mol %) for 16–24 h. After cooling, the reaction mixture was concentrated and the product was purified by flash chromatography (EtOAc/hexanes).

5-[(2-Chloro-α,α,α,6-tetrafluoro-p-tolyl)oxy]-3-isopropylideneindolin-2-one (17). Heating **10a** in acetone containing piperidine (200 mol %) gave the desired product as a yellow solid in 74% yield: mp 194–195 °C; ^{1}H NMR ($CDCl_3$) δ 9.17 (s, 1 H), 7.57 (s, 1 H), 7.38 (dd, J = 1.5, 6.6, 1 H), 7.27 (d, J = 1.8, 1 H), 6.77 (d, J = 9.0, 1 H), 6.60 (dd, J = 1.8, 8.4, 1 H), 2.61 (s, 3 H), 2.33 (s, 3 H); IR 1709, 1621, 1592 cm^{-1}; CIMS 386 (MH^+). Anal. Calcd for $C_{18}H_{12}ClF_4NO_2$: C, 56.05; H, 3.14; N, 3.63. Found: C, 56.01; H, 3.20; N, 3.51.

5-[(2-Chloro-α,α,α,6-tetrafluoro-p-tolyl)oxy]-3-isopropylidene-1-methylindolin-2-one (15a) was prepared as a beige solid in 78% yield by heating **14** and piperidine (200 mol %) in acetone at reflux: mp 121–124 °C; ^{1}H NMR ($CDCl_3$) δ 7.60 (s, 1 H), 7.38 (dd, J = 2.1, 9.6, 1 H), 7.31 (s, 1 H), 6.63 (s, 2 H), 3.21 (s, 3 H), 2.63 (s, 3 H), 2.34 (s, 3 H); IR 1686, 1621 cm^{-1}; CIMS 400 (MH^+). Anal. Calcd for $C_{19}H_{14}ClF_4NO_2$: C, 57.09; H, 3.53; N, 3.51. Found: C, 57.02; H, 3.68; N, 3.52.

Alternatively, **15a** was prepared by treatment of **17** with dimethyl sulfate to give **15a** in 69% yield. See N-Alkylation of 3-Alkylidene-Substituted Indolin-2-ones below.

5-[(2-Chloro-α,α,α,6-tetrafluoro-p-tolyl)oxy]-3-cyclopentylidene-1-methylindolin-2-one (15b) was prepared as a yellow solid in 82% yield by treatment of **14** with cyclopentanone (500 mol %) and piperidine (200 mol %) in toluene at reflux: mp 120–122 °C; ^{1}H NMR ($CDCl_3$) δ 7.58 (s, 1 H), 7.39 (d, J = 9.3, 1 H), 7.18 (s, 1 H), 6.67 (br s, 2 H), 3.23 (s, 3 H), 3.15 (br s, 2 H), 2.81 (br s, 2 H), 1.86 (br s, 4 H); IR 1694, 1640, 1624 cm^{-1}; CIMS 426 (MH^+). Anal. Calcd for $C_{21}H_{16}ClF_4NO_2$: C, 59.24; H, 3.79; N, 3.29. Found: C, 58.96; H, 3.93; N, 3.30.

5-[(2-Chloro-α,α,α,6-tetrafluoro-p-tolyl)oxy]-3-cyclohexylidene-1-methylindolin-2-one (15c) was prepared as a yellow solid in 73% yield by treatment of **14** with cyclohexanone (500 mol %) and piperidine (200 mol %) in toluene at reflux: mp 110–112 °C; ^{1}H NMR ($CDCl_3$) δ 7.55 (s, 1 H), 7.42 (s, 1 H), 7.36 (d, J = 9.0, 1 H), 6.62–6.58 (m, 2 H), 3.35 (t, J = 5.7, 2 H), 3.16 (s, 3 H), 2.78 (t, J = 5.7, 2 H), 1.80–1.66 (m, 6 H); IR 1684, 1611 cm^{-1}; CIMS 440 (MH^+). Anal. Calcd for $C_{22}H_{18}ClF_4NO_2$: C, 60.08; H, 4.13; N, 3.18. Found: C, 60.31; H, 4.23; N, 3.09.

N-Alkylation of 3-Alkylidene-Substituted Indolin-2-ones. A solution of **17**, K_2CO_3 (125 mol %), and the appropriate alkylating agent (110 mol %) was heated at reflux in 2-butanone (ca. 0.1 M) for 24 h. After cooling, the reaction mixture was partitioned between EtOAc and H_2O. The phases were separated, the aqueous phase was back-extracted, and the combined organic phases were dried and concentrated. The residue which contained the desired product and some unreacted starting material was purified by flash chromatography (EtOAc/hexanes, 15/85).

Ethyl 5-[(2-chloro-α,α,α,6-tetrafluoro-p-tolyl)oxy]-3-isopropylidene-α-methyl-2-oxo-1-indolineacetate (15d) was prepared from **17** and ethyl bromoacetate as a yellow solid in 46% yield: mp 142–144 °C; ^{1}H NMR ($CDCl_3$) δ 7.57 (s, 1 H), 7.38 (dd, J = 1.8, 8.4, 1 H), 7.33 (d, J = 1.8, 1 H), 6.63 (dd, J = 2.4, 8.7, 1 H), 6.56 (d, J = 8.4, 1 H), 4.47 (s, 2 H), 4.20 (q, J = 7.2, 2 H), 2.63 (s, 3 H), 2.36 (s, 3 H), 1.25 (t, J = 7.2, 3 H); IR 1744, 1736, 1694, 1636, 1616 cm^{-1}; CIMS 472 (MH^+). Anal. Calcd for $C_{22}H_{18}ClF_4NO_4$: C, 56.00; H, 3.85; N, 2.97. Found: C, 55.95; H, 3.86; N, 3.03.

Reduction of 3-Alkylidene-Substituted Indolin-2-ones. General Procedure. A solution of the appropriate alkylidene-substituted indolin-2-one in DME/EtOH (1/1) was hydrogenated over PtO_2 (5–10 wt %) at 50 psi until reduction was complete (usually 4–7 h). The catalyst was filtered, washed with fresh EtOH, and concentrated to afford essentially pure material.

5-[(2-Chloro-α,α,α,6-tetrafluoro-p-tolyl)oxy]-3-isopropyl-1-methylindolin-2-one (16a) was obtained from the reduction of **15a** as a tan solid in 90% yield: mp 76–79 °C; ^{1}H NMR ($CDCl_3$) δ 7.56 (s, 1 H), 7.37 (d, J = 9.3, 1 H), 6.96 (s, 1 H), 6.77–6.69 (m, 2 H), 3.33 (d, J = 3.3, 1 H), 3.16 (s, 3 H), 2.49–2.41 (m, 1 H), 1.02 (d, J = 6.9, 3 H), 0.86 (d, J = 6.9, 3 H); IR 1697, 1624, 1603 cm^{-1}; CIMS 402 (MH^+); HRMS calcd for $C_{19}H_{17}ClF_4NO_2$ (MH^+) 402.0884, found 402.0883.

5-[(2-Chloro-α,α,α,6-tetrafluoro-p-tolyl)oxy]-3-cyclopentyl-1-methylindolin-2-one (16b) was obtained from the reduction of **15b** as a white solid in 91% yield: mp 114–117 °C; ^{1}H NMR ($CDCl_3$) δ 7.57 (s, 1 H), 7.37 (d, J = 9.3, 1 H), 6.99 (s, 1 H), 6.77–6.69 (m, 2 H), 3.48 (d, J = 4.8, 1 H), 3.16 (s, 3 H), 2.46–2.40 (m, 1 H), 1.86–1.33 (m, 8 H); IR 1697, 1625, 1599 cm^{-1}; CIMS 428 (MH^+). Anal. Calcd for $C_{21}H_{18}ClF_4NO_2$: C, 58.96; H, 4.24; N, 3.27. Found: C, 58.64; H, 4.35; N, 3.18.

5-[(2-Chloro-α,α,α,6-tetrafluoro-p-tolyl)oxy]-3-cyclohexyl-1-methylindolin-2-one (16c) was obtained from the reduction of **15c** as a beige solid in 90% yield; mp 95–102 °C; ^{1}H NMR ($CDCl_3$) δ 7.54 (s, 1 H), 7.35 (d, J = 9.6, 1 H), 6.97 (s, 1 H), 6.71–6.62 (m, 2 H), 3.28 (br s, 1 H), 3.12 (s, 3 H), 2.11–2.04 (m, 1 H), 1.70–1.12 (m, 10 H); IR 1704, 1625, 1605 cm^{-1}; CIMS 442 (MH^+). Anal. Calcd for $C_{22}H_{20}ClF_4NO_2$: C, 59.80; H, 4.56; N, 3.17. Found: C, 59.39; H, 4.55; N, 3.13.

Ethyl 5-[(2-chloro-α,α,α,6-tetrafluoro-p-tolyl)oxy]-3-isopropyl-α-methyl-2-oxo-1-indolineacetate (16d) was obtained from the reduction of **15d** as a yellow solid in 98% yield: mp 85–88 °C; ^{1}H NMR ($CDCl_3$) δ 7.51 (s, 1 H), 7.31 (dd, J = 2.1, 9.9, 1 H), 6.92 (d, J = 1.8, 1 H), 6.69 (dd, J = 2.4, 8.4, 1 H), 6.52 (d, J = 8.7, 1 H), 4.52 (d, J = 17.1, 1 H), 4.19 (d, J = 17.1, 1 H), 4.12 (q, J = 7.2, 2 H), 3.37 (d, J = 3.3, 1 H), 2.48–2.38 (m, 1 H), 1.66 (t, J = 7.2, 3 H), 0.99 (d, J = 6.6, 3 H), 0.88 (d, J = 6.6, 3 H); IR 1742, 1709 cm^{-1}; CIMS 474 (MH^+). Anal. Calcd for $C_{22}H_{20}ClF_4NO_4$: C, 55.76; H, 4.25; N, 2.96. Found: C, 56.03; H, 4.54; N, 2.71.

5-[(2-Chloro-α,α,α,6-tetrafluoro-p-tolyl)oxy]-3-isopropylindolin-2-one (16e) was obtained from the reduction of **17** as a pale yellow solid in 84% yield: mp 139–141 °C; ^{1}H NMR ($CDCl_3$) δ 9.56 (s, 1 H), 7.57 (s, 1 H), 7.38 (d, J = 9.3, 1 H), 6.95 (s, 1 H), 6.83 (d, J = 8.4, 1 H), 6.71 (d, J = 8.4, 1 H), 3.40 (d, J = 3.0, 1 H), 2.50–2.44 (m, 1 H), 1.08 (d, J = 6.6, 3 H), 0.93 (d, J = 6.6, 3 H); IR 1705, 1688 cm^{-1}; CIMS 388 (MH^+). Anal. Calcd for $C_{18}H_{14}ClF_4NO_2$: C, 55.76; H, 3.64; N, 3.61. Found: C, 56.02; H, 3.78; N, 3.44.

A New Bis(indole) Alkaloid from a Deep-Water Marine Sponge of the Genus *Spongosorites*

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Received February 18, 1992 (Revised Manuscript Received May 29, 1992)

A number of bis(indole) alkaloids have been reported from the marine environment over the past few years. Some examples reported from sponges include: the topsentins reported from *Topsentia genitrix*,[1] *Spongosorites* spp.,[2] and *Hexadella* sp.,[3] which have a ketone and imidazole spacer between the two indole rings; the dragmacidins reported from both *Dragmacidon* sp.[4] and *Hexadella* sp.[5] which have a piperazine spacer; the nortopsentins reported from a *Spongosorites* sp. which lack the ketone observed in the topsentins;[6] and fascaplysin, a fully aromatized compound reported from *Fascaplysinopsis* sp.[7] Bis(indole) alkaloids have also been reported from the ascidians *Dendroda grossularia*[8] and *Didemnum candi-*

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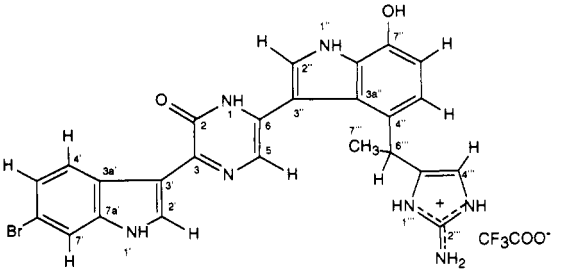
Table I. ^1H and ^{13}C NMR Data for 1 in DMSO-d_6 and Methanol-d_4

atom no.	^{13}C δ^a mult	^1H δ^a mult (J, Hz)	long-range ^1H–^{13}C correlations from C to:[a]	^{13}C δ^b mult	^1H δ mult (J, Hz)[b]	long-range ^1H–^{13}C correlations from C to:[b]
1						
2	155.10 s		H-5 and/or H-2″	156.98 s		
3	148.46 s		H-5	149.81 s		H-5
4						
5	123.87 d	7.50 s		125.40 d	7.51 s	
6	131.16 s		H-5 and/or H-2″	132.17 s		H-5, H-2″
1′		11.75 d (2.7)				
2′	131.51 d	8.80 d (2.7)		133.56 d	8.67 s	
3′	112.17 s		H-1′, H-2′	113.14 s		H-2′
3a′	125.25 s		H-1′, H-2′, H-7′, H-5′	126.29 s		H-2′, H-5′, H-7′
4′	124.60 d	8.58 d (8.6)	H-5′	125.25 d	8.55 d (8.6)	
5′	123.32 d	7.27 dd (8.6, 1.7)	H-7′	124.78 d	7.34 dd (8.6, 1.8)	H-7′
6′	115.11 s		H-4′, H-7′	116.94 s		H-4′, H-5′, H-7′
7′	114.55 d	7.69 d (1.7)	H-5′	115.32 d	7.68 d (1.8)	H-5′
7a′	137.44 s		H-1′, H-2′, H-4′	138.81 s		H-2′, H-4′
1″		11.62 d (2.6)				
2″	127.35 d	7.52 d (2.6)	H-1″	127.80 d	7.43 s	
3″	107.52 s		H-1″, H-2″	108.51 s		H-5, H-2″
3a″	126.94 s		H-1″, H-2″, H-5″	126.93 s		H-2″, H-5″, H-6‴
4″	125.89 s		H-5″, H-6‴, H-7‴	125.63 s		H-6″, H-6‴, H-7‴
5″	118.56 d	6.61 s[c]	H-6‴	120.02 d	6.85 d (7.9)	H-6‴
6″	106.54 d	6.61 s[c]	H-5‴	107.38 d	6.65 d (7.9)	
7″	143.10 s		H-5″ or H-6″	144.42 s		H-5″, H-6″
7a″	125.59 s		H-1″, H-2″, H-6″	128.46 s		H-2″, H-6″
1‴		11.85 bs				
2‴	147.48 s		H-1‴ or H-3‴, H-4‴	148.49 s		H-4‴
3‴		11.88 bs				
4‴	108.98 d	6.37 s	H-1‴ or H-3‴, H-6‴	109.90 d	6.05 s	H-6‴
5‴	131.43 s		H-1‴ or H-3‴, H-4‴, H-6‴, H-7‴	133.78 s		H-4‴, H-6‴, H-7‴
6‴	31.22 d	4.33 q (6.8)	H-7‴	32.97 d	4.35 q (6.9)	H-5″, H-7‴
7‴	20.48 q	1.33 d (6.8)	H-6‴	20.60 q	1.54 d (6.9)	H-6‴
2‴-NH_2		7.34 bs (2H)				

[a] In DMSO-d_6 containing a trace of TFA. [b] In methanol-d_4. [c] Assignments may be interchanged.

dum.[9] One of the compounds from *D. candidum* contains a piperazine spacer similar to that observed in the dragmacidin series. In this paper, we report the isolation and structure elucidation of a new bis(indole) alkaloid which we call dragmacidin d, **1**, from a deep-water sponge of the genus *Spongosorites*. Dragmacidin d inhibits the growth of the feline leukemia virus, the opportunistic fungal pathogens *Cryptococcus neoformans* and *Candida albicans* and the P388 and A549 tumor cell lines. Structurally, it varies from the previously reported dragmacidins in the further oxidation of the piperazine ring to a 1(2*H*)-pyrazinone and the addition of a 2-aminoimidazole-containing side chain on one of the indole rings.

Dragmacidin d was first detected in our laboratory as part of a study to determine the utility of secondary metabolites as chemotaxonomic markers in the Halichondrida.[10] A number of samples of *Spongosorites* were analyzed by thin-layer chromatography and the secondary metabolites compared. One sample lacked the topsentins and nortopsentins which are characteristic of most species of *Spongosorites* but appeared to contain a more polar related metabolite. Insufficient quantities of this sponge were available for full chemical characterization at the time, but fortunately, a second sample of this sponge was subsequently collected at York Bay, St. Vincent, Grenadines. A crude ethanol extract of this sample was found to show activity against feline leukemia virus which increased our interest in this organism. Reversed-phase chromatography led to the isolation of the trifluoroacetate salt of **1** (≈98% pure) as a reddish-orange glass which was used in the NMR studies. Further purification by HPLC led to material which was used in the bioassays.



1

HR FABMS suggested a formula $C_{25}H_{21}BrN_7O_2$ for dragmacidin d (Δ 0.6 mmu). This formula requires 19.5 unsaturation equivalents and suggested that compound **1** is a salt. The ^1H NMR (Table I), ^{13}C NMR (Table I), and UV [λ_{max} 213 (43 000), 270 (14 400), 278 sh, 383 (20 700)] spectra were reminiscent of those of the topsentins and dragmacidins and consistent with the presence of indole functionality in **1**.[1-5] ^1H homonuclear decoupling as well as 2D-COSY experiments were used to determine proton connectivities while one and multiple bond ^{13}C–^1H connectivities were determined by the XHCORR experiment[11] optimized for 140 Hz and the proton detected HMBC experiment,[12] respectively. All experiments were run in both methanol-d_4 and DMSO-d_6 containing a trace of TFA. The most obvious difference between the proton NMR spectrum of **1** and those of the topsentins and dragmacidins was the presence of a methine proton (δ 4.35 (q, J =

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6.8 Hz) which was coupled to a methyl resonance (δ 1.50, J = 6.8 Hz), suggesting the presence of a 1,1-disubstituted ethane moiety in 1. The proton NMR spectrum also contained one additional aromatic resonance while the carbon NMR spectrum contained three additional sp^2-hybridized carbon resonances. The indole rings were assigned as a 6-bromoindol-3-yl moiety and a 7-hydroxy-3,4-dialkyl-substituted indole based upon interpretation of the NMR data (Table I). The presence of a protonated 2-aminoimidazole unit in 1 was suggested by the carbon resonances observed at δ 147.9 (s), 131.4 (s), and 108.9 (d) and the ^{1}H NMR resonances observed at δ 6.37 (s), 7.34 (2 H, bs, exchangeable), 11.87 (bs, exchangeable), and 11.88 (bs, exchangeable) which are similar to those observed for the same structural unit in oroidin,[13] stevensine,[14] and hymenidin.[15] All correlations observed in the ^{1}H–^{13}C HMBC experiment were consistent with this assignment. Long-range ^{1}H–^{13}C correlations observed between the methine proton observed at 4.35 ppm (H-6‴) and both C-4″ and C-5″ of the 6-hydroxyindole as well as to C-4‴ and C-5‴ of the 2-aminoimidazole moiety tied these fragments together.

The NMR resonances which remain to be assigned are attributable to four sp^2-hybridized carbons observed at δ 155.1 (s), 148.4 (s), 131.1 (s), and 123.8 (d) and an aromatic proton observed at δ 7.50 (s). Two nitrogen atoms and one oxygen atom also remain to be placed in 1. In the topsentin series these atoms are assigned as an imidazole and ketone which link the two indole rings. The high-field chemical shift of the carbon observed at 155.0 ppm in 1 is inconsistent with a ketone functionality but would fit that of an amide. Morris et al. have proposed the replacement of the imidazole/ketone functionality in topsentin c and 4,5-dihydro-6″-deoxybromotopsentin which have similar amide resonances (δ 157.5 and 160.49) with a 2-ketodehydropiperazine ring.[16] Similarly, the unassigned resonances in the NMR spectra of 1 could be assigned as a 3,6-dialkyl-substituted 2(1*H*)-pyrazinone ring. Comparison of the NMR and IR data to those of known 2(1*H*)-pyrazinones allowed for assignment of the remaining atoms.[17] The 4-alkyl-7-hydroxyindole ring has been attached at C-6 of the pyrazinone based upon the observation of two low-intensity correlations (H-5 to C-3″ and H-2″ to C-6) in the methanol-d_4 HMBC spectrum. Further support for this assignment is the observation of a 3% enhancement of H-5 when H-6‴ was irradiated in a difference NOE experiment. This leaves the 6-bromoindole ring to be placed at C-3 of the pyrazinone completing the planar structure of 1. A series of NOE difference experiments were carried out which lend further support to the proposed structure (Table II). The stereochemistry at C6‴ could not be determined from these experiments.[18] The proton on N-1 was not observed, but this is most likely due to rapid exchange caused by equilibration between the 2(1*H*)-pyrazinone and 2-hydroxypyrazine forms of 1.[17b]

Table II. NOE Difference Enhancements for 1

^{1}H irradiated	^{1}H enhanced (DMSO-d_6)	^{1}H enhanced (methanol-d_4)
H-5	*a*	H-6‴ (weak)
H-1′	H-2′, H-7′	
H-2′	H-1′	none
H-4′	H-5′	H-5′
H-5′	H-4′	H-4′
H-7′	None	none
H-1″	H-2″	
H-2″	*a*	none
H-5″[b]	none	H-6″, H-7‴
H-6″[b]	none	H-5″
H-1‴[c]	2‴-NH_2, H-6‴, H-5″ or H-6″, H-4‴	
H-3‴[c]	2‴-NH_2, H-6‴, H-5″ or H-6″, H-4‴	
H-4‴	H-1″ and/or H-3‴, H-6‴, H-7‴, H-5″ or H-6″	H-5″
H-6‴	H-5″ or H-6″	H-5, H-5″ (weak), H-4‴
H-7‴	H-5″ or H-6″, H-4‴, H-5, H-1‴ or H-3‴, H-6‴	H-5 (weak), H-5″, H-4‴, H-6‴
2‴-NH_2	H-1‴ and/or H-3‴	

[a] In DMSO-d_6 the protons are very close together and difficult to irradiate independently. [b] In DMSO-d_6 the protons overlap. Enhancements are reported for both protons irradiated simultaneously. [c] In DMSO-d_6 the protons overlap. Enhancements are reported for both protons irradiated simultaneously.

Treatment of 1 with acid (HCl or TFA) results in the formation of a deep red color with the expected bathochromic shift in the UV spectrum. This may be due to the formation of a more planar fully conjugated pyrazine. In some solvents (acetonitrile and DMSO when no acid is present) the compound appears to be greenish in color, suggesting a different nonplanar conformation.

Dragmacidin d adds a new twist to the growing class of bis(indole)-derived sponge metabolites. To the best of our knowledge, this is the first of the marine derived bis(indole) compounds to have alkyl substitution on C-4 of an indole ring, the first to incorporate the 2-aminoimidazole functionality which has been reported previously in the Agelasidae,[19] Axinellidae,[19] and Verongidae[20] sponges, and the first to have the 2(1*H*)-pyrazinone spacer. Dragmacidin d exhibits a broad spectrum of biological activity. It inhibits in vitro replication of feline leukemia virus (FeLV) with a minimum inhibitory concentration of 6.25 μg/mL (ELISA assay). It has antimicrobial activity with the following minimum inhibitory concentrations: *Escherichia coli*, 15.6 μg/mL; *Bacillus subtilis*, 3.1 μg/mL; *Pseudomonas aeruginosa*, 62.5 μg/mL; *Candida albicans*, 15.6 μg/mL; and *Cryptococcus neoformans*, 3.9 μg/mL. It also inhibits the in vitro growth of the P388 murine and A549 human lung tumor cell lines with IC_{50}s of 1.4 and 4.4 μg/mL, respectively. It was recently suggested that the 6-bromotryptophan-derived alkaloids may be produced by associated microorganisms.[9] A number of 2(1*H*)-pyrazinones have been reported from microbial sources.[21] Research to investigate this possible source of dragmacidin d and related bis(indole) alkaloids from *Spongosorites* is currently in progress in our laboratories.

Experimental Section

General Experimental Procedure. Spectral data were measured on the following instruments: IR, Bruker FTIR with microscope probe; UV/visible, Perkin-Elmer Lamda 3B; NMR,

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Bruker AM360 with the Aspect 3000 computer; HRFAB, Kratos MS-80RFA, thiothreitol matrix (Chemical Instrumentation Center, Yale University); [α], JASCO DIP-360 Digital polarimeter. ^{1}H NMR chemical shifts are reported as δ values in ppm relative to DMSO-d_6 (2.49 ppm) or methanol-d_4 (3.31 ppm). ^{13}C NMR chemical shifts are reported as δ values in ppm relative to DMSO-d_6 (39.1 ppm) or methanol-d_4 (49.0 ppm). ^{13}C multiplicities were measured using the DEPT sequence. One bond ^{1}H–^{13}C connectivities were determined via the XHCORR experiment and multiple-bond ^{1}H–^{13}C connectivities were determined through the proton-detected HMBC experiment.

Collection and Taxonomy. A sample of *Spongosorites* n. sp. (Phylum Porifera, Class Demospongiae, Order Halichondrida, Family Halichondriidae, Genus *Spongosorites*, HBOI no. 31-III-89-1-010) was collected by the Johnson-Sea-Link manned submersible at a depth of 292 ft at York Bay, St. Vincent, Grenadines. This new species is a massive, amorphous, thickly encrusting sponge, dark yellow alive and dark brown in ethanol preservative. Vermetid gastropods are associated with and incorporated in the sponge. The consistency is firm but crumbly. The genus is characterized by a distinct dermal layer of smaller spicules arranged tangentially to the surface and a confused choanosomal arrangement of spicules with sporadic spicule tracks (30–100 μm in width) running parallel to the surface. In our sponge, there are two size categories of oxeas, some of which are slightly flexed at the mid-point. This new species is most similar to *S. ruetzleri* (van Soest and Stentoft, 1988)[22] from which it is distinguished by the absence of bromotopsentin. A voucher specimen of the sponge has been deposited at the Harbor Branch Oceanographic Museum, catalog number 003:00544.

Isolation of 1. The frozen sponge (100 g) was extracted exhaustively with ethanol by macerating in a Waring blender. The extract was filtered through a bed of Celite and then concentrated to an orange oil by distillation under reduced pressure. The residue was chromatographed under vacuum column chromatographic conditions on an RP-18 stationary phase. The column used had a volume of 360 mL and was 4 cm in height. The column was eluted with a step gradient of acetonitrile–water–trifluoroacetic acid. The extract was applied adsorbed onto a small amount (5 g) of RP-18 packing as a slurry in water containing 0.05% trifluoroacetic acid (TFA) to the top of the column. The column was eluted as follows: fraction 1, 500 mL of water containing 0.05% TFA; fraction 2, 250 mL of water containing 0.05% TFA; fraction 3, 200 mL of water–ACN–TFA (160:40:0.1); fraction 4, 200 mL of water–ACN–TFA (120:80:0.1); fraction 5, 200 mL of water–ACN–TFA (80:120:0.1); fraction 6, 200 mL of water–ACN–TFA (40:160:0.1); fraction 7, 500 mL of ACN. Dragmacidin d eluted in fractions 3, 4, and 5 dependent upon loading of the column. Yield from 100 g of sponge: 534 mg. ^{1}H NMR: see Table I. ^{13}C NMR: see Table I. IR: FT IR (neat, microscope) ν_{max} (cm^{-1} 3165 broad, 1678, 1637, 1531, 1447, 1408, 1244, 1200, 1136, 955, 806. UV: EtOH λ_{max} 213 (47 870), 270 sh, 278 (14 470), 383 (20 740) after addition of 1 drop of HCl to a 2-mL cell; 214 (54 000), 280 (16 400), 452 (19 946). FABMS: 530/532 (M^+), 449/447 (M^+ – (2-aminoimidazole)). HRFABMS: M^+_{obsd} 532.0916, M^+_{calcd} 532.0922.

Biological Methods: Antimicrobial Assays. Minimum inhibitory concentrations (MICs) were determined by standard microdilution broth techniques[23] in a total volume of 50 μL. The growth media used were as follows: *Candida albicans*, Sabouraud dextrose broth; *Cryptococcus neoformans*, Emmon's modification of Sabouraud dextrose broth; Bacteria, Mueller-Hinton broth supplemented with Ca^{2+} and Mg^{2+}. Plates were incubated at 37 °C for either 24 h (bacteria and *C. albicans*) or 48 h (*C. neoformans*). The MIC was determined as the lowest concentration of the drug which completely inhibited growth.

Antitumor and Antiviral Assays. The FeLV assay is an ELISA assay developed by Dr. Sue Cross at HBOI; full details have been published elsewhere.[24] The antitumor assays were run using standard protocols in 96-well plates and MTT to detect cytotoxicity.[25]

Acknowledgment. We would like to thank Dr. Eberhard Essich, Dr. Ross Longley, and Mr. Allen Ebalo for the antitumor assay data, and the Harbor Branch Collection Team and Marine Operations for assistance with collection of the sample. This is Harbor Branch Contribution Number 919.

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1-(Benzenesulfonyl)- and 1-(*p*-Toluenesulfonyl)-3-methylimidazolium Triflates: Efficient Reagents for the Preparation of Arylsulfonamides and Arylsulfonates

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Received March 25, 1992

Arylsulfonyl substituents have served as effective protecting groups for both oxygen and nitrogen functionalities.[1] As arylsulfonates and arylsulfonamides they provide strong chromophores and are stable to a variety of reaction conditions.[1] Subsequently, the arylsulfonyl group can be removed from the amine[2] and the arylsulfonate can be hydrolyzed, displaced, or eliminated. As a consequence of this versatility of sulfonamides, the arylsulfonyl group has found particular application for the masking of amine and guanidine functions[1] and for the protection of α-amino acids in which the carbonyl group is destined to undergo reaction with an organometallic reagent.[3]

The preparation of toluenesulfonyl and benzenesulfonyl derivatives generally relies on the use of the corresponding sulfonyl chloride or anhydride in the presence of pyridine or aqueous base in a Schotten–Bauman type reaction.[1] These procedures fail or are limited when the nucleophiles are insufficiently nucleophilic or sterically encumbered. Side reactions are possible due to the presence of base or the liberated chloride nucleophile, especially under forcing conditions with relatively non-nucleophilic substrates. It would thus be highly desirable to have an arylsulfonating reagent that would operate under mild conditions in the absence of base and competing nucleophile and that could sulfonate relatively non-nucleophilic substrates. Additionally, it would be advantageous if this reagent could be applied in an organic solvent under homogeneous conditions rather than in an aqueous or a mixed phase. With these properties, such a reagent also would be useful for

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0022-3263/92/1957-4775$03.00/0