3-Oxo-3-phenylpropanonitrile (2) was prepared by the general procedure from 0.62 g (15 mmol) of acetonitrile and 1.65 g of *N*-methoxy-*N*-methylbenzamide in ether (-78 °C, 3 h: 0 °C, 1 h). After standard workup, 1.3 g (90%) of an orange solid was obtained, which was contaminated with a trace of starting amide. The solid was triturated with methylcyclohexane (2×), filtered, and then distilled in a Kugelrohr apparatus to give 0.90 g (62%) of **2** as a pale yellow solid: mp 78–80 °C (lit.[19] mp 80–81 °C); NMR δ 7.90 (m, 2 H), 7.65 (m, 1 H), 7.50 (m, 2 H), 4.09 (s, 2 H).

1-Phenyl-1,3-hexanedione (3) was prepared by the general procedure from 1.03 g (12 mmol) of 2-pentanone and 1.65 g of *N*-methoxy-*N*-methylbenzamide in ether (-78 °C, 3 h; ambient temperature, 24 h). After a standard workup, 1.5 g of an oil was isolated, which was contaminated with approximately 25% of the starting amide (NMR). The oil was purified by chromatography, eluting with 19:1 hexane–ethyl acetate, and Kugelrohr distillation to give 0.90 g (47%) of diketone **3** as a colorless oil: NMR (enol form) δ 7.88 (m, 2 H), 7.5–7.4 (m, 3 H), 6.17 (s, 1 H), 2.40 (t, J = 7.5 Hz, 2 H), 1.72 (sextet, J = 7.5 Hz, 2 H), 0.99 (t, J = 7.5 Hz, 3 H). Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.97; H, 7.45.

1-Phenyl-1,3-butanedione 3-(Dimethylhydrazone) (4). A solution of diisopropylamine (1.7 mL, 12 mmol) in 10 mL of THF was cooled under N_2 in an ice bath, and 12 mmol of *n*-butyllithium in hexane was added. The resulting solution was stirred at 0 °C for 15 min, and a solution of 1.2 g (12 mmol) of acetone dimethyl hydrazone in 1 mL of THF was added dropwise. The resulting mixture was stirred at 0 °C for 40 min, when a solution of 1.65 g (10 mmol) of *N*-methoxy-*N*-methylbenzamide in 1 mL of THF was slowly added. The resulting solution was stirred at 0 °C for 30 min, poured into aqueous NH_4Cl, and extracted with two portions of ether. The combined organic layers were dried over Na_2SO_4 and evaporated to dryness. The residue was distilled in a Kugelrohr apparatus (100 °C, 0.07 mmHg) to give 2.00 g (98%) of **4** as a yellow oil: NMR (enol form) δ 7.84 (m, 2 H), 7.38 (m, 3 H), 5.55 (s, 1 H), 2.58 (s, 6 H), 2.15 (s, 3 H). Anal. Calcd for $C_{12}H_{16}N_2O$: C, 70.55; H, 7.90; N, 13.72. Found: C, 70.16; H, 7.80; N, 13.77.

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A Second Shermilamine Alkaloid from a Tunicate *Trididemnum* sp.

Anthony R. Carroll, Niranjala M. Cooray, Anthony Poiner, and Paul J. Scheuer*

Department of Chemistry, University of Hawaii at Manoa, Honolulu, Hawaii 96822

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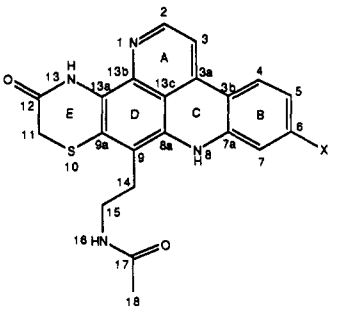
Recent chemical studies of colonial tunicates have shown them to be rich sources of fused tetra- and pentacyclic aromatic alkaloids.[1] In our earlier work on *Trididemnum* sp., a purple colonial tunicate from Pago Bay, Guam, we isolated a thiazinone-containing pentacyclic alkaloid, shermilamine A (**1**).[2] Further fractionation of the extracts has yielded a second shermilamine alkaloid, shermilamine B (**2**), lacking C6 bromination. The structure of shermilamine B was determined by interpretation of spectral data. Furthermore, a ^{1}H-detected heteronuclear multiple bond ^{1}H–^{13}C correlation experiment (HMBC)[3] has facilitated the complete and unambiguous assignment of ^{1}H and ^{13}C resonances for both shermilamine A and B. As a result of this experiment, a number of the spectral properties previously reported for shermilamine A have been revised.[4]



Optimized extraction of the tunicate with a mixture of chloroform/methanol (1:1) containing 1% of a concentrated ammonium hydroxide solution, followed by extraction of the orange pigments into an aqueous hydrochloric acid solution, and finally purification of the pigment fraction on normal-phase MPLC yielded shermilamine A, orange prisms from chloroform/methanol (94:6), mp >300 °C (0.006%, wet weight), and shermilamine B, orange prisms from methanol, mp 254 °C dec (0.02%, wet weight).

HREIMS established the molecular formula, $C_{21}H_{18}N_4O_2S$, for **2**, suggesting that it might be the nonbrominated analogue of **1**. This proposal was supported by close similarities in the UV, IR, ^{1}H NMR, and ^{13}C NMR spectra (Table I) of **2** with those of **1**. In particular, the ^{1}H NMR and ^{13}C NMR spectra for the two compounds were almost identical. The only major differences were the resonances associated with the spin system of the B ring. Proton decoupling and a COSY experiment indicated that the three protons on C4, C5, and C7 in the ^{1}H NMR spectrum of **1** were replaced in the ^{1}H NMR spectrum of **2** by a four-proton spin system in which the protons are attached to contiguous carbons. This is best explained by a hydrogen replacing the bromine at C6. The presence of another protonated aromatic carbon (δ 131.8) in the DEPT (distortionless enhancement of polarization transfer) spectrum and the absence of one quarternary carbon in the broad band decoupled ^{13}C NMR spectrum of **2** as compared with **1** was also in accord with the proposed structure assignment for **2**.

To complete the unambiguous assignment of structures for shermilamine A and B, ^{1}H–^{13}C long range coupling information was obtained from an HMBC experiment (Table II). Since the structure of **1** had already been solved by an X-ray crystallographic study,[2] an analysis of its long range $^{2\text{-}3}J_{C\text{-}H}$ ^{1}H–^{13}C couplings has allowed us to trace indirectly the complete carbon skeleton of the molecule, thus confirming the structure by a second method. It has also allowed us to unambiguously assign the ^{1}H and ^{13}C resonances for **1**. The ^{13}C resonances for **2**

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(4) The ^{1}H NMR data in DMSO-d_6 and the ^{13}C NMR data for shermilamine A reported previously were data for shermilamine B. The mass spectral data previously presented were those of a mixture of shermilamine A and B.

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Table I. ^{13}C (75 MHz) and ^{1}H (300 MHz) Nuclear Magnetic Resonance Data for Shermilamine A (1) and B (2) (DMSO-d_6)

	shermilamine A: chemical shift, ppm			shermilamine B: chemical shift, ppm	
atom	^{13}C (mult)	^{1}H (mult, J (Hz), intgrtn)	atom	^{13}C (mult)	^{1}H (mult, J (Hz), intgrtn)
2	150.57 (d)	8.43 (d, 4.8 1 H)	2	150.56 (d)	8.50 (d, 5.1, 1 H)
3	107.46 (d)	7.39 (d, 4.8, 1 H)	3	107.07 (d)	7.49 (d, 5.1, 1 H)
3a	138.49 (s)		3a	139.30 (s)	
3b	114.71 (s)		3b	115.34 (s)	
4	125.90 (d)	7.86 (d, 8.7, 1 H)	4	123.87 (d)	8.01 (dd, 7.8, 1.2, 1 H)
5	123.33 (d)	7.07 (dd, 8.7, 1.8, 1 H)	5	120.76 (d)	7.02 (ddd, 7.8, 7.8, 1.2, 1 H)
6	124.97 (s)		6	131.80 (d)	7.44 (ddd, 7.8, 7.8, 1.2, 1 H)
7	118.22 (d)	7.49 (d, 1.8, 1 H)	7	116.43 (d)	7.39 (dd, 7.8, 1.2, 1 H)
7a	141.10 (s)		7a	139.90 (s)	
8		10.17 (s, 1 H)	8		10.24 (s, 1 H)
8a	130.44 (s)		8a	131.07 (s)	
9	109.32 (s)		9	108.56 (s)	
9a	122.01 (s)		9a	121.40 (s)	
11	29.26 (t)	3.54 (s, 2 H)	11	29.25 (t)	3.33 (s, 2 H)
12	163.48 (s)		12	163.41 (s)	
13		9.22 (s, 1 H)	13		9.26 (s, 1 H)
13a	121.31 (s)		13a	121.21 (s)	
13b	136.55 (s)		13b	136.60 (s)	
13c	116.27 (s)		13c	116.27 (s)	
14	27.62 (t)	2.80 (m, 2 H)	14	27.66 (t)	2.82 (m, 2 H)
15	37.03 (t)	3.05 (m, 2 H)	15	37.07 (t)	3.00 (m, 2 H)
16		8.55 (t, 4.8, 1 H)	16		8.57 (t, 4.8, 1 H)
17	171.53 (s)		17	171.62 (s)	
18	22.45 (q)	1.90 (s, 3 H)	18	22.38 (q)	1.92 (s, 3 H)

Table II. $^{2-3}J_{C-H}$ Correlations from HMBC Experiment for Shermilamine A (1) (DMSO-d_6)[a]

proton no.	long-range correlations to carbon no.
H-2	C3, C3a, C13b
H-3	C2, C3b, C13c
H-4	C3a, C3b, C6, C7, C7a
H-5	C3b, C7
H-7	C3b, C5
H_2-11	C9a, C12
H-13	C9a
H_2-14	C8a, C9, C9a
H_3-18	C17

[a] Spectra were recorded on a General Electric GN OMEGA 500 spectrometer.

could then be assigned by direct comparison with the ^{13}C assignments for 1.

Experimental Section

General Procedures. Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 1420 spectrometer and ultraviolet spectra on a Hewlett-Packard Model 8452A diode array spectrophotometer. Mass spectra were measured on a VG-70SE instrument and NMR spectra on a General Electric QE-300 instrument at 300 MHz (^{1}H) and 75 MHz (^{13}C) respectively and on a General Electric GN OMEGA 500 instrument for the HMBC experiment. Solvents were freshly distilled before use.

Isolation. Animals that were collected in September 1987 in Pago Bay, Guam, were frozen until examined. The frozen tunicates (1.73 kg) were extracted, first with methanol, followed by repeated extraction with chloroform/methanol (1:1) containing 1% of a 30% ammonium hydroxide solution. The extracts were combined and concentrated. The aqueous residue was acidified with 1 M hydrochloric acid and partitioned against hexane and chloroform. The aqueous layer was basified with 10% ammonium hydroxide and partitioned against chloroform. The basic chloroform extract was concentrated, yielding an orange/red solid (1.20 g). This residue was filtered through silica gel (BondElut, elution with chloroform) and then subjected to MPLC on silica gel (elution with chloroform/methanol, 97:3), resulting in shermilamine A (1, 98 mg, 0.006%) and shermilamine B (2, 340 mg, 0.019%).

Shermilamine A (1): orange prisms from chloroform/methanol (96:4); mp >300 °C; UV (MeOH) λ_{max} 238 (log ϵ = 4.52), 282 (4.45), 298 (4.39), 350 (3.90), 392 (3.71), 470 nm (3.76); UV ($MeOH_2^+$) λ_{max} 242 (log ϵ = 4.40), 286 (4.36), 312 (4.55), 320 (4.54), 364 (3.74), 382 (3.75), 536 nm (3.77); IR (solution in chloroform) ν_{max} 3680, 1665, 1650, 1630, 1605, 1595, 1500, 1460, 1435, 1375, 1335, 1010, 930, 830 cm^{-1}; HREIMS, m/z 468.0260 ($C_{21}H_{17}{}^{79}BrN_4O_2S$ requires 468.0255); EIMS, m/z 470 (85), 468 (82), 398 (55), 396 (65), 207 (60), 177 (100), 147 (30), 135 (40), 91 (25), 73 (30), 57 (68).

Shermilamine B (2): fine orange prisms from methanol; mp 254 °C dec; UV (MeOH) λ_{max} 234 (log ϵ = 4.54), 282 (4.45), 298 (4.39), 348 (3.97), 390 (3.76), 468 nm (3.81); UV ($MeOH_2^+$) λ_{max} 232 (log ϵ = 4.44), 282 (4.40), 302 (4.53), 318 (4.69), 364 (3.78), 382 (3.79), 536 nm (3.83); IR (film from chloroform) ν_{max} 3290, 3265, 2980, 1640, 1630, 1600, 1580, 1550, 1450, 1420, 1350, 1310, 1190, 1120, 1070, 900, 840, 800, 740, 650 cm^{-1}; HREIMS, m/z 390.1204 ($C_{21}H_{18}N_4O_2S$ requires 390.1259), 318.0645 ($C_{18}H_{12}N_3OS$ requires 318.0590); EIMS, m/z 390 (100), 318 (80), 212 (45), 162 (90).

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Generation and Cycloaddition Reactions of Phenylsulfonyl-Substituted 1,3-Butadienes

Albert Padwa,* Brian Harrison, S. Shaun Murphree, and Philip E. Yeske

Department of Chemistry, Emory University, Atlanta, Georgia 30322

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Phenylsulfonyl-substituted 1,3-dienes exhibit high regio- and stereoselectivity toward dienophiles, and consequently these dienes are becoming well established as useful intermediates in organic synthesis.[1] Some of the procedures

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