a 0.1 M solution of iodine in THF-2,6-lutidine-water (2:2:1, v/v/v, 1 mL) for 1 min. Then the CPG was washed with pyridine followed by dichloromethane and further treated with a solution of 1% TFA. The condensation yield was estimated by colorimetry of released dimethoxytrityl cation in 60% $HClO_4$-ethanol (6:4, v/v) at 498 nm.

Solid-Phase Synthesis of Dodecathymidylate: Using 5a as a Building Block. An aminopropyl CPG was functionalized with 5'-dimethoxytrityl-N^3-benzoylthymidine 3'-*O*-succinate (14 μmol/g) by a literature procedure.[24] The fully protected dodecathymidylate was synthesized in 88% yield from the anchored N^3-benzoylthymidine on the CPG (0.05 g, 0.7 μmol) by repetition of the chain elongation cycle (Table III). Compound **5a** (0.016 g, 21 mmol) and BDCP (0.034 g, 31.5 μmol) were used for each cycle. The fully protected dodecamer on the CPG was treated with concentrated NH_3-pyridine (9:1, v/v, 20 mL) at room temperature for 12 h and then at 50 °C for 6 h. The CPG gel was filtered off and the filtrate was concentrated to a small volume. The aqueous solution was washed with ether three times, concentrated to a small volume (2 mL), and lyophilized to obtain 50 A_{260} units (0.56 μmol) of the crude product. It was further chromatographed by C_{18} reversed phase HPLC to obtain pure dodecathymidylate (33 A_{260} units, 0.37 μmol, 53% based on N^3-benzoylthymidine on the CPG). The chromatographic behavior and the UV spectrum of the product were identical with that of the authentic sample.[9b] UV: λ_{max} 265 nm (pH 7.0), λ_{min} 234 nm (pH 7.0).

Using 7a as a Building Block. The fully protected dodecathymidylate was synthesized in 92% yield from the anchored N^3-benzoylthymidine on the CPG (0.05 g, 0.7 μmol) by the procedure described above. Compound **7a** (0.015 g, 21 μmol) and BDCP (0.034 g, 31.5 μmol) were used for each cycle. After chain elongation, the CPG was treated with benzenethiol-triethylamine-dioxane (1:1:2, v/v/v, 0.5 mL) at room temperature for 30 min, washed with methanol, and finally treated with concentrated NH_3-pyridine (9:1, v/v, 20 mL) at room temperature for 12 h and then at 50 °C for 6 h. The CPG gel was filtered off and the filtrate was concentrated to a small volume. The aqueous solution was washed with ether three times and concentrated to a small volume (2 mL). The crude mixture was chromatographed by C_{18} reversed phase HPLC to obtain pure dodecathymidylate (16 A_{260} units, 0.18 μmol, 26% based on N^3-benzoylthymidine on the CPG). The chromatographic behavior and the UV spectrum of the product were identical with that of the authentic sample.[9b] UV: λ_{max} 265 nm (pH 7.0), λ_{min} 234 nm (pH 7.0).

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Registry No. **1a**, 868-85-9; **1b**, 762-04-9; **1c**, 1809-20-7; **1d**, 1809-19-4; **1e**, 13086-84-5; **1f**, 4712-55-4; **3a**, 3743-07-5; **3b**, 589-57-1; **3c**, 41662-51-5; **3d**, 4124-92-9; **3e**, 78543-77-8; **3f**, 5382-00-3; **4a**, 102573-69-3; **4b**, 64325-78-6; **4c**, 68892-40-0; **4d**, 90662-86-5; **4e**, 87036-65-5; **5a**, 130983-89-0; **5b**, 119484-01-4; **5c**, 130954-58-4; **5d**, 130954-59-5; **5e**, 130983-90-3; **6b**, 98796-53-3; **7a**, 130954-60-8; **7b**, 130249-64-8; **7c**, 130954-61-9; **7d**, 130954-62-0; **8a**, 130954-63-1; **9a**, 130954-64-2; **10a**, 130954-65-3; **10b**, 119484-02-5; **10c**, 130954-66-4; **10d**, 130954-67-5; **10e**, 130983-91-4; **11a**, 130954-68-6; **11b**, 78635-96-8; **11c**, 130954-69-7; **11d**, 130954-70-0; **12a**, 130954-71-1; **13a**, 131041-15-1; **13b**, 119484-03-6; **13c**, 130954-72-2; **13d**, 130954-73-3; **13e**, 130983-92-5; **14a**, 130983-93-6; **14b**, 130954-74-4; **14c**, 130983-94-7; **14d**, 130983-95-8; **15a**, 109946-76-1; **15b**, 119484-04-7; **15c**, 130983-96-9; **15d**, 130983-97-0; **15e**, 130983-98-1; **16a**, 102538-11-4; **16b**, 126733-74-2; **16c**, 130954-75-5; **16d**, 130954-76-6; **17a**, 130954-77-7; **17b**, 71100-65-7; **17c**, 130954-78-8; **17d**, 130954-79-9; **17e**, 130954-80-2; **18a**, 130954-81-3; **18b**, 130983-99-2; **18c**, 130954-82-4; **18d**, 130954-83-5; BDCP, 15493-07-9; H-dThd(*N*-Bz)-Bz, 94189-81-8.

New Spongian Diterpenoids from a Great Barrier Reef Sponge, *Spongia* sp.

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Four new spongian diterpenes, **4-6** and **8**, have been isolated from a *Spongia* sp. of sponge collected on the Great Barrier Reef. Two of the diterpenes have ring-A lactones instead of the conventional cyclohexane rings. Structures were determined primarily by proton and carbon-13 NMR analyses. One of the metabolites is slightly cytotoxic to murine leukemia cells.

A variety of spongian diterpenoids typified by epispongiadiol (**1**)[1] with a ring D furan and functionalized ring A have been isolated from sponges of the genus *Spongia*, order Dictyoceratida, collected from widely diverse geographical sites such as Australia, the Mediterranean, the Red Sea, and the Caribbean.[2,3] Additional relatives of **1** with the intact furan ring have been isolated from other Dictyoceratid sponges[3,4] and also nudibranchs,[3] although the ultimate source of the nudibranch diterpenes is considered most likely to be a sponge in the mollusk's diet. Another set of diterpenoids with the spongian carbon skeleton, but with saturated A rings and functionalization in ring D or even more extensively cleaved versions of this skeleton, e.g. **2**[5] and **3**,[6] have been reported from sponges from the Pacific, the Mediterranean, and the Caribbean, as well as from nudibranchs.[3] We report here additional members of the former group of spongians, including the first example of a nor-spongian with a ring-A γ-lactone.

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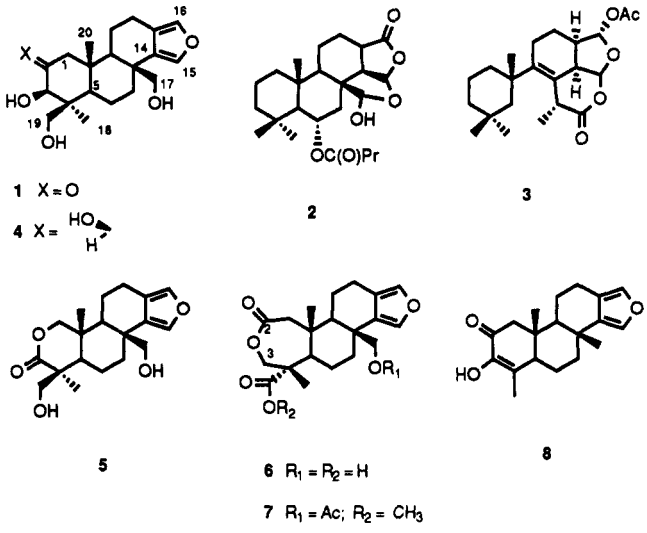
An unidentified *Spongia* sp., order Dictyaceratida, family Spongidae, was collected at Dalton Reef, Great Barrier Reef, and immediately frozen. Chromatographic separation of the methylene chloride extracts of the freeze-dried sponge yielded the spongians 1, 4–6, and 8.



The identity of 3β,17,19-trihydroxyspongia-13(16),14-dien-2-one (1) was established by comparison of its spectral properties with those reported.[1] In particular the NMR chemical shift of C-3, 83.8 ppm, is characteristic of the 3β-hydroxy configuration in compounds of this type.[1,2,4] Further confirmation of this configurational question was obtained by irradiation of the H-3 signal and noting that one of the H-19 signals sharpened. This confirms that the H-3 and the 19-CH_2OH group are diaxially disposed and that this is indeed the 3β-epimer.

All of the remaining metabolites, 4–6 and 8, were recognized as being members of the spongian family of terpenoids by their proton and ^{13}C data which paralleled that of 1 for the furan ring, C-17 CH_2OH (or C-17 Me), two quaternary methyls, and carbons of rings B and C. Hence, the unique features of the new metabolites were determined to be confined to ring A in all cases.

Metabolite 4, $C_{20}H_{30}O_5$ by LRMS (M^+ 350) and $^{13}C/^1H$ NMR, exhibited hydroxyl (3400 cm^{-1}, br) but not carbonyl absorption in the infrared and hence was presumed to be an alcohol resulting from reduction of the carbonyl group in 1. This was confirmed by proton NMR data taken in pyridine-d_5 where good resolution of the relevant signals was obtained. Coupling between H-3, H-2, and both H-1's was evident from a COSY spectrum and was also confirmed by conventional decoupling. The signal for H-1β was identified through the NOE it experienced upon irradiation of the quaternary methyl signal at 1.56 ppm. Signals from one C-19 and one C-17 proton were also enhanced in this NOE experiment, thus demonstrating that the 1.56 signal is indeed due to H-20 and also that C-17, -19, and -20 are all β-oriented. Irradiation of the alternate quaternary methyl signal, 1.60 ppm, produced NOE's on H-3, both H-19's, and very slight enhancement of H-1β and one H-19 signal, the latter two NOE's being due to partial saturation of the 1.56 signal.

The alcohol at C-2 is assigned the β-configuration since the 2-H methine proton exhibits only small couplings to its neighboring protons. The 3β-OH assignment is based on the fact that the H-1α signal occurs at ~1.25 ppm rather than much farther downfield as would be expected if the 3-OH were α and hence in a 1,3-diaxial relationship with H-1.[7] Also, the ^{13}C NMR chemical shifts of the two methine carbinol carbons, 72.0 and 82.1 ppm, are consistent with one axial and one equatorial alcohol group.[4]

Metabolite 5, $C_{19}H_{26}O_5$ by HRMS, exhibited infrared absorption for hydroxyl (3300–3650 cm^{-1}) and carbonyl (1700 cm^{-1}) groups. The ^{13}C NMR spectrum contained only one signal in the carbonyl region, 179.4 ppm, which was indicative of an ester group. Comparison of the ^1H and ^{13}C NMR data of 5 with that of 1 supported the presence of an identical B, C, D ring structure in both these compounds, along with two quaternary methyls and two CH_2OH groups. An isolated, oxygenated methylene group was revealed by a carbon triplet signal at 81.9 ppm and mutually coupled one-proton doublets at 3.90 and 4.28 ppm (J = 11 Hz). The 3.90 ppm signal showed slight W coupling with the quaternary methyl group resonating at 1.05 ppm. Irradiation of this 1.05 ppm methyl signal in a NOE experiment produced enhancements of the doublet at 4.28 ppm and one of each of the H-17 and H-19 methylene protons. This result is only compatible with the 1.05 signal being due to the axial C-20 methyl group as shown in 4 with C-17 and C-19 also being β and in 1,3-diaxial relationships with C-20, and with the oxygenated methylene group being at C-1. Insertion of the unassigned carbonyl carbon to the C-4 position completes the structure of 4. The rather low frequency infrared absorption for this lactone carbonyl group may be due to intramolecular hydrogen bonding of the C-19 OH with the carbonyl oxygen.

Compound 6 was difficult to purify in its native state, but after esterification (CH_2N_2) and acetylation it could be chromatographed nicely on silica gel. The derivatized product 7, $C_{23}H_{30}O_7$ by HRMS, showed carbonyl absorptions at 1732 (slt shoulder at 1720 cm^{-1}) and was confirmed to have three carbonyl carbons by ^{13}C NMR spectroscopy, singlets at 170.7, 173.3, and 174.7 ppm. The B, C, D rings of the spongiadiene skeleton of 1 were postulated to be present in 7 by comparison of ^{13}C NMR data and the resolved proton resonances for H-7 to H-12, H-15, H-16, and H-17. The architecture of ring A was resolved as follows. First, the methyl singlet at 1.09 ppm was confirmed to be due to methyl-20 by noting that irradiation of this signal in a difference NOE experiment produced signals for the other quaternary methyl signal at 1.31, one of the H-17 protons, and H-11 (~1.70, dq). Irradiation of the methyl-20 signal (1.09 ppm) in a decoupling experiment slightly sharpened a broad doublet occurring at 2.70, which in turn was coupled only with another broad doublet at 2.97 ppm. These two protons must therefore be H-1α and H-1β, respectively, and their chemical shifts are consistent with location α to a carbonyl group. Irradiation of the methyl-19 signal (1.31 ppm) caused a NOE on the proton doublet absorbing at 3.93 ppm and since this proton is coupled to a doublet at 4.43 ppm, this pair of protons must be at C-3 of the homo ring A. The overall structure of lactone 7 is the same as that of spongialactone A reported by Hirsch and Kashman,[2] but 7 differs from spongialactone A in having oxygenation at C-17 and being epimeric to it at C-4. The stereochemistry at C-4 could arise by oxidative cleavage at C-2, -3 followed by rotation about the C-4, -5 bond and lactone formation between a C-3 hydroxyl group and C-2.

Diosphenol 8, $C_{19}H_{24}O_3$ by high-resolution MS, exhibited ^1H and ^{13}C NMR signals, see Tables I and II, indicative of rings B, C, and D plus quaternary methyls-17 and -20 of the spongiadiene compounds such as spongialactone A[2] and 1.[1] The absence of the 17-OH group causes a noticeable upfield shift of C-8 in 8 relative to that of 1, 4, 5,

(7) For examples of the downfield shift caused by axial hydroxyl groups, see: Ksebati, M. B.; Schmitz, F. J. *Steroids* **1984**, *43*, 639.

Table I. Partial Proton NMR Data for 1, 4, 5, 7, and 8[a]

H no.	1[b]	4[c]	4[b]	5[b]	7[b]	8[b]
1	2.06, d (12.5)		1.16	3.91, d (11.0)	2.70, d (14.2)	2.08, d (16.7)
1β	2.61, d (12.5)	2.47, dd (13.9, 3.2)	2.21, dd (11, 3)	4.28, d (11.0)	2.97, d (14.2)	2.82, d (16.7)
2α		4.52, ddd (3.7, 3.7, 3.5)	4.02, q (3.5)			
3α	3.95, s	3.66, d (3.5)	3.28, d (3.5)		3.93, 4.43, d (12.7)	
5					2.21, dd	2.48–2.54, m
7α				1.27, m	(12, 2)	
7β	2.43, m	2.84, ddd (13.0, 3.1, 3.1)	2.38, ddd	2.51, ddd (14.2, 3.1, 3.1)	2.32, ddd 13.3, 3.1, 3.1	
12α	2.43, m	2.54, m	2.41	2.52, ddd (16.8, 11.5, 5.2)	2.63, ddd (16.3, 11.5, 5.2)	2.48–2.54, m
12β	2.73, dd (15.8, 4.7)	2.75, ddd (15.9, 3.5, 3.5)	2.69, dd (11, 6)	2.79, dd (16.8, 6.8)	2.87, dd (16.3, 5.2)	2.81, ddd (16.5, 5.7, 2.8)
15	7.11, br s	7.32, s	7.09, s	7.18, s	7.09, s	7.07, s
16	7.08, br s	7.32, s	7.09, s	7.14, s	7.09, s	7.11, s
17	3.67, d (10.9)	3.77, d (10.6)	3.35, d	3.56, d (11.0)	4.17, d (10.9)	1.25
17′	3.35, d (10.9)	4.20, d (10.6)	3.73, d (11)	3.79, d (11.0)	4.35, d (10.9)	
18	1.30, s	1.60, s	1.18	1.35, s		1.90, d (2)
19	3.27, d (11.6)	3.94, d (10.2)	3.35, d	3.47, d (10.9)	1.31	
19′	3.60, d (11.6)	5.17 (10.2)	4.54, d (11)	3.80, d (10.9)		
20	0.77, s	1.56, s	1.11	1.05, s	1.09	0.90, s

[a] 75 MHz. [b] $CDCl_3$ or $CDCl_3$ with few drops of CD_3OD. [c] Py-d_5.

Table II. ^{13}C NMR Data for 1, 4, 5, 7, and 8[a]

C no.	1[b]	4[c]	5[c]	7[d]	8[d]
1	52.9	38.1	81.9	45.8	51.7
2	210.1	72.0		170.7	193.6
3	83.8	81.1	179.4	73.0	143.8
4	49.6	43.4	47.3	(45.8)[e]	130.7
5	55.2	57.4	51.6	53.9[f]	49.0
6	17.8	19.2	19.6	19.0	20.2
7	34.2	36.6	35.4	34.4	39.6
8.	40.2	41.4	40.6	39.2	33.7
9.	56.0	59.3	54.3	53.9[f]	52.5
10.	42.7	44.9	37.0	38.7	41.7
11.	20.0	21.5	21.0	21.8	21.1
12.	18.2	19.4	19.5	20.6	18.3
13.	119.2	120.9	120.6	119.2	119.3
14.	129.3	131.6	130.9	129.7	136.7
15.	137.5	138.1	138.3	137.5	134.9
16.	137.7	139.1	139.3	137.3	137.1
17.	61.5	62.9	62.8	64.1	14.5
18.	23.5	24.4	25.4	173.3	25.9
19.	63.9	66.7	66.3	21.0	
20.	17.5	19.0	14.8	14.3	13.3
CH_3CO				21.0	
CH_3CO				174.7	
OCH_3				52.6	

[a] 75 MHz. Multiplicities determined by APT experiments.[11] [b] $CDCl_3/CD_3OD$ (2:1). [c] CD_3OD. [d] $CDCl_3$. [e] Assumed peak; not observed in $CDCl_3$ or C_6D_6 or in a spectrum of 6 in D_2O. [f] Observed as separate peaks in C_6D_6 at 52.2, 52.6 ppm.

and 7. Infrared absorptions at 3450, 1665, and 1640 cm^{-1} indicated the presence of hydroxyl and conjugated ketone groups, and the latter was supported by ^{13}C NMR signals at 193.6, 143.8, and 130.7 ppm. Irradiation of the upfield quaternary methyl signal (assigned to C-20 by analogy with 1, 5, 7) revealed that it was *W*-coupled to a methylene proton doublet at 2.08 ppm (converse decoupling also observed) which in turn was coupled to a one-proton doublet at 2.82 ppm (J = 16.7 Hz). This methylene pair must, therefore, be at position C-1. The rather low field vinyl methyl doublet, 1.90 ppm, J = 2.2 Hz, was coupled to an allylic signal, 2.50 ppm (overlapped by the H-12α signal), which was attributed to H-5. This vinyl methyl unit was combined with the remaining elements of the formula, i.e., a carbonyl group, a quaternary sp^2 carbon, and a hydroxyl group, to give the diosphenol moiety C-(O)C(OH)=C(CH_3), which could be inserted to give a completed ring A as in 7. This arrangement accounts for the coupling between H-5 and the vinyl methyl group. Biogenetically, structure 7 is also logical as it could arise from loss of the C-4 hydroxymethyl group in the C-3 keto analogue of 1.

A more definitive confirmation of the coupling between H-5 and the C-4 vinyl methyl group was observed in a measurement carried out at 500 MHz in C_6D_6 at 60 °C where both these signals were clearly resolved from other resonances. Irradiation of the vinyl methyl signal, 1.68 ppm, which integrated for three protons, collapsed a one-proton doublet of multiplets, 1.95 ppm (major J = 13 Hz) to a doublet of doublets (J = 13, ~3 Hz), in full agreement with structure 7. Although this type of coupling is not routinely manifested so distinctly, the clarity of the coupling in this case can be explained by the fact that the vinyl methyl group experiences coupling only to the H-5 proton whereas a vinyl methyl group more commonly would also be coupled to a vinyl hydrogen and homoallylic methine or methylene protons, thus leading to a broad unresolved vinyl methyl signal. The ^{13}C NMR shifts of C-2, -3, and -4, and the vinyl methyl group are in agreement with those of other diosphenols[8] as are the three cited infrared absorptions.[9] One of the other spongiadiene type compounds isolated to date from sponges and nudibranchs has a diosphenol feature in ring A, but interestingly it occupies positions C-1 to C-3 with the carbonyl group at the latter site.[10]

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Compound 5 showed marginal cytotoxicity to murine leukemia cells (P388), ED50 = 3.5 μg/mL, but the other compounds in the group were inactive.

Experimental Section

The sponge, a *Spongia* sp., was collected at Dalton Reef, Queensland, Australia, in 1983 and immediately frozen. The specimens were freeze dried (246 g), cut into small pieces, and extracted three times with methylene chloride at room temperature assisted by agitation in a sonication bath. The combined extracts were concentrated on a rotary evaporator, and the residue (6.0 g) was chromatographed on a column of silica gel (180 g, 230–400 mesh) beginning with $CHCl_3$ and then using $CHCl_3$ with increasing amounts of CH_3OH.

3β,17,19-Trihydroxyspongia-13(16),14-dien-2-one (1). Fraction 10 from above, eluted with $CHCl_3$ (~400 mg), was rechromatographed over silica gel (10 g) using 1.5% MeOH in $CHCl_3$ to give four fractions. Purification of fraction 2 by HPLC using a reversed-phase column (C-18, 5 μm) with 40% aqueous CH_3OH afforded 1 (18 mg) and 3 (9 mg). For 1: mp 157–159 °C (lit.[1] mp 194.7–197 °C);[12] IR (KBr) 3500, 3430, 3390, 1695, and 1030 cm^{-1}; mass spectrum (12 eV, low resolution), *m/e* (relative intensity) 348 (M^+, 4), 318 (25), 317 (12), 288 (17), 287 (100), 269 (23), 251 (3), 241 (7), 213 (10), 199 (5), 187 (7), 185 (7), 161 (7), 159 (5), 147 (42), 135 (25), 133 (33), 121 (8), 105 (15), and 91 (21).

2β,3β,17,19-Tetrahydroxyspongia-13(16),14-diene (4). Fraction 15 of the initial chromatography, eluted with 2% MeOH–$CHCl_3$, on purification by HPLC using a reversed-phase column (C-18, 5 μm) with 40% H_2O–MeOH yielded a crude polar fraction and compound 2 as a gum (5.1 mg): IR (KBr) 3400 (br) cm^{-1}; mass spectrum (12 eV, low resolution), *m/e* 350 (M^+, 36), 320 (24), 319 (100), 301 (32), 287 (24), 283 (35), 271 (14), 265 (9), 253 (11), 227 (5), 225 (6), 187 (5), 185 (6), 173 (7), 161 (8), 149 (12), 147 (39), 135 (20), 132 (9), 121 (12), 119 (19), and 95 (4).

2-Oxa-17,19-dihydroxyspongia-13(16),14-dien-3-one (5): colorless gum; IR ($CHCl_3$) 3480, 1702 cm^{-1}; mass spectrum (12 eV, low resolution), *m/e* 334 (M^+, 1), 305 (6), 304 (28), 303 (4), 285 (1), 274 (19), 273 (100), 255 (1), 227 (2), 200 (3), 199 (14), 187 (2), 147 (21), 132 (5), and 121 (2); high-resolution mass spectrum, observed *m/z* (composition, calculated millimass) 334.17997 ($C_{19}H_{26}O_5$, 334.17803).

(12) In ref 1, the 3α-epimer of 1 is reported to have mp 157.5–160.5 °C. Since our ^{13}C data clearly matches that of 1 in ref 1, we presume an error was made in reporting the melting points of these epimers initially.

17-Acetoxy-4-epispongialactone A Methyl Ester (7). The crude polar fraction obtained in the isolation of 2 was purified by HPLC using a reversed-phase (C-18, 5 μm) HPLC column with 70% H_2O–CH_3OH to give impure 6 (13 mg). Impure 6 (13 mg) was dissolved in 16 mL of H_2O–CH_3OH–diethyl ether (1:2:5) and methylated at 5 °C with excess CH_2N_2 to give a methyl ester which was then acetylated with pyridine–acetic anhydride (9:1, 5 mL) at room temperature overnight. The usual workup, afforded crude ester 7, which was purified using a SiO_2 Sep-Pak column with chloroform elution to give pure 7: gum (6 mg); IR ($CHCl_3$) 1732, 1720 (sh) cm^{-1}; mass spectrum (12 eV, low resolution), *m/z* 418 (M^+, 22), 360 (2), 359 (4), 358 (7), 347 (16), 346 (64), 345 (100), 328 (2), 327 (4), 313 (5), 304 (13), 303 (29), 299 (4), 286 (4), 285 (12), 271 (6), 258 (5), 249 (3), 225 (2), 199 (2), 185 (3), 169 (4), 149 (1), and 84 (1); high-resolution mass spectrum, observed *m/e* (composition, calculated millimass) 418.20338 ($C_{23}H_{30}O_7$, M^+, 418.19916).

19-Nor-3-hydroxyspongia-3,13(16),14-trien-2-one (8). Fraction 4 that eluted with $CHCl_3$ (~30 mg) on the first open column chromatography was further resolved by HPLC using a reversed-phase column (C-18, 5 μm) and 20% aqueous CH_3OH as eluent to give 8 as white crystals (6 mg): mp 145–147 °C ($CHCl_3$); $[\alpha]_D$ = 3.0° (*c* 0.1, $CHCl_3$); IR ($CHCl_3$) 3460, 1665, 1640, cm^{-1}; mass spectrum (12 eV, low resolution), *m/e* 300 (M^+, 100), 285 (19), 282 (11), 267 (7), 229 (7), 215 (5), 201 (10), 200 (13), 185 (13), 161 (7), 151 (7), 149 (8), 148 (8), 147 (10), 135 (8), and 121 (8); high-resolution mass spectrum, observed *m/z* (composition, calculated millimass) 300.17024 ($C_{19}H_{24}O_3$, M^+, 300.17255).

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Epoxidation of Styrene with Aqueous Hypochlorite Catalyzed by a Manganese(III) Porphyrin Bound to Colloidal Anion-Exchange Particles

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Epoxidation of styrene in aqueous sodium hypochlorite solution was catalyzed by the tetrasodium salt of 5,10,15,20-tetrakis(2,6-dichloro-3-sulfonatophenyl)porphinatomanganese(III) chloride (1). Manganese porphyrin 1 was more active bound to 60 nm diameter colloidal anion exchange particles than in aqueous solution: 0.12 mol % of 1 bound to four different types of particles gave 71–81% conversion of 1.2 mmol of styrene to styrene oxide with 1.5 mmol of hypochlorite in 1 h at room temperature. Although the activity of the catalyst decreased with time due to oxidative degradation of the porphyrin, 620 mol of styrene oxide per mol of catalyst were produced in the presence of excess oxidant. The conditions were highly selective for epoxidation of styrene: substituted styrenes epoxidized more slowly, and aliphatic alkenes did not react. Visible spectra indicated that oxidized forms of 1 were present in the hypochlorite solutions, and that the form of 1 in solution was different from that in the particles.

Introduction

Colloidal polymer particles in water, also known as latexes, are produced by emulsion polymerization in large amounts for synthetic rubber and for paints. They also are promising catalyst supports because of their high surface areas and their ability to concentrate organic reactants in the active catalyst phase by absorption from water.[1] In the absence of organic solvent aqueous colloidal

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