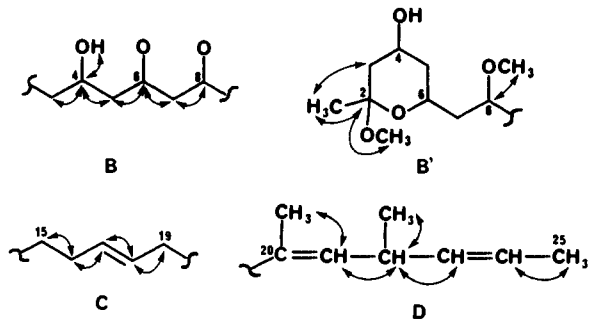

Figure 2. Partial structures B–D. Arrows indicate ^1H–^1H COSY (B, C, D) and HMBC (B').

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 12 000). 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, $COCH_3$).

(11) Toda, F. *^{13}C-NMR Data Book*; Oshima, T., Ed.; Sankyo-Shuppan: Tokyo, 1981; p 13.

(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).

(13) Ishibashi, M.; Moore, R. E.; Patterson, G. M. L.; Xu, C.; Clardy, J. *J. Org. Chem.* **1986**, *51*, 5300–5306.

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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(1) (a) Pool, R. *Science* **1990**, *247*, 1410. (b) Georger, J. H.; Singh, A.; Price, R. P.; Schnur, J. M.; Yager, P.; Schoen, P. E. *J. Am. Chem. Soc.* **1987**, *109*, 6169. (c) Martin, C. R.; Van Dyke, L. S.; Cai, Z.; Liang, W. *J. Am. Chem. Soc.* **1990**, *112*, 8976. (d) Schnur, J. M.; Price, R.; Schoen, P.; Yeager, P.; Calvert, J. M.; Georger, J.; Singh, A. *Thin Solid Films* **1987**, *152*, 181.

(2) Schoen et al. have developed a chemical template synthesis of such tubules. Price, R. R.; Baral, S.; Schoen, P. E., Naval Research Laboratory, personal communication, 1990.

(3) (a) Cai, Z.; Martin, C. R. *J. Am. Chem. Soc.* **1989**, *111*, 4138. (b) Liang, W.; Martin, C. R. *J. Am. Chem. Soc.* **1990**, *112*, 9666.

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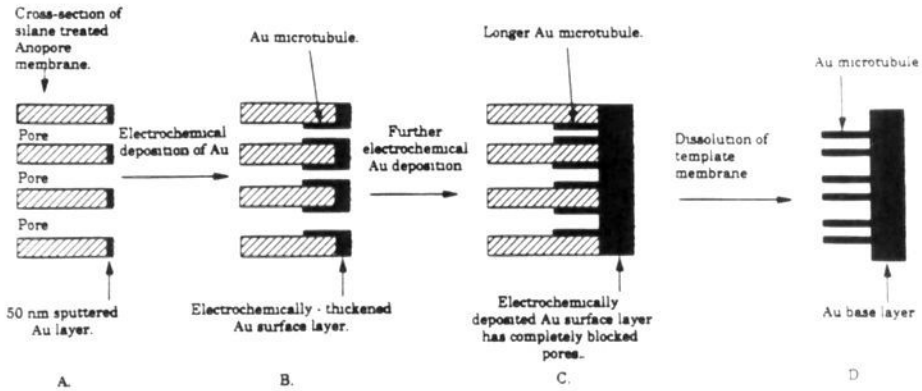


Figure 1. Schematic representation of procedure used to prepare Au microtubules.

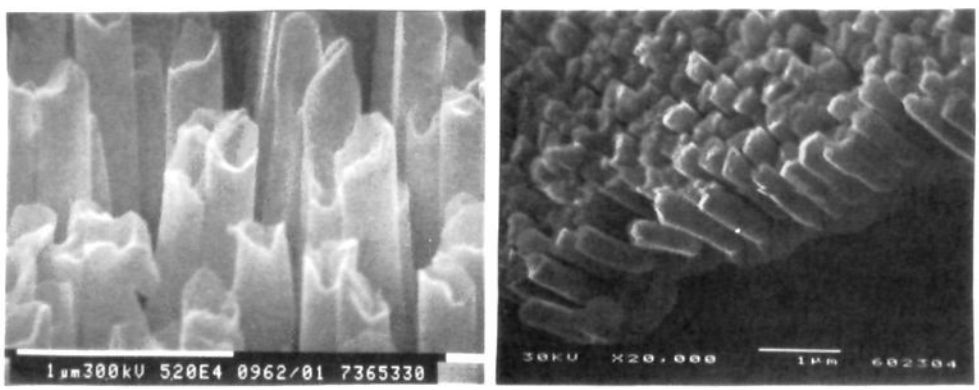
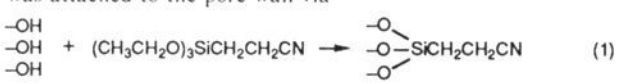


Figure 2. Electron micrographs of (A) Au microtubules (left) and (B) solid Au fibers obtained if organocyanide molecular anchor is not used (right).

an organocyanide, (2-cyanoethyl)triethoxysilane, as the molecular anchor to bind the electrochemically-deposited Au to the walls of the template membrane. Soriaga et al. have shown that organocyanides strongly chemisorb to Au.[4] This molecular anchor was attached to the pore wall via[5]



(1)

where the -OH's represent hydroxyl groups on the pore wall.

A schematic representation of the procedure used to synthesize the Au microtubules is shown in Figure 1. A 50-nm layer of Au was first sputter-deposited, from an Ar plasma, onto one face of the silane-treated Anopore membrane. This layer was too thin to block the pores in the Anopore membrane but converted the surface of the membrane into an electrode (Figure 1A). The electrochemical cell consisted of this Au/Anopore cathode and a large-area platinized niobium mesh (Technics) anode. The anode faced the Au-coated side of the membrane; the opposite configuration caused solid Au fibers, rather than tubules, to form. Au was deposited galvanostatically at current densities of 0.5–2.0 mA cm^{-2}; 1.0–4.0 C cm^{-2} was passed.

As indicated in Figure 1B, Au is deposited on the surface of the Anopore membrane and along the walls of the pores in this membrane. The gold deposited along the walls forms the Au microtubules. Deposition along the walls continues (i.e., the microtubules grow longer) until the pores become completely blocked by the Au surface layer (Figure 1C). To date, we have obtained Au microtubules that are as long as 2 μm.

After tubule synthesis, the Anopore membrane can be dissolved away,[6] to expose the Au microtubules. An upright ensemble of microtubules connected via a common Au base layer is obtained (Figure 1D). An electron micrograph of such an ensemble is shown in Figure 2A. The organocyanide molecular anchor is essential to this tubule formation process. If the electrochemistry illustrated in Figure 1 is conducted at an *underivatized* Anopore membrane, *solid Au fibrils* (Figure 2B) are obtained. We are currently exploring the mechanism of this novel tubule formation process.

It is not clear from Figure 2A how far down their lengths the tubules remain hollow. We have conducted several experiments that address this issue. First, electron micrographs of tubules that were broken near the base (i.e., near the Au surface layer)[7] show that the tubules are hollow to within several hundred nanometers of the base. Second, while solution will not flow through the membrane when the Au surface layer is intact (i.e., Figure 1C), dissolution of the Au layer, in aqua regia, allows for solution flow through the tubule-impregnated membrane. Finally, electron micrographs of the membrane after dissolution of the Au surface layer show that the exposed bases of the tubules are hollow. It is worth noting that dissolution of the Au base layer disconnects the tubules from each other. If the Anopore membrane is then dissolved,[6] the isolated fibrils can be collected by filtration.[3]

We believe that the silanization chemistry illustrated in eq 1 might provide a very general method for attaching many different types of molecular anchors to the Anopore (alumina) pore walls.[5] For example, tubules composed of a vinyl polymer might be synthesized by attaching a silane that contains an active vinyl group to the pore walls, and tubules composed of an ionic polymer might be synthesized by attaching a silane that contains a counterionic group to the pore walls. We are currently exploring these possibilities.

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(4) Brovo, B. G. Ph.D. Dissertation, Texas A&M University, 1990.
(5) (a) Miller, C. J.; Majda, M. *Anal. Chem.* **1988**, *60*, 1168. (b) The Anopore surfaces were silanized by sonicating the membrane for 30 s in a 0.1% (v/v) solution of (2-cyanoethyl)triethoxysilane in anhydrous hexadecane. The membrane was removed from this solution and heated overnight at 100 °C. The silane probably forms not as a monolayer but as a thin polymer film.
(6) Van Dyke, L. S.; Martin, C. R. *Langmuir* **1990**, *6*, 1118.
(7) Electron micrographs like those shown in Figure 2 were obtained by breaking the Anopore membrane in half. This frequently caused the tubules near the cleaved edge to break.