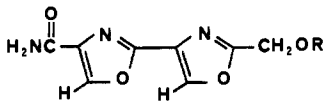
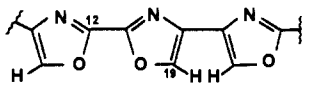
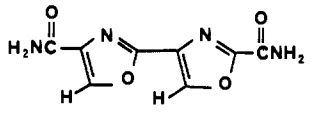


3 R = Ac
4 R = H



5



6

has been reported. Three contiguous disubstituted oxazoles became apparent from a fully coupled $^{13}C$ spectrum including one-, two-, and three-bond couplings and from long-range heteronuclear coupling experiments (Table III).

Selective decoupling of H-14 collapsed the C-14 (207 Hz)[13] and C-12 (8 Hz) doublets to singlets and sharpened the broad C-10 resonance, thereby elucidating oxazole I. Since H-14 is also linked to H-9 (vide supra), C-12 must be bonded to oxazole II.

C-22 ($\delta$ 163) of oxazole III is linked to H-26 ($\delta$ 6.94) by long-range C-H decoupling data. C-24 exhibits a C-H coupling of 213 Hz, which necessitates C-20 linkage to oxazole II.

Oxazole II may be inserted between I and III as shown in **1** (C-12-15 and C-17-20) or by linking C-12 to C-17 and C-15 to C-20. Three-bond coupling between H-19 ($\delta$ 8.09) and C-12 ($\delta$ 154) was not observed; hence oxazole II was initially placed as in **5**, where H-19 and C-12 are separated by four bonds, although biogenetic considerations favored **1**.

Although few biosynthetic models for oxazoles are known,[14] the symmetrical disposition of the trisoxazole as in **2** appeared attractive and we secured experimental evidence that favors **2**.

Hydrolysis of **3** (powdered $K_2CO_3$, MeOH overnight) furnished alcohol **4**, $C_8H_7N_3O_4$,[15] which was transformed to the bisamide **6**.[16,17] The $^1H$ NMR spectrum of **6**[18] had two singlets at $\delta$ 8.72 and 8.51 and four broad amide signals at $\delta$ 8.43, 8.09, 7.68, and 7.59. This spectrum does not fit a bisamide derived from **5**, which should display only a single aromatic proton resonance. Hence the ulapulaides have structures **1** and **2**.

The nudibranch *Hexabranchus sanguineus*, which lays the eggmasses, also contains the ulapualides though in low concentration. *H. sanguineus* feeds on the calcareous sponge *Leucetta solida*,[19] but our examination of *L. solida* yielded no ulapualides. An interesting pteridine, leucettidine, has been reported from *L. microraphis* from Bermuda.[20,21]

**Acknowledgment.** We thank Steve Coval, Nanda Gulavita, Roy Okuda, Debbie Roll, and Bülent Terem for help with collections and NMR measurements; Walter Niemczura and Lars Bergknut for NMR and MS determinations, Dr. J. Michael Geckle of Bruker Medical Instruments and the Southern California and Carnegie Mellon NMR facilities for high-field NMR data, Professors A. L. Burlingame (UCSF) and K. Nakanishi (Columbia) for MS data, Manabu Nukina for helpful discussions, and the National Science Foundation and the University of Hawaii Sea Grant College Program under Institutional Grant NA81AA-D-0070 from NOAA, Office of Sea Grant, U.S. Department of Commerce, for financial support.

**Supplementary Material Available:** Table I-VI list complete NMR spectral data (7 pages). Ordering information is given on any current masthead page.

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(13) C-H couplings in oxazoles: C-2, $J$ = 231 Hz; C-4, $J$ = 195 Hz; C-5, $J$ = 209 Hz; cf.: Hiemstra, H.; Houwing, H. A.; Possel, O.; van Leusen, A. M. *Can. J. Chem.* **1979**, *59*, 3168-3170.
(14) In the alkaloid annuloline (O'Donovan, D. G.; Horan, H. *J. Chem. Soc. C* **1971**, 331-334) the oxazole is derived from an amide, in the macrolide virginiamycin M (Kingston, D. G. I.; Kolpak, M. X. *J. Am. Chem. Soc.* **1980**, *102*, 5964-5966) from an acylserine.
(15) **4**: $^1H$ NMR ($Me_4SO$-$d_6$) $\delta$ 8.81 (1 H, s), 8.65 (1 H, s), 7.67 (1 H, br s), 7.54 (1 H, br s); HREIMS; $m/z$ found 209.0499; calcd for $C_8H_7N_3O_4$, 209.0436; FTIR (film) 3300, 1670, 1616 $cm^{-1}$; UV (MeOH) $\lambda_{max}$ 245 nm ($\epsilon$ 6000).
(16) **4** (0.5 mg); THF, -20 °C, dry $NH_3$ for 30 min; XS $NiO_2$ added over 1 h, stirred for 10 h at -20 °C; purified on BondElut RP-18, then HPLC RP-18 ($MeOH/H_2O$, 2:8).
(17) Nakagawa, K.; Onoue, H.; Minami, K. *J. Chem. Soc., Chem. Commun.* **1966**, 17-18.
(18) **6**: $^1H$ NMR ($Me_2SO$-$d_6$) $\delta$ 8.72 (1 H, s), 8.51 (1 H, s), 8.43 (1 H, br s), 8.09 (1 H, br s), 7.68 (1 H, br s), 7.59 (1 H, br s); HREIMS, $m/z$ found 222.0374; calcd for $C_8H_6N_4O_4$, 222.0389; FTIR (film) 3480, 3330, 1646 (br) $cm^{-1}$.
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## Kabiramide C, a Novel antifungal Macrolide from Nudibranch Eggmasses[1]

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Nudibranch eggmasses seem immune to predation in spite of their brilliant colors ranging from yellow to red and of flowerlike shapes. Although a variety of chemical defense substances of nudibranchs have been reported,[2-6] the chemistry of the eggmasses is totally unknown.[7] In the course of our search for bioactive substances of Japanese marine invertebrates, we found that the lipophilic extract of eggmasses of an unidentified nudibranch collected at Kabira Bay in Ishigaki-jima Island of the Ryukyus showed considerable antifungal activity, while eggmasses of *Dendrodoris nigra* in the Gulf of Sagami were inactive. We have isolated from the Kabira collection a major active compound, named kabiramide C, which has been assigned a novel macrolide structure. Kabiramide C showed marked antifungal activity.[8]

(1) Part 13 of the bioactive marine metabolites series. Part 12: Fusetani, N.; Yasukawa, K.; Matsunaga, S.; Hashimoto, K. *Tetrahedron Lett.* **1985**, *26*, 6449.
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(7) Faulkner, D. J. *Nat. Prod. Rep.* **1984**, *1*, 551.
(8) Zones of inhibition found by using a quarter portion of 8-mm-diameter filter paper disk saturated with a 250 $\mu$g/mL solution of kabiramide C: *Candida albicans* ATCC 10234 (7.7 mm); *Aspergillus niger* ATCC 9642 (30.7 mm); *Penicillium citrium* ATCC 9849 (20.0 mm); *Trichophyton interdigitae* (21.1 mm).

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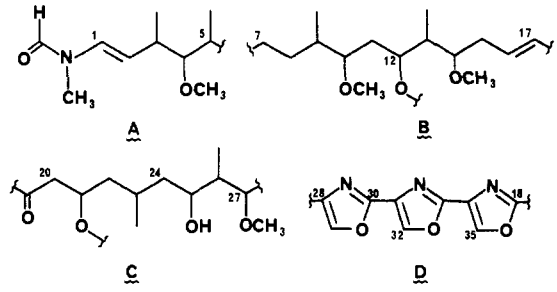
The ether-soluble portion of the MeOH extract of the eggmasses (120 g, 12 pieces) was subjected to silica gel column chromatography ($CHCl_3$–MeOH, 98:2) followed by reversed-phase HPLC (ODS, 76% MeOH) to obtain 30 mg of kabiramide C (**1**)



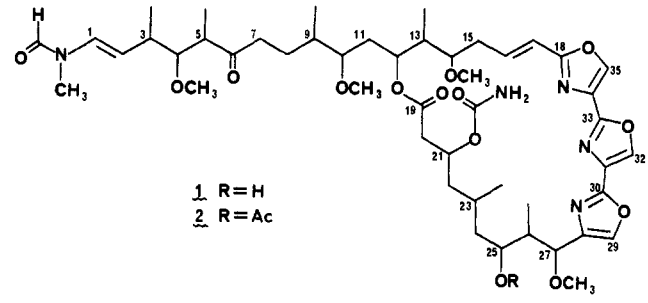
A B C D

as a colorless noncrystalline solid $[\alpha]^{23}_D$ +20° (*c* 0.1, $CHCl_3$). Its UV spectrum exhibited broad absorption with an apparent $\lambda_{max}$ (MeOH) at 245 nm ($\epsilon$ 26000). The IR absorptions at 3450, 3350, and 3150 $cm^{-1}$ indicated the presence of OH and NH functionalities, while the presence of ester and amide groups was implied by bands at 1720 and 1650 $cm^{-1}$. A molecular formula of $C_{48}H_{71}N_5O_{14}$ was obtained by high-resolution FAB mass spectrum ($MH^+$, *m/z* 942.5106 for $C_{48}H_{72}N_5O_{14}$, $\Delta$ –0.5 mmu).

Although kabiramide C eluted as a sharp symmetrical peak in reversed-phase HPLC, it showed some doublets in a 1:2 ratio in the $^{13}C$ NMR, which suggested the presence of two slowly interconverting conformers. $^1H$ and $^{13}C$ NMR[9] revealed the presence of four *O*-methyl, one *N*-methyl, and six secondary methyl groups, and seven methylenes, seven oxygen-bearing methines, six C-methines, two disubstituted double bonds, three heteroaromatic protons, one formamide, one ketone, one OH, and one $NH_2$. Since overlapping signals at $\delta$ 1.65 (3 H), 1.83 (2 H), 2.40 (3 H), and 2.49 (2 H) prevented further structural analyses, we overcame this problem by applying two-dimensional ($^1H$, $^{13}C$) shift correlation experiments,[10] which differentiated methine and methylene protons in the overlapping region. Interpretation of the COSY[11] spectrum was facilitated by this experiment and gave rise to partial structures A, B, and C.

Partial structure A was identical with an end portion reported for tolytoxin isolated from a blue-green alga.[12] All $^{13}C$ NMR signals and $^1H$ NMR signals for H-1,2,5 and the *N*-methyl formyl group in A were doubled. It was observed that difference in chemical shifts within the doublets was proportional to the distance from the *N*-methyl formyl group, suggesting that the doubled signals are attributable to restricted rotation of the amide C–N bond. *E* geometry for the $\Delta^{1,2}$ double bond was assigned on the basis of a coupling constant of 14.0 Hz between the H-1 and H-2 signals. The presence of an *O*-methyl group at C-4 was determined by a difference NOE experiment;[13] irradiation at $\delta$ 3.31 enhanced the C-3 methyl signal, though enhancement for the H-4 methine was not observed due to perturbation caused by irradiation.

Starting from the H-17 olefinic proton at $\delta$ 6.26 partial structure B was deduced from the COSY spectrum. *E* geometry of the $\Delta^{16,17}$ double bond was assigned on the basis of a coupling constant of 16.0 Hz between the H-16 and H-17 signals. Two methoxy groups were located by difference NOE experiments; irradiation at $\delta$ 3.40 and 3.30 enhanced H-14 and H-10 signals, respectively. The chemical shift at 5.29 ppm for the H-12 proton indicated that the hydroxyl group on C-12 must be esterified. It should be noted that the $^{13}C$ NMR signals for C-7–9 and -11 were doubled.



**1** R=H
**2** R=Ac

Partial structure C was deduced from the COSY spectrum starting from the H-27 proton at $\delta$ 4.78. The presence of an *O*-methyl group at C-27 was confirmed by a difference NOE experiment; irradiation at $\delta$ 3.42 enhanced the H-27 signal. Presence of a free hydroxyl group at C-25 was inferred from a coupling between the H-25 proton and a hydroxyl proton at $\delta$ 3.13. This was supported by acetylation of kabiramide C: treatment of **1** with acetic anhydride in pyridine (room temperature, 16 h) gave the monoacetate **2** [FABMS, *m/z* 984 ($MH^+$)], with an H-25 signal at $\delta$ 5.10. Chemical shifts for the H-20 methylene protons ($\delta$ 2.39, 2.56) indicated that this methylene carbon was adjacent to a carbonyl group. A chemical shift at 5.13 ppm for the H-21 proton implied that the hydroxyl group at C-21 must be substituted.

The presence of heteroaromatic rings was deduced from low-field signals in the $^1H$ and $^{13}C$ NMR spectra. $^1H$ NMR chemical shifts for H-29, -32, and -35 ($\delta$ 7.55, 8.07, and 8.01, respectively), large $^1J_{C-H}$ values (211 Hz each), $^{2,3}J_{C-H}$ values, and $^{13}C$ NMR chemical shifts for the remaining carbons were reminiscent of oxazole ring systems.[14] The relationship of the three oxazole rings was determined by a long-range selective proton decoupling (LSPD) experiment.[15] Irradiation at $\delta$ 7.55 collapsed the C-28 signal ($\delta$ 141.6, dd, *J* = 14, 5 Hz) into a doublet (*J* = 5 Hz) and the C-30 signal ($\delta$ 155.4, d, J = 8 Hz) into a singlet. Irradiation at $\delta$ 8.07 not only collapsed two doublets for C-31 ($\delta$ 131.1, *J* = 13 Hz) and C-33 ($\delta$ 156.4, *J* = 8 Hz) into singlets but also sharpened the C-30 signal ($W_{1/2}$, 2.6 → 2 Hz). Irradiation at $\delta$ 8.01 also sharpened the C-33 signal and collapsed the C-34 ($\delta$ 129.9, d, *J* = 14 Hz) as well as the C-18 ($\delta$ 163.4, dd, *J* = 6, 8 Hz) signals. These results evidenced the presence of a three contiguous oxazole ring system D.

There was one ketone group that was influenced by the *N*-methyl formyl moiety ($\delta$ 214.0, 214.1). Partial structure A could be connected at C-5 to C-7 of partial structure B through this carbon, which was verified by a difference NOE experiment; irradiation of the H-5 proton at $\delta$ 2.66 enhanced low-field portion of the AB multiplet signal for the H-7 methylene at $\delta$ 2.49. Partial structure B should be also linked at C-17 to C-18 of partial

(9) $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 214.0 (214.1) (s, C-6), 171.6 (s, C-19), 163.2 (s, C-18), 162.1 (160.8) (d, C-1-NCHO), 157.3 (s, C-21-$CONH_2$), 156.4 (s, C-33), 155.4 (s, C-30), 142.0 (d, C-16), 141.6 (s, C-28), 137.1 (d, C-35), 136.8 (d, C-32), 135.5 (d, C-29), 131.1 (s, C-31), 129.9 (s, C-34), 128.7 (124.8) (d, C-1), 115.4 (d, C-17), 111.4 (113.1) (d, C-2), 87.3 (87.4) (d, C-4), 82.0 (d, C-10), 79.2 (d, C-14), 78.3 (d, C-27), 74.1 (d, C-12), 73.4 (d, C-25), 69.3 (d, C-21), 61.3 (q, C-4–OMe), 57.9 (q, C-10–OMe), 57.6 (q, C-27–OMe), 57.4 (q, C-14–OMe), 49.0 (49.1) (d, C-5), 45.1 (t, C-22), 43.6 (t, C-24), 43.0 (t, C-20), 42.3 (42.4) (t, C-7), 40.5 (d, C-13), 37.4 (37.6) (d, C-3), 37.3 (d, C-26), 34.6 (34.7) (d, C-9), 34.0 (t, C-15), 32.9 (33.0) (t, C-11), 27.6 (33.1) (q, C-1-NMe), 25.1 (d, C-23), 25.0 (25.1) (t, C-8), 19.3 (19.4) (q, C-3-Me), 18.2 (q, C-23-Me), 15.5 (q, C-9-Me), 13.5 (13.6) (q, C-5-Me), 10.6 (q, C-26-Me), 8.4 (C-13-Me); $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 8.26 (8.04) (s, 1-NCHO), 8.07 (s, 32-H), 8.01 (s, 35-H), 7.55 (d, *J* = 1 Hz, 29-H), 7.44 (ddd, *J* = 5.5, 9.5, 16.0 Hz, 16-H), 6.43 (7.10) (d, *J* = 14.0 Hz, 1-H), 6.26 (br d, *J* = 16.0 Hz, 17-H), 5.29 (ddd, *J* = 2.0, 6.0, 10.5 Hz, 12-H), 5.13 (br t, *J* = 10.0 Hz, 21-H), 5.08 (5.10) (dd, *J* = 9.5, 14.0 Hz, 2-H), 4.78 (br s, 27-H), 3.81 (m, 25-H), 3.65 (m, 14-H), 3.42 (3 H, s, 27-OMe), 3.40 (3 H, s, 14-OMe), 3.31 (3 H, s, 4-OMe), 3.30 (3 H, s, 10-OMe), 3.28 (dd, *J* = 2.0, 9.5 Hz, 4-H), 3.13 (br, s, 25-OH), 3.00 (3.05) (3 H, s, 1-NMe), 2.99 (ddd, *J* = 2.0, 4.0, 9.5 Hz, 10-H), 2.78 (dddd, *J* = 2.0, 5.0, 5.5, 14.5 Hz, 15-H), 2.66 (2.63) (dd, *J* = 7.0, 9.5 Hz, 5-H), 2.56 (dd, *J* = 9.5, 14.5 Hz, 20-H), 2.49 (2 H, m, 7-$H_2$), 2.40 (m, 3-H), 2.39 (m, 20-H), 2.38 (m, 15-H), 2.13 (ddq, *J* = 2.0, 3.5, 7.0 Hz, 26-H), 1.89 (m, 23-H), 1.82 (2H, m, 13-H, 22-H), 1.75 (m, 8-H), 1.69 (m, 9-H), 1.66 (2H, m, 24-$H_2$), 1.63 (ddd, *J* = 2.0, 10.0, 14.5 Hz, 11-H), 1.44 (ddd, *J* = 2.0, 10.5, 14.5 Hz, 11-H), 1.31 (ddd, *J* = 2.0, 10.5, 14.0 Hz, 22-H), 1.25 (m, 8-H), 1.13 (3 H, d, *J* = 7.0 Hz, 3-Me), 0.97 (3 H, d, *J* = 7.0 Hz, 26-Me), 0.89 (3 H, d, *J* = 7.0 Hz, 23-Me), 0.87 (3 H, d, *J* = 7.0 Hz, 5-Me), 0.85 (3 H, d, *J* = 7.0 Hz, 13-Me), 0.80 (3 H, d, *J* = 7.0 Hz, 9-Me).

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structure D, which was substantiated by an $LSPD_2$ experiment; irradiation of the H-16 proton at $\delta$ 7.44 collapsed the C-18 (dd) signal into a doublet ($J$ = 8 Hz). It was concluded that C-27 in C was linked to C-28 in D, which was supported by a 1-Hz allylic coupling between H-27 and H-29. This was also evidenced by an LSPD experiment; irradiation at $\delta$ 4.78 affected the C-28 and the C-29 signals. Then the C-12 oxygen moiety in B can be linked to the C-19 carbonyl group in C to make an ester linkage. This was also shown by an LSPD experiment; irradiation at $\delta$ 5.29 changed the shape of the signal at $\delta$ 171.6. The last group to be assigned possessed a composition of $CH_2NO$ including a $^{13}C$ NMR signal at $\delta$ 157.3 and a $^1H$ NMR signal at $\delta$ 6.48 (2 H, br s, exchangeable). These features are characteristic of a carbamate group. A $^3J_{C\text{-}H}$ (3 Hz) observed between H-21 and the carbamate carbon led us to place the carbamate group at C-25. The configuration of the 13 chiral centers remains to be elucidated.

Kabiramide C possesses an unprecedented three contiguous oxazole ring system, which might be biosynthesized by a cyclization of a triserine moiety. Nudibranch eggmasses from Kabira Bay contained considerable amounts of kabiramide C (0.03% of wet weight), whose roles and origin, whether it is produced by the nudibranch or derived from a food source, are interesting subjects.

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**Supplementary Material Available:** $^1H$ NMR, $^{13}C$ NMR, ($^1H$, $^1H$) COSY, and ($^1H$, $^{13}C$) COSY spectra (4 pages). Ordering information is given on any current masthead page.

## Cascade Molecules:[1] Synthesis and Characterization of a Benzene[9]$^3$-Arborol

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The synthetic aspects of a novel class of cascade molecules called arborols have recently been described.[1] Tomalia et al.[3] have recently reported a similar class of cascades called "Starburst-Dendritic" polymers. Our initial unidirectional cascade design, derived from the Leeuwenberg model for trees,[4] generated a unique spherical hydrophilic surface covering a compact lipophilic core. Application of the synthetic techniques to a three-*directional* model (Figure 1) has led to the herein described benzene[9]$^3$-arborol (**1**), in which the three cascade spheres are attached to a central benzene seed. Further, with increasing spherical volume it should be possible to visualize a triad using electron microscopy, thus affording direct substantiation of the arborol concept.

**Figure 1.**

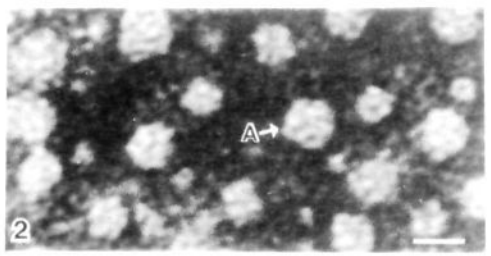


**Figure 2.** Transmission electron micrograph of **1**, negatively stained with 2% phosphotungstic acid. Note aggregation of **1** into micelles of ca. 200-Å diameter. Bar = 200 Å; 390000× magnification; 80-KV accelerating voltage.

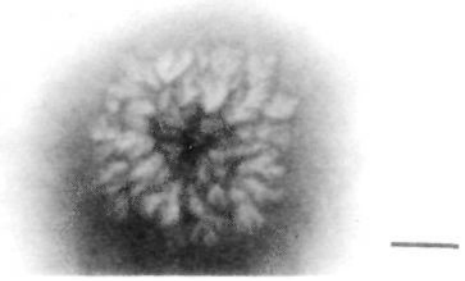

**Figure 3.** Microcrystalline region of transmission electron micrograph of **1**. Bar = 100 nm; 100000× magnification.

The synthesis of **1** (Scheme I) proceeded by selective free radical bromination[5] of mesitylene with *N*-bromosuccinimide in $CCl_4$ to give (30%) 1,3,5-tris(bromomethyl)benzene (**2**), which upon treatment with 3 equiv of $NaC(CO_2Et)_3$[6] afforded (88%) the nonaester **3** [oil; $^1H$ NMR $\delta$ 1.21 (t, $CH_2CH_3$, $J$ = 7.2, 27 H), 3.41 (s, $ArCH_2$, 6 H), 4.20 (q, $CH_2CH_3$, $J$ = 7.2 Hz, 18 H), 7.02 (s, Ar H, 3 H); $^{13}C$ NMR $\delta$ 38.4 ($ArCH_2$), 66.6 ($CH_2C$), 166.4 (*C*O);[7] IR (neat) 1746 (C=O) cm$^{-1}$]. The second tier, which incorporates the polar functional groups, was introduced by amide formation; thus, treatment of **3** with tris(hydroxymethyl)aminomethane at 70 °C in $Me_2SO$ gave (40%) the benzene[9]$^3$-arborol (**1**) [mp 135–140 °C; $^{13}C$ NMR ($D_2O$) $\delta$ 64.0 ($HN^{4°}C$), 64.4 ($ArCH_2C$), 174.6 (CO); IR 1682 (C=O) cm$^{-1}$]. Even with a mass of 1485, this arborol is highly water-soluble.

For complete characterization, **1** was converted into its benzoate derivative by treatment with benzoyl chloride[8] to afford (90%) the tris(nonabenzoate) **4** [mp 88–90 °C; $^{13}C$ NMR $\delta$ 166.2 (CONH), 162.8 (CO), 133.6 (C4), 129.8 & 128.6 (C2 and C3), 127.2 (C1); IR 1725 (ester), 1680 (amide) cm$^{-1}$]. The NMR ($^1H$ and $^{13}C$) spectra of ester **4** exhibited considerable line broadening in the aromatic region, which is attributed to the expected steric overcrowding.[9] Ester **4** is highly soluble in most organic solvents ($CHCl_3$, $C_6H_6$, $CH_3COCH_3$) and completely insoluble in water; it is, however, very hygroscopic!

In order to provide insight into the mode and size of aggregation, arborol **1** (0.7 mmol solution) was negatively stained, air dried, and examined by transmission electron microscopy; a representative micrograph is shown in Figure 2, where aggregates[10]

† Department of Chemistry.
‡ Botany Department.

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