X ²
1	Me	H	SMe	Cl
2	H	H	SMe	Cl
3	Me	H	H	Cl
8	Me	Me	H	H
9	H	Me	H	H
10	Me	H	H	H



	X ¹	X ²
4	SMe	Cl
5	SMe	H
6	H	Cl



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The uv spectrum of a MeOH solution of **8** [214 nm (δ 9000), 245 nm (ε 21000), 347 nm (ε 7200), 516 nm (ε

500)] was similar enough to that of batzelline A [1] to lead us to consider closely related structures. Comparison of the ^1H - and ^{13}C -nmr data of **8** with those of quinone **10** (see Table 1) led to the conclusion that damirone A is the N^5 -methyl derivative of quinone **10**. The new N -methyl signal appears at δ 3.01 in the ^1H -nmr spectrum and at δ 39.8 in the ^{13}C -nmr spectrum, and the C-4 signal shows the expected downfield carbon shift from δ 41.1 in **10** to δ 51.7 in **8**. A series of NOEDS experiments supported the proposed structure; irradiation of the N^5 -methyl signal at δ 3.01 caused enhancements of the signals at 5.20 (H-6, 9%) and 3.55 (H-4, 8%), and irradiation of the H-3 signal at 2.88 caused an 8% enhancement of the H-2 signal at 6.60. All other data were also consistent with the structural assignment.

The hrms of damirone B [9] indicated a molecular formula of $\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}_2$, which is the same as that of quinone **10**.

The uv spectrum of damirone B was similar to that of damirone A. The structure of damirone B [9] was proposed on the basis of a comparison of the ^1H - and ^{13}C -nmr spectra with those of damirone A [8] and quinone **10** (see Table 1). The signals at δ 3.05 (s, 3H) in the ^1H -nmr spectrum and at 38.6 (q) in the ^{13}C -nmr spectrum were appropriate for the N^5 -methyl group. Damirone B [9] is therefore an isomer of quinone **10** that is methylated at the alternative nitrogen atom.

The discovery of related metabolites in *Damiria* sp. and *Batzella* sp. may be of chemotaxonomic interest since both sponges are classified on the basis of negative characters (R. van Soest, personal communication).

EXPERIMENTAL

COLLECTION, EXTRACTION, AND ISOLATION PROCEDURES.—*Damiria* sp. (22 g dry wt), a black, thickly encrusting sponge, was collected by hand using scuba at Ngemelis drop-off (-20 m), Republic of Palau. Although this specimen

TABLE 1. ^{13}C - (50 MHz, δ) and ^1H - (360 MHz, δ , mult) nmr Data for Damirone A [8], Damirone B [9], and Quinone **10**.

Carbon	Compound					
	8^a		9^a		10^b	
	^{13}C	^1H	^{13}C	^1H	^{13}C	^1H
N^1H				3.70 (br s)		
C-2	127.1	6.60 (s)	127.4	6.58 (s)	128.6	7.07 (s)
C-2a	115.6		118.6		116.0	
C-3	20.3	2.80 (t) ^c	20.9	2.84 (t) ^c	19.0	2.69 (t) ^c
C-4	51.7	3.55 (t) ^c	53.3	3.60 (t) ^c	41.1	3.47 (t) ^c
N^5H						8.19 (br s)
C-5a	153.8		159.0		153.7	
C-6	93.5	5.20 (s)	93.1	5.22 (s)	92.5	5.02 (s)
C-7	171.7		172.4		171.5	
C-8	179.3		180.5		177.7	
C-8a	124.9		no ^d		124.3	
C-8b	124.7		no		123.9	
N^1Me	35.9	3.83 (s)			35.4	3.82 (s)
N^5Me	39.8	3.01 (s)	38.6	3.05 (s)		

^aRecorded in $\text{MeOH}-d_4$.

^bRecorded in $\text{DMSO}-d_6$.

^c $J = 7.0$ Hz.

^dno = not observed.

lacks any obvious external characteristics, it possesses a unique spicule complement of tylotes and strongyles, both with acanthose endings, and smooth strongyles; without microscleres. The sponge was stored at -20° until it was extracted with MeOH. The MeOH extract was concentrated in vacuo to obtain an aqueous suspension that was extracted sequentially with hexane, CH_2Cl_2 , and EtOAc. The CH_2Cl_2 extract was chromatographed on Sephadex LH-20 using CH_2Cl_2 -MeOH (1:1) as eluent to obtain a purple-colored fraction. The purple fraction was separated on a Si gel column into two fractions that gave damirone A [**8**] (8 mg, 0.04% dry wt) and damirone B [**9**] (8 mg, 0.04% dry wt) as purple microcrystalline solids.

DAMIRONE A [**8**].—Purple solid, mp 240 – 242° (dec); ir (CHCl_3) 1675 , 1600 cm^{-1} ; uv (MeOH) 214 nm (ϵ 9000), 245 (ϵ 21000), 347 (ϵ 7200), 516 (ϵ 7200); $^1\text{H nmr}$ (360 MHz, MeOH- d_4) see Table 1; $^{13}\text{C nmr}$ (50 MHz, MeOH- d_4) see Table 1; hreims m/z 216.0903 ($\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_2$ requires 216.0899); eims m/z (intensity, %) 216 (100), 188 (68), 159 (33), 118 (31).

DAMIRONE B [**9**].—Purple solid, mp $>250^{\circ}$

(dec); ir (CHCl_3) 1670 cm^{-1} ; uv (MeOH) 243, 348, 492 nm; $^1\text{H nmr}$ (360 MHz, MeOH- d_4) see Table 1; $^{13}\text{C nmr}$ (50 MHz, MeOH- d_4) see Table 1; hreims m/z 202.0768 ($\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}_2$ requires 202.0742); eims m/z (intensity, %) 202 (100), 174 (71), 145 (46), 118 (42), 104 (41).

ACKNOWLEDGMENTS

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