[$Q(^{185}Re) = 2.8 \times 10^{24}/cm^2$, $Q(^{187}Re) = 2.6 \times 10^{24}/cm^2$], the magnitude of Q' reflects the concentration of charge along the z axis, which induces a large electric field gradient in the complex.[15] As evident in Table I, Q' generally increases in the order $ReO^{4+} < ReN^{3+} < ReO_2^{2+}$. In addition, estimated LF energies ($d_{xy} \rightarrow d_{xz}, d_{yz}$) increase with Q',[12-14,18] consistent with an increase in π-bonding on going from monooxo to mononitrido to *trans*-dioxo axial units. Thus the combined spectroscopic evidence emphasizes dramatically the strong axially compressed tetragonal ligand field associated with the *trans*-dioxo moiety.

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Registry No. *trans*-$[ReO_2(dmap)_4]PF_6$, 131892-43-8; *trans*-$[ReO_2(dmap)_4]^{2+}$, 131892-42-7.

Supplementary Material Available: Tables of crystallographic data, bond lengths, angles, positional parameters, and thermal parameters for *trans*-$[ReO_2(dmap)_4](PF_6)_2$ and description of EPR simulation procedure (13 pages); table of observed and calculated structure factors for *trans*-$[ReO_2(dmap)_4](PF_6)_2$ (15 pages). Ordering information is given on any current masthead page.

Hennoxazoles: Bioactive Bisoxazoles from a Marine Sponge

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Oxazole-containing marine alkaloids,[1] first described in 1986 from nudibranch egg masses[2,3] and subsequently from sponges,[4-7] possess significant bioactivities including antifungal, cytotoxic, anthelmintic, and tumor-promoting properties. We now report hennoxazoles A-D (**1-4**) from a sponge, *Polyfibrospongia* sp.[8]

Table I. NMR Data for Hennoxazole A (**1**) in Acetone-d_6

C no.	δ_C	δ_H (J, Hz)	HMBC	COSY
1	23.9, q	1.23, 3 H, s		
2	99.9, s		1, 29	
3	45.7, t	1.98, 1 H, ddd (12.6, 4.6, 1.6)	1, OH	3′, 4
3′		1.22, 1 H, t (11.7)		3, 4
4	64.1, d	3.89, 1 H, m	OH	3,3′, 5,5′, OH
5	41.4, t	1.89, 1 H, dtd (12.4, 4.5, 2.3)	7, OH	4, 5′
5′		1.11, 1 H, q (11.6)		4, 5, 6
6	66.3, d	3.51, 1 H, m	7, 8	5′, 7
7	41.2, t	2.06, 2 H, m	8	6, 8
8	73.1, d	4.45, 1 H, dd (7.7, 6.5)	7, 28	7
9	156.1, s		7, 8	
10	137.5, d	7.96, 1 H, s	8	
11	142.1, s		10	
12	131.2, s			
13	139.4, d	8.38, 1 H, s		
14	165.9, s		13, 15, 16	
15	28.4, t	2.88, 2 H, t (7.5)	16, 17	16
16	30.2, t	2.49, 2 H, q (6.9)	15, 17, 18	15, 17
17	129.5, d	5.50, 1 H, dt (15.3, 6.2)	16, 18	16, 18
18	129.9, d	5.44, 1 H, dt (15.3, 6.1)	16, 17	17, 19
19	35.6, t	2.67, 2 H, m	17, 18, 21, 27	18
20	132.5, s		27	
21	130.8, d	4.94, 1 H, d (9.3)	26, 27	22, 27
22	35.7, d	3.01, 1 H, m	24, 26	21, 23
23	136.8, d	5.32, 1 H, m	25, 26	22, 25
24	122.7, d	5.32, 1 H, m	25	25
25	17.9, q	1.58, 3 H, br s	23	23, 24
26	21.6, q	0.94, 3 H, d (6.9)		
27	23.3, q	1.58, 3 H, br s		21
28	56.1, q	3.21, 3 H, s	8	
29	47.7, q	3.01, 3 H, s	2	
OH		3.74, 1 H, d (4.8)		4

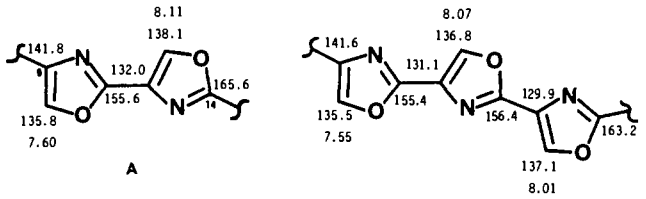
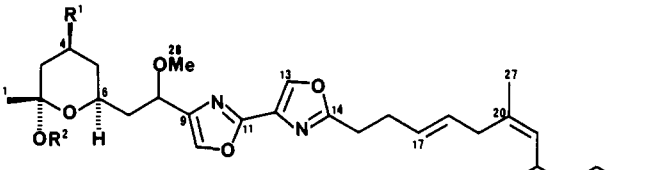


Figure 1. Comparison of NMR data ($CDCl_3$) for partial structure A and the trisoxazole moiety of kabiramide A.

Hennoxazole A (**1**) is active against herpes simplex virus type 1 (IC_{50} 0.6 μg/mL) and displays peripheral analgesic activity comparable with that of indomethacin, when assayed in the phenylquinone-induced writhing assay in mice.[9]



	R^1	R^2
1	OH	$^{29}CH_3$
2	OH	$^{29}CH_2{}^{30}CH_3$
3	OH	$^{29}CH_2CH_2CH_2{}^{32}CH_3$
4	H	$^{29}CH_3$

Polyfibrospongia sp. (4.5 kg) collected by scuba divers was extracted by steeping in acetone. After concentration, the resulting aqueous suspension was extracted with chloroform, yielding an oil (20 g), which was separated by vacuum flash chromatography on silica gel with a stepwise gradient of hexane/ethyl acetate/methanol. A fraction eluting with ethyl acetate was chromato-

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(8) The sponge classified tentatively as a species of the genus *Polyfibrospongia* (family Thorectidae, order Dictyoceratida) is bowl-shaped with a diameter of 10-20 cm and many processes on the surface. It was found sporadically on rock walls at a depth of 20-35 m, where underwater currents are fairly strong. The names of the compounds are derived from the collection site, Agari*hen*nazaki on the island of Miyako, Okinawa, Japan.
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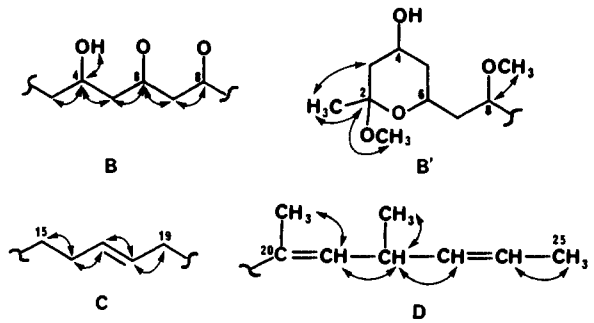

Figure 2. Partial structures B–D. Arrows indicate ^1H–^1H COSY (B, C, D) and HMBC (B').

graphed on Sephadex LH-20 ($MeOH/CH_2Cl_2$, 2:1), and the resulting fractions having UV absorption at 254 nm were further separated by HPLC (ODS, $MeOH/H_2O$, 9:1) to furnish hennoxazoles A (480 mg), B (21.2 mg), C (23.1 mg), and D (25.6 mg), all as light yellow oils. Structure determination was carried out mostly with hennoxazole A (**1**): $C_{29}H_{42}N_2O_6$ (HR EIMS m/z 514.3045, calcd 514.3025); $[\alpha]^{25}_D$ -47° (c 3.116, $CHCl_3$); UV (MeOH) λ_{max} 254 nm (ϵ 12000). The IR spectrum ($CHCl_3$) indicated a hydroxyl group (3580, 3380 cm^{-1}), which was confirmed by acetylation to a monoacetate [1730 cm^{-1}, δ 1.94 (3 H, s)].[10] Two methoxy groups [δ 3.21 (3 H, s), 3.01 (3 H, s); δ 56.1 (q), 47.7 (q)] and a ketal carbon (δ 99.9) were implied by ^1H and ^{13}C NMR data. Two low-field singlets (δ 8.40, 7.96) in the ^1H NMR and several sp^2-carbon resonances including singlets at δ 165.9 and 156.1 in the ^{13}C NMR spectrum (acetone-d_6) suggested two disubstituted oxazole rings. Indeed, when the spectra ($CDCl_3$) were compared with those for the trisoxazole portion of ulapualides[2] and kabiramide A,[3b] a bisoxazole (partial structure A) was deduced (Figure 1).

Three additional partial structures B–D were derived from ^1H–^1H COSY and $^1J_{CH}$ (CSCM, chemical shift correlation method) spectra (Figure 2). An HMBC spectrum (heteronuclear multiple bond correlation spectroscopy) revealed the connectivity of the ketal carbon (C2) to a methyl (H1) and a methoxy (H29), and the correlation of H1 with C3. Thus, partial structure B was expanded to B', in which another methoxy group (δ 3.21) was connected to C8 by H28–C8 correlation. Observed correlation of H8 with C9 and C10 connected B' to partial structure A. Connectivities of A to C and C to D were established by correlations to C14 to H15 and H16 and of C19 to H21 and H27. The geometry of the C17–C18 double bond was based on a 15.3-Hz coupling constant while the Z geometry of the C20–C21 double bond resulted from NOE between H21 and H27. The C23–C24 (E) double bond (overlapping signal at δ 5.32) was assigned by comparison of the ^{13}C NMR chemical shift of C25 (δ 17.8) with those of C1 in (E)-4-methyl-2-pentene (δ 17.6) and (Z)-4-methyl-2-pentene (δ 12.3).[11] The configuration of the six-membered ring was proposed by NOESY in which correlations were observed between H29, H4, and H6 and indicated an axial relationship of the methoxy group at C2 and protons at C4 and C6 in the chair conformation of the tetrahydropyran ring. Thus, gross structure **1** can be depicted for hennoxazole A, with stereochemistry at C8 and C22 undetermined.

Structures for the minor constituents, hennoxazoles B–D, were similarly elucidated. Hennoxazoles B (**2**) and C (**3**) were substituted at C2 by an ethoxy and an n-butoxy group, respectively, instead of a methoxy group as in **1** (NMR data).[12] Except for these substituents, the NMR data for **2** and **3** were virtually identical with those for **1**. However, the IR spectrum of hennoxazole D (**4**)[12] lacked hydroxyl bands, and in its ^{13}C NMR spectrum, three triplets at δ 31.6 (C3), 19.6 (C4), and 36.2 (C5) replaced signals at δ 45.7 (t, C3), 64.1 (d, C4), and 41.4 (t, C5) in **1**. All other signals corresponded to resonances of **1**, and thus, hennoxazole D (**4**) is a 4-dehydroxyhennoxazole A.

As suggested[13] for the biogenesis of the trisoxazole functionality of ulapualides and kabiramides, the biogenesis of the bisoxazole may also involve a polyketide intermediate.

Registry No. 1, 132564-95-5; **2**, 132564-96-6; **3**, 132564-97-7; **4**, 132564-98-8.

(10) Hennoxazole A acetate: light yellow oil; ^1H NMR (acetone-d_6) δ 5.02 (1 H, m, 4-H_{ax}), 2.08 (1 H, m, 3-H_{eq}), 1.98 (1 H, m, 5-H_{eq}), 1.94 (3 H, s, $COCH_3$), 1.37 (1 H, t, J = 11.7 Hz, 3-H_{ax}), and 1.24 (1 H, q, J = 10.4 Hz, 5-H_{ax}); ^{13}C NMR (acetone-d_6) δ 170.3 (s, $COCH_3$), 68.2 (d, C4), 41.8 (t, C3), 37.4 (t, C5), and 21.1 (q, $COCH_3$).

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(12) **2**: ^1H NMR (acetone-d_6) δ 3.28 (2 H, m, H29) and 0.87 (3 H, t, J = 7.0 Hz, H30); ^{13}C NMR (acetone-d_6) δ 55.6 (t, C29) and 15.6 (q, C30); EIMS m/z 480 (M^+ - 48, 15), 464 (100), 449 (23), 442 (18), and 432 (78 rel %); HR EIMS m/z 480.2619 (calcd for $C_{28}H_{36}N_2O_5$ 480.2614). **3**: ^1H NMR (acetone-d_6) δ 3.20 (2 H, m, H29) and 0.74 (3 H, t, J = 7.0 Hz, H32); ^{13}C NMR (acetone-d_6) δ 60.0 (t, C29), 32.9 (t, C30), 20.2 (t, C31), and 14.3 (q, C32); EIMS m/z 556 (M^+, 1), 483 (4), 464 (93), 449 (16), 446 (13), 432 (100), 421 (23), 417 (30), and 403 (23 rel %); HR EIMS m/z 464.2676 (calcd for $C_{28}H_{36}N_2O_4$ 464.2677). **4**: ^{13}C NMR (acetone-d_6) δ 98.3 (s, C2), 67.4 (d, C6), 36.2 (t, C5), 31.6 (t, C3), and 19.6 (t, C4); EIMS m/z 446 (M^+ - 32, 27), 423 (10), 395 (22), 356 (36), 341 (43), 304 (34), 273 (41), 163 (45), 107 (59), and 89 (100 rel %); HR EIMS m/z 466.2837 (calcd for $C_{28}H_{38}N_2O_4$ 466.2842).

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Template Synthesis of Metal Microtubules

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Organic microtubules have recently caused a great deal of excitement in the chemistry, physics, and materials science communities.[1] We have developed a novel "template" method for synthesizing organic tubules.[1c] This method entails using the pores in a microporous membrane as templates for tubule formation. We have used this method to prepare microtubules composed of various heterocyclic polymers.[1c] It seems likely that the template method could be used to synthesize microtubules composed of other materials; metals are an obvious choice. We describe, in this paper, an electrochemical template synthesis of gold microtubules.[2]

In general, the template method entails synthesis of a material within the pores of a microporous membrane.[1c,2,3] Either solid fibrils[3b] or hollow tubules[1c,2] will be obtained. Tubules will only be obtained if "*molecular anchors*" *are present on the pore wall*; these anchors assure that the material forms as a thin "skin" which lines the pore wall.[1c] The challenges in synthesizing metal microtubules, then, are (1) to identify chemistry for forming the metal within the pores of the membrane, (2) to identify a suitable molecular anchor, and (3) to develop chemistry for attaching this anchor to the pore walls in the membrane.

Gold microtubules were prepared by electrochemically depositing Au into the pores of microporous alumina (Anopore, Anotech Ltd.)[3b] membranes. These membranes have 200 nm diameter pores and enormous pore densities.[3b] A commercial Au plating solution (Orotemp 24, Technics) was employed. We chose

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