procedure for the preparation of **3d** described below is typical for the syntheses of all **3**.

o-Isopropylphenol (0.05 mol), dissolved in aqueous ethanol, was treated with a slight molar excess of aqueous Br_2–KBr (6.4 mL of Br_2, 30 g of KBr, 200 mL of water) at room temperature. The solution was stirred for 1 h before an equal volume of water was added, and the dibromophenol was extracted with several portions of ether. The extracts were successively washed with 5% $NaHCO_3$, water, and saturated aqueous NH_4Cl and then dried over anhydrous $MgSO_4$. The ether was removed using a rotary evaporator, and the residue was dissolved in 7 mL of water containing 1.9 g of NaOH. This solution was added slowly and without external heating to a well-stirred mixture of 1,2-dibromoethane (0.063 mol, 5.5 mL) plus water (26 mL). The solution was then refluxed for 6 h, cooled, and extracted with ether. The extracts were washed sequentially with water and saturated NH_4Cl and then dried over anhydrous $MgSO_4$. The ether was removed at room temperature using a rotary evaporator, and the remainder was fractionated under reduced pressure. The first distillate was mostly unreacted dibromoethane. The fraction boiling at 134 °C (ca. 15.5 Torr) was 2,4-dibromo-6-isopropylphenoxyethyl bromide which solidified on cooling. It was identified by its ^{13}C NMR spectrum.

To 15 mmol of this material, dissolved in 100 mL of dry tetrahydrofuran plus 25 mL of cyclohexane (both solvents distilled from sodium benzophenone ketyl) in a dry nitrogen atmosphere at −100 °C (methanol–liquid nitrogen bath), was slowly added with stirring 17 mmol of *n*-butyllithium (2.5 M in hexane) at such a rate that the temperature did not rise by more than 5 °C. Stirring was continued at −100 °C for another 30 min before an additional 17-mmol portion of *n*-butyllithium in hexane was added. Following this, the reaction mixture was stirred for 1 h at −100 °C. Then it was quenched by slowly adding 30 mmol of methanol in 20 mL of THF. Stirring was continued for another 30 min, and then the mixture was allowed to come to room temperature. It was poured into 150 mL of water, the layers were separated, and the aqueous phase was extracted three times with 150 mL of ether. The ether extracts and organic layer were combined, dried over anhydrous $MgSO_4$, concentrated to a smaller volume at room temperature using a rotary evaporator, and fractionally distilled from CaH_2 under reduced pressure. The first fraction was residual THF; the second, 7-isopropyl-2,3-dihydrobenzofuran **3d**, bp 79–81 °C (15 Torr), was identified by its ^{13}C NMR spectrum.

NMR Measurements. A series of ^{13}C NMR spectra of 0.5 M solutions of the anisoles in $CDCl_3$, titrated with successive portions of TFA, were recorded at 301 ± 2 K on a Bruker WN-250 (5-mm tubes) spectrometer, operating at 62.9 MHz. The peaks of the base were referenced to internal cyclohexane (1%, v/v) because of the reported sensitivity of the ^{13}C chemical shift of Me_4Si to medium and temperature effects.[48] The conversion to the TMS scale is $\delta(^{13}C(Me_4Si)) = \delta(^{13}C(C_6H_{12})) + 26.92$ ppm.

Peak assignments were based on coupled spectra, the attached proton test, and comparisons with peak assignments in similar systems.

Variable-Temperature Titrations of 3a. Four sets of ^{13}C NMR spectra were obtained by titrating **3a**, 0.5 M in $CDCl_3$ containing 1% (v/v) each of Me_4Si and C_6H_{12}, with successive portions of TFA at 250, 263, 280, and 301 K. The peaks of **3a** were referenced to the internal C_6H_{12}. The chemical shift of Me_4Si, relative to C_6H_{12} in deuteriochloroform solutions of **3a** containing no TFA, varied linearly with temperature: $\delta^T(^{13}C(Me_4Si)) = -0.00469T + 1.37856$ ppm (correlation coefficient, 0.998). In each titration of **3a** the shift of Me_4Si relative to C_6H_{12} moved upfield with increasing stoichiometric acid:base ratio. Plots of these shifts versus the acid:base ratio at the four temperatures were parallel curves with a vertical separation of ca. $0.00469\Delta T$. Thus, after the addition of each aliquot of TFA in the titration of **3a**, return of the sample to the proper temperature could be monitored by observing the position of the Me_4Si signal.

The chemical shift of the para carbon of **3a**, 0.5 M in TFA containing 1% (v/v) C_6H_{12} plus 5% (v/v) Me_4Si, was measured relative to internal C_6H_{12} at six temperatures giving the correlation: $\delta^{TFA}C4(\mathbf{3a}) = -0.00329T + 123.7842$ ppm (correlation coefficient, 0.992). This relation was used to obtain the para carbon shift change associated with fully hydrogen bonding **3a** in neat TFA (ΔC in eq 2) at each of the four temperatures at which the titration was carried out.

Acknowledgment. The author wishes to express her special thanks to Professor Kurt Mislow (Princeton University) for his generosity in providing her access to the NMR facility at Princeton University.

Supplementary Material Available: Substituent chemical shifts of the alkyl groups of arenes in deuteriochloroform, TFA, and TFE (Table V) and ^{13}C NMR shifts of cyclic ethers **3** and **4′** in deuteriochloroform and in TFA (Tables VI and VII) (the corresponding chemical shifts for **1** and **2** have been deposited previously[14]) (3 pages). Ordering information is given on any current masthead page.

(48) Ziessow, D.; Carroll, M. *Ber. Bunsenges.* **1972**, *76*, 61.

Isotactic Polymethoxy-1-alkenes from Blue-Green Algae. Synthesis and Absolute Stereochemistry

Yuji Mori,* Yasunori Kohchi, and Makoto Suzuki

Faculty of Pharmacy, Meijo University, Tempaku, Nagoya 468, Japan

Shmuel Carmeli, Richard E. Moore, and Gregory M. L. Patterson

Department of Chemistry, University of Hawaii, Honolulu, Hawaii 96822

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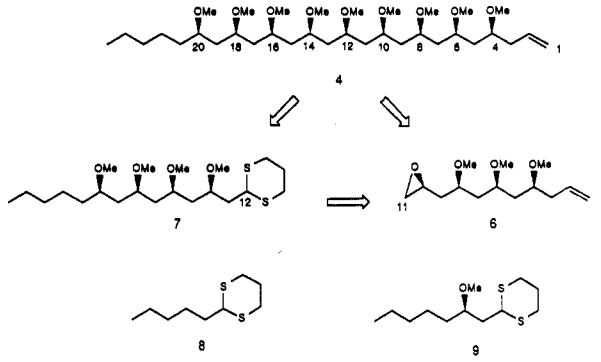
Novel isotactic polymethoxy-1-alkenes **1**–**4** were isolated from tolytoxin-producing blue-green algae belonging to the family Scytonemataceae. *Scytonema mirabile* produced **1** and **2**, whereas **3** and **4** were isolated from *S. burmanicum*. The gross structures and relative stereochemistries were determined by mass and NMR spectral analyses. The absolute configurations of **1**–**4** were established by direct comparison with optically active synthetic samples.

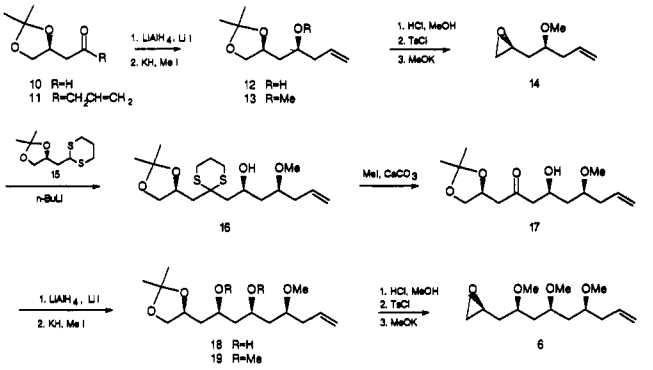
Isotactic polymethoxy-1-alkenes were first found in a field-collected sample of tolytoxin-producing blue-green alga *Tolypothrix conglutinata* var. *colorata* Ghose from Fanning Island.[1] Recently, however, we have been able

0022-3263/91/1956-0631$02.50/0

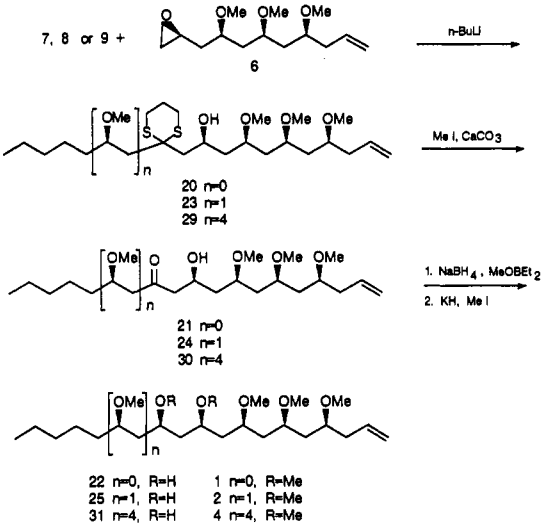
Scheme I



Scheme II

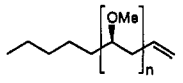


Scheme III



to isolate these compounds from several cultured, toly-toxin-producing blue-green algae belonging to the family scytonemataceae, e.g., *Scytonema mirabile* (Dillwyn) Bornet and *S. burmanicum* Skuja. 4,6,8,10,12-Pentamethoxy-1-heptadecene (1) and 4,6,8,10,12,14-hexamethoxy-1-nonadecene (2) were isolated from *S. mirabile*, whereas 4,6,8,10,12,14,16,18-octamethoxy-1-tricosene (3) and 4,6,8,10,12,14,16,18,20-nonamethoxy-1-pentacosene (4) were isolated from *S. burmanicum*. Compounds 3 and 4, along with a small amount of 4,6,8,10,12,14,16,18,20,22-decamethoxy-1-heptacosene (5), were the isotactic polymethoxy-1-alkenes that had been isolated from *T. conglutinata*. The gross structures and relative stereochemistries of 1–4 were determined by mass and NMR spectral analyses as previously described.[1]

In this paper we report the syntheses and absolute configurations of the polymethoxy-1-alkenes 1–4.



1 n=5
2 n=6
3 n=8
4 n=9
5 n=10

Syntheses of the four polymethoxy-1-alkenes required a convergent method, where use of a common synthetic intermediate would provide efficient routes to 1–4. As depicted in Scheme I, a logical retrosynthesis of 4 began with dissection of C(11)–C(12) to provide two segments 7 and 6. As the dithioacetal group of 7 could be obtained from a terminal olefin, segment 7 could be further dissembled into segment 6 and a C_4 unit upon disconnection at the C(21)–C(22). Polymethoxyalkenes 1 and 2 could be accessed by using epoxide 6 and the dithiane anions from 8 and 9, respectively, and contraction of 4 would provide octamethoxy compound 3. Thus, 6 was chosen to be the common synthetic intermediate.

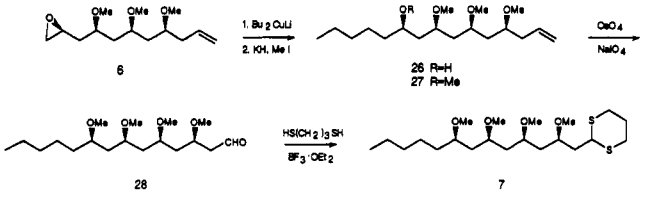
Synthesis of Key Intermediate 6. Our route to 6, which utilizes lithium aluminum hydride–lithium iodide reduction of β-alkoxy ketones to provide syn-1,3-diols,[2] is shown in Scheme II. Reduction of ketone 11, prepared from the aldehyde 10, with lithium aluminum hydride in the presence of lithium iodide afforded, after separation of the major diastereoisomer from the 94:6 mixture, compound 12 (84%), which was methylated to give 13 in 99% yield. Conversion of the ketal 13 into epoxide 14 was achieved in 65% overall yield by routine synthetic operations, viz. acetal hydrolysis, tosylation, and cyclization. The epoxide was treated with the lithium salt of the dithiane 15, which is a useful chiral building block for 1,3-polyol synthesis,[3] to provide hydroxydithiane 16 (91%). Removal of the dithioketal group with methyl iodide and calcium carbonate in aqueous acetonitrile gave hydroxy ketone 17 in 95% yield. Alkoxy-directed reduction of 17 with lithium aluminum hydride–lithium iodide led to a 96:4 mixture of separable diastereoisomers, the major one being the desired 18 (89%). Synthesis of the key intermediate 6 was completed in 62% overall yield by methylation of the diol to 19 followed by three steps to form the oxirane.

Synthesis of 4,6,8,10,12-Pentamethoxy-1-heptadecene. The synthesis of optically active 1 is summarized in Scheme III. Coupling of epoxide 6 with the anion generated from 2-pentyl-1,3-dithiane (8) and *n*-butyllithium gave bisalkylated dithiane 20 (60%) and deprotection of the dithioketal group provided hydroxy ketone 21 in 72% yield. Highly stereoselective reduction of the C(12) keto functionality to the desired 12*R* stereochemistry was effected by using a syn-stereoselective reduction with sodium borohydride–diethylmethoxyborane[4] at −70 °C, giving diol 22 in 79% yield. The selectivity of the reduction was syn:anti = 98:2, judging from the ^{1}H NMR spectrum in benzene-d_6 where the methoxy signals of the reduction products were nicely separated. Finally, methylation of 22 afforded (4*S*,6*S*,8*R*,10*R*,12*R*)-4,6,8,10,12-pentamethoxy-1-heptadecene (1), $[\alpha]_D$ +7.57° ($CHCl_3$), in 90% yield.

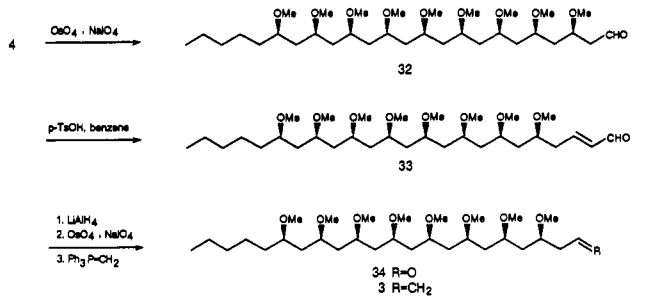
Natural 1 had a specific rotation of $[\alpha]_D$ +7.39° ($CHCl_3$) and a ^{1}H NMR spectrum identical with those of synthetic

(1) Mynderse, J. S.; Moore, R. E. *Phytochemistry* **1979**, *18*, 1181.
(2) Mori, Y.; Tekeuchi, A.; Kageyama, H.; Suzuki, M. *Tetrahedron Lett.* **1988**, *29*, 5423.
(3) Mori, Y.; Kuhara, M.; Takeuchi, A.; Suzuki, M. *Tetrahedron Lett.* **1988**, *29*, 5419.
(4) Chen, K.-M.; Hardtmann, G. E.; Prasad, K.; Repic, O.; Shapiro, M. J. *Tetrahedron Lett.* **1987**, *28*, 155.

Scheme IV



Scheme V



1, indicating that the absolute configuration of 1 is as shown.

Synthesis of 4,6,8,10,12,14-Hexamethoxy-1-nonadecene. The synthesis of the hexamethoxy derivative 2 was carried out in a similar manner as described for the pentamethoxy compound 1 (Scheme III). Addition of the lithiated dithiane 9, prepared from (*S*)-(−)-butane-1,2,4-triol,[5] to epoxide 6 gave alcohol 23 (58%), which was deprotected to hydroxy ketone 24 in 80% yield. Syn-stereoselective reduction of 24 with sodium borohydride–diethylmethoxyborane[4] (syn:anti = 94:6) followed by methylation gave the hexamethoxy-1-nonadecene (2), $[\alpha]_D$ +6.26° ($CHCl_3$), in 80% overall yield. Comparison of the ^1H NMR spectrum and the specific rotation, $[\alpha]_D$ +6.23° ($CHCl_3$), of the natural sample with those of the synthetic compound led to the absolute configuration of 4*S*,6*S*,8*S*,10*R*,12*R*,14*R* for natural 2.

Synthesis of 4,6,8,10,12,14,16,18,20-Nonamethoxy-1-pentacosene. Nonamethoxy-1-pentacosene (4) has recently been synthesized in optically active form by Oishi and his co-workers.[6] As shown in Scheme I the nonamethoxy compound could arise from two segments 6 and 7, each having four stereocenters with a 1,3-relationship. Segment 7 could be prepared from 6, the key intermediate of our synthesis (Scheme IV).

Treatment of epoxide 6 with (di-*n*-butylcopper)lithium afforded alcohol 26 (87%), which was methylated to give tetramethoxy olefin 27 in 96% yield. The terminal olefin was cleaved by Lemieux–Johnson oxidation[7] and the resulting aldehyde 28 was protected as its dithioacetal to obtain the segment 7 in 80% yield. The final bond connection was achieved by the coupling 6 and lithiated 7 to yield 29 in 64% yield. Removal of the dithioketal group afforded hydroxy ketone 30 (96%). Synthesis of 4 was completed by 1,3-syn-stereoselective reduction[4] of 30 followed by methylation of diol 31 (86% in two steps).

The ^1H NMR spectra and specific rotations of synthetic and natural samples were identical: the $[\alpha]_D$ values of synthetic and natural 4 were found to be +4.45° ($CHCl_3$) and +4.73° ($CHCl_3$), respectively. Therefore, 4 is (4*S*,6*S*,8*S*,10*S*,12*R*,14*R*,16*R*,18*R*,20*R*)-nonamethoxy-1-pentacosene.

Synthesis of 4,6,8,10,12,14,16,18-Octamethoxy-1-tricosene. Nonamethoxy compound 4 was converted to octamethoxy derivative 3 as outlined in Scheme V. Oxidative cleavage of the double bond of 4 gave aldehyde 32 (83%). Elimination of the C(4) methoxy group by heating 32 with *p*-toluenesulfonic acid to 50 °C in benzene afforded unsaturated aldehyde 33 in 51% yield (77% based on consumed starting material). Since the second oxidative cleavage of the conjugated double bond of 33 by Lemieux–Johnson oxidation[7] resulted in a low yield of 34, the carbonyl group of 33 was first reduced with lithium aluminum hydride and the resulting allylic alcohol was subjected to Lemieux–Johnson oxidation to give aldehyde 34 in 72% overall yield. Condensation of 34 with methylenetriphenylphosphorane accomplished the synthesis of octamethoxy-1-tricosene 3 in 80% yield.

Comparison of synthetic 3, $[\alpha]_D$ +5.22° ($CHCl_3$), with the natural sample, $[\alpha]_D$ +5.44° ($CHCl_3$), established the 4*S*,6*S*,8*S*,10*S*,12*R*,14*R*,16*R*,18*R* configuration for 3.

In conclusion, novel isotactic polymethoxy-1-alkenes 1–4 have been isolated from the tolytoxin-producing blue-green algae *S. mirabile* and *S. burmanicum* and their absolute configurations established unambiguously by synthesis.

Experimental Section

Spectral Analysis. NMR spectra were determined on a GN-OMEGA instrument operating at 500 Mz for proton and 125 Mz for carbon-13 and on a JEOL JNM-GX 400 instrument operating at 400 MHz for proton and 100 MHz for carbon-13. Proton chemical shifts are referenced in benzene-d_6 to the residual benzene signal (7.15 ppm) and in chloroform-*d* to TMS (0 ppm); ^{13}C chemical shifts are referenced in benzene-d_6 to the solvent signal (128 ppm). Homonuclear ^1H connectivities were determined by using the COSY experiment. Heteronuclear ^1H–^{13}C connectivities were determined by heteronuclear multiple quantum coherence (HMQC) and heteronuclear multiple bond connectivity (HMBC) experiments.[8,9] IR spectra were measured in chloroform. Mass spectra, including high resolution mass measurements, were determined in either the EI, FD, or FAB mode with a VG Analytical 70 SE instrument equipped with a 11-250J data system and in the CI mode with a Shimadzu GCMS QP-1000 instrument. Optical rotations were determined on a JASCO DIP-181 digital polarimeter.

Culture Conditions. *S. mirabile*, designated strain number BY-8-1, was cultured as described elsewhere.[10] Yields of lyophilized cells averaged 0.125 g/L of culture.

An aerial form of *S. burmanicum*, designated strain number D0-4-1, was isolated from an algal sample at Moon Beach, Okinawa. The alga was mass cultivated in 20–25-L glass bottles using the procedure described for *Hapalosiphon fontinalis*.[11] Harvest times were typically 28–32 days. Yields of lyophilized cells averaged 0.22 g/L of culture.

Isolation. Isotactic 4,6,8,10,12-pentamethoxy-1-heptadecene (1) and 4,6,8,10,12,14-hexamethoxy-1-nonadecene (2) were isolated in 0.12 and 0.04% yields, respectively, from *S. mirabile* as previously described.[10]

Isotactec 4,6,8,10,12,14,16,18-octamethoxy-1-tricosene (3) and 4,6,8,10,12,14,16,18,20-nonamethoxy-1-pentacosene (4) were isolated from *S. burmanicum* as follows: Freeze-dried alga (49 g) was extracted with 3 × 2 L portions of 7:3 EtOH/water (24 h for each extraction). The total extract (5.2 g) was flash chromato-

(5) Mori, K.; Takigawa,T.; Matsuo, T. *Tetrahedron* **1979**, *35*, 933. Treatment of (3*S*)-3,4-dihydroxybutanal acetonide with 1,3-propanedithiol and boron trifluoride etherate in CH_2Cl_2 for 12 h and, then, 2,2-dimethoxypropane for 30 min gave 9 in 76% yield.

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(9) Bax, A.; Summers, M. F. *J. Am. Chem. Soc.* **1986**, *108*, 2093.

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graphed on a RP-18 column (60 mL of YMC-GEL, ODS 120A). The chromatogram was developed with 300 mL of each of the following solvents: H_2O followed by 3:7, 1:1, 1:3, and 1:9 H_2O/MeOH mixtures, MeOH, MeCN, and ethyl acetate. Eight fractions (300 mL each) were collected.

Fraction 5 from the RP-18 column was further flash chromatographed on a silica gel column (EM Science kieselgel 60, 230–400 mesh, 60 mL). The column was eluted with 6:4 hexane/ethyl acetate and fractions of 100 mL were collected. The third fraction contained pure **3** (325 mg) and the fifth fraction contained pure **4** (255 mg). A mixture of **3** and **4** (105 mg) was in the fourth fraction.

The polymethoxy-1-alkenes had the following R_f values on silica gel (kieselgel 60 F_{254}) plates using 30% ethyl acetate/hexane: **1**, 0.35; **2**, 0.21; **3**, 0.10; **4**, 0.06. The spots were visualized with 1% ceric sulfate/10% H_2SO_4.

4,6,8,10,12-Pentamethoxy-1-heptadecene (1): $[\alpha]^{25}_D$ +7.39° (c = 0.77, $CHCl_3$); ^1H NMR (500 MHz, benzene-d_6) δ 5.12 (ddt, J = 17.1, 2.5 and 1.2 Hz, H-1Z), 5.08 (br d, J = 10.0, 2.0, and 1.2 Hz, H-1E), 5.90 (ddt, J = 17.1, 10.0, and 7.0 Hz, H-2), 2.31 (dddd, J = 1.2, 2.5, 5.4, and 7.0 Hz, H-3 and H-3′), 3.39 (m, H-4), 3.19 (s, OMe on C-4), 1.68 (m, H-5), 1.95 (m, H-5′), 3.58 (m, H-6), 3.22 (s, OMe on C-6), 1.75 (m, H-7), 2.00 (m, H-7′), 3.60 (m, H-8), 3.24 (s, OMe on C-8), 1.75 (m, H-9), 2.00 (m, H-9′), 3.60 (m, H-10), 3.25 (s, OMe on C-10), 1.65 (m, H-11), 1.96 (m, H-11′), 3.36 (m, H-12), 3.23 (s, OMe on C-12), 1.44 (m, H-13), 1.57 (m, H-13′), 1.43 (m, H-14), 1.55 (m, H-14′), 1.31 (m, H-15), 1.43 (m, H-15′), 1.33 (m, H-16 and H-16′), 0.92 (t, J = 7.0 Hz, H_3-17); ^{13}C NMR (125 MHz, benzene-d_6) δ (multiplicity, carbon position) 117.00 (t, C-1), 135.23 (d, C-2), 38.18 (t, C-3), 77.55 (d, C-4), 56.11 (q, OMe on C-4), 37.95 (t, C-5), 75.56 (d, C-6), 55.88 (q, OMe on C-6), 38.40 (t, C-7), 75.68 (d, C-8), 55.91 (q, OMe on C-8), 38.43 (t, C-9), 75.71 (d, C-10), 55.91 (q, OMe on C-10), 38.26 (t, C-11), 78.06 (d, C-12), 56.00 (q, OMe on C-12), 33.88 (t, C-13), 25.02 (t, C-14), 32.47 (t, C-15), 23.04 (t, C-16), 14.26 (q, C-17); FDMS m/z (intensity) 389 (MH^+, 38.5), 347 ($MH^+ - C_3H_6$, 100); FABMS m/z 389 (MH^+), 357 (MH^+ – MeOH), 325 (MH^+ – 2MeOH), 293 (MH^+ – 3MeOH), 261 (MH^+ – 4MeOH), 229 (MH^+ – 5MeOH).

4,6,8,10,12,14-Hexamethoxy-1-nonadecene (2): $[\alpha]^{25}_D$ +6.23° (c = 0.30, $CHCl_3$); ^1H NMR (500 MHz, benzene-d_6) δ 5.12 (ddt, J = 17.1, 2.5, and 1.2 Hz, H-1Z), 5.08 (br d, J = 10.0, 2.0, and 1.2 Hz, H-1E), 5.90 (ddt, J = 17.1, 10.0, and 7.0 Hz, H-2), 2.31 (dddd, J = 1.2, 2.5, 5.4, and 7.0 Hz, H-3 and H-3′), 3.39 (m, H-4), 3.16 (s, OMe on C-4), 1.68 (m, H-5), 1.95 (m, H-5′), 3.58 (m, H-6), 3.20 (s, OMe on C-6), 1.75 (m, H-7) 2.00 (m, H-7′), 3.60 (m, H-8), 3.23 (s, OMe on C-8), 1.75 (m, H-9), 2.00 (m, H-9′), 3.60 (m, H-10), 3.24 (s, OMe on C-10), 1.75 (m, H-11), 2.00 (m, H-11′), 3.60 (m, H-12), 3.25 (s, OMe on C-12), 1.65 (m, H-13), 1.96 (m, H-13′), 3.36 (m, H-14), 3.21 (s, OMe on C-14), 1.44 (m, H-15), 1.57 (m, H-15′), 1.43 (m, H-16), 1.55 (m, H-16′), 1.31 (m, H-17), 1.43 (m, H-17′), 1.33 (m, H-18 and 18′), 0.92 (t, J = 7.0 Hz, H_3-19); ^{13}C NMR (125 MHz, benzene-d_6) δ (multiplicity, carbon position) 117.02 (t, C-1), 135.24 (d, C-2), 38.21 (t, C-3), 77.58 (d, C-4), 56.15 (q, OMe on C-4), 38.02 (t, C-5), 75.62 (d, C-6), 55.90 (q, OMe on C-6), 38.57 (t, C-7), 75.72 (d, C-8), 55.95 (q, OMe on C-8), 38.61 (t, C-9), 75.72 (d, C-10), 55.95 (q, OMe on C-10), 38.61 (t, C-11), 75.79 (d, C-12), 55.95 (q, OMe on C-12), 38.32 (t, C-13), 78.10 (d, C-14), 56.06 (q, OMe on C-14), 33.93 (t, C-15), 25.08 (t, C-16), 32.51 (t, C-17), 23.09 (t, C-18), 14.28 (q, C-19): FDMS m/z (intensity) 447 (MH^+, 45), 405 ($MH^+ - C_3H_6$, 100).

4,6,8,10,12,14,16,18-Octamethoxy-1-tricosene (3): $[\alpha]^{25}_D$ +5.44° (c = 0.50, $CHCl_3$); ^1H NMR (500 MHz, benzene-d_6) δ 5.12 (ddt, J = 17.1, 2.5, and 1.2 Hz, H-1Z), 5.08 (br d, J = 10.0, 2.0, and 1.2 Hz, H-1E), 5.90 (ddt, J = 17.1, 10.0, and 7.0 Hz, H-2), 2.31 (dddd, J = 1.2, 2.5, 5.4, and 7.0 Hz, H-3 and H-3′), 3.39 (m, H-4), 3.15 (s, OMe on C-4), 1.68 (m, H-5), 1.95 (m, H-5′), 3.58 (m, H-6), 3.19 (s, OMe on C-6), 1.75 (m, H-7), 2.00 (m, H-7′), 3.60 (m, H-8), 3.22 (s, OMe on C-8), 1.75 (m, H-9), 2.00 (m, H-9′), 3.60 (m, H-10), 3.23 (s, OMe on C-10), 1.75 (m, H-11), 2.00 (m, H-11′), 3.60 (m, H-12), 3.25 (s, OMe on C-12), 1.75 (m, H-13), 2.00 (m, H-13′), 3.60 (m, H-14), 3.25 (s, OMe on C-14), 1.75 (m, H-15), 2.00 (m, H-15′), 3.60 (m, H-16), 3.25 (s, OMe on C-16), 1.65 (m, H-17), 1.96 (m, H-17′), 3.36 (m, H-18), 3.20 (s, OMe on C-18), 1.44 (m, H-19), 1.57 (m, H-19′), 1.43 (m, H-20), 1.55 (m, H-20′), 1.31 (m, H-21), 1.43 (m, H-21′), 1.33 (m, H-22 and 22′), 0.92 (t, J = 7.0 Hz, H_3-23); ^{13}C NMR (125 MHz, benzene-d_6) δ (multiplicity, carbon position) 117.01 (t, C-1), 135.22 (d, C-2), 38.21 (t, C-3), 77.56 (d, C-4), 56.13 (q, OMe on C-4), 38.00 (t, C-5), 75.58 (d, C-6), 55.90 (q, OMe on C-6), 38.57 (t, C-7), 75.70 (d, C-8), 55.95 (q, OMe on C-8), 38.60 (t, C-9), 75.70 (d, C-10), 55.95 (q, OMe on C-10), 38.60 (t, C-11), 75.70 (d, C-12), 55.95 (q, OMe on C-12), 38.60 (t, C-13), 75.70 (d, C-14), 55.95 (q, OMe on C-14), 38.60 (t, C-15), 75.79 (d, C-16), 55.95 (q, OMe on C-16), 38.32 (t, C-17), 78.10 (d, C-18), 56.06 (q, OMe on C-18), 33.93 (t, C-19), 25.08 (t, C-20), 32.51 (t, C-21), 23.09 (t, C-22), 14.28 (q, C-23).

4,6,8,10,12,14,16,18,20-Nonamethoxy-1-pentacosene (4): $[\alpha]^{25}_D$ +4.73° (c = 0.43, $CHCl_3$); ^1H NMR (500 MHz, benzene-d_6) δ 5.12 (ddt, J = 17.1, 2.5, and 1.2 Hz, H-1Z), 5.08 (br d, J = 10.0, 2.0, and 1.2 Hz, H-1E), 5.90 (ddt, J = 17.1, 10.0, and 7.0 Hz, H-2), 2.31 (dddd, J = 1.2, 2.5, 5.4, and 7.0 Hz, H-3 and H-3′), 3.39 (m, H-4), 3.15 (s, OMe on C-4), 1.68 (m, H-5), 1.95 (m, H-5′), 3.58 (m, H-6), 3.19 (s, OMe on C-6), 1.75 (m, H-7), 2.00 (m, H-7′), 3.60 (m, H-8), 3.22 (s, OMe on C-8), 1.75 (m, H-9), 2.00 (m, H-9′), 3.60 (m, H-10), 3.23 (s, OMe on C-10), 1.75 (m, H-11), 2.00 (m, H-11′), 3.60 (m, H-12), 3.25 (s, OMe on C-12), 1.75 (m, H-13), 2.00 (m, H-13′), 3.60 (m, H-14), 3.25 (s, OMe on C-14), 1.75 (m, H-15), 2.00 (m, H-15′), 3.60 (m, H-16), 3.25 (s, OMe on C-16), 1.75 (m, H-17), 2.00 (m, H-17′), 3.60 (m, H-18), 3.26 (s, OMe on C-18), 1.65 (m, H-19), 1.96 (m, H-19′), 3.36 (m, H-20), 3.20 (s, OMe on C-20), 1.44 (m, H-21), 1.57 (m, H-21′), 1.43 (m, H-22), 1.55 (m, H-22′), 1.31 (m, H-23), 1.43 (m, H-23′), 1.33 (m, H-24 and 24′), 0.92 (t, J = 7.0 Hz, H_3-25); ^{13}C NMR (125 MHz, benzene-d_6) δ (multiplicity, carbon position) 117.02 (t, C-1), 135.23 (d, C-2), 38.21 (t, C-3), 77.56 (d, C-4), 56.13 (q, OMe on C-4), 38.00 (t, C-5), 75.56 (d, C-6), 55.90 (q, OMe on C-6), 38.57 (t, C-7), 75.70 (d, C-8), 55.95 (q, OMe on C-8), 38.60 (t, C-9), 75.70 (d, C-10), 55.95 (q, OMe on C-10), 38.60 (t, C-11), 75.70 (d, C-12), 55.95 (q, OMe on C-12), 38.60 (t, C-13), 75.70 (d, C-14), 55.95 (q, OMe on C-14), 38.60 (t, C-15), 75.70 (d, C-16), 55.95 (q, OMe on C-16), 38.60 (t, C-17), 75.79 (d, C-18), 55.95 (q, OMe on C-18), 38.32 (t, C-19), 78.11 (d, C-20), 56.06 (q, OMe on C-20), 33.93 (t, C-21), 25.08 (t, C-22), 32.51 (t, C-23), 23.09 (t, C-24), 14.28 (q, C-25).

Uniform ^{13}C Enrichment of 1. *S. mirabile* BY-8-1 was grown in a 10-L glass vessel containing 8 L of an inorganic medium from which buffer had been omitted and 4.0 g of $Na^{15}NO_3$ (99 atom %) was added as the sole nitrogen source. The culture was stirred, incubated at 24 ± 2 °C, illuminated at an incident intensity of 150 mEinstein m^{-2} s^{-1} with cool-white fluorescent lighting for a continuous period of 16 h per day, and aerated at roughly 100 mL/min with ordinary air (no extra CO_2 added). The culture vessel was equipped with acid (0.5 N HCl) and base ($NaH^{13}CO_3$ solution) addition ports and an autoclavable pH electrode. The pH was kept at 7.85 ± 0.05 by continuous monitoring with a pH controller and automatic addition of acid. A 1-L aqueous solution of 5.0 g of $NaH^{13}CO_3$ (99 atom %) was added continuously over 26 days.

After 28 days, the 8-L culture (medium and cells) was lyophilized and the solid residue extracted twice with 1 L of ethanol/water (7:3) for 12 h. Workup as described above resulted in the isolation of ^{13}C-labeled **1** (5.1 mg); inspection of its ^{13}C NMR spectrum indicated uniform ^{13}C enrichment to about 37%. Unambiguous assignments of all the carbon signals of **1** could be made from the INADEQUATE spectrum.

(2*S*,6*S*,8*S*)-1,2-*O*-Isopropylidene-8-methoxy-4-(trimethylenedithio)-10-undecene-1,2,6-triol (16). To a stirred solution of 2-[(2*S*)-2,3-*O*-isopropylidene-2,3-dihydroxypropyl]-1,3-dithiane (**15**) (1.67 g, 7.1 mmol) in dry THF (20 mL) at −40 °C under nitrogen was added 1.6 M *n*-butyllithium in hexane (5 mL, 8 mmol). The solution was stirred at −30 °C for 2 h and then a solution of **14**[10] (924 mg, 6.5 mmol) in dry THF (5 mL) was added. The reaction vessel was closed under a positive pressure of nitrogen and stored at −20 °C for 43 h. The reaction mixture was quenched with aqueous NH_4Cl and extracted with ether. The extract was washed with water and brine, dried ($MgSO_4$), and evaporated. Flash chromatography (15–20% ethyl acetate/hexane) gave **16** (2.05 g, 87%): $[\alpha]^{25}_D$ +25.22° (c = 1.0, $CHCl_3$); IR ($CHCl_3$) 3450, 1635, 1420, 1375, 1365, 1230, 1080, 915 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.34 (3 H, s, Me), 1.39 (3 H, s, Me), 1.56 (1 H, ddd, J = 14.1, 4.6, and 2.9 Hz), 1.74 (1 H, ddd, J = 14.1, 9.5, and 8.3 Hz), 1.88–2.38 (8 H), 2.75–3.00 (4 H), 3.37 (3 H, s, OMe), 3.52 (1 H, m), 3.55 (1 H, t, J = 8.1 Hz), 3.82 (1 H, d, J = 1.2 Hz, OH), 4.13 (1 H, dd, J = 8.1 and 6.1 Hz), 4.15 (1

H, m), 4.40 (1 H, m), 5.09 (1 H, br d, J = 10.2 Hz), 5.10 (1 H, br d, J = 17.1 Hz), 5.80 (1 H, ddt, J = 17.1, 10.2, and 7.1 Hz); high-resolution EIMS m/z 376.1752 (M^+), calcd for $C_{18}H_{32}O_4S_2$, mmu error 1.2.

(2*S*,6*S*,8*S*)-1,2-*O*-Isopropylidene-8-methoxy-4-oxo-10-undecene-1,2,6-triol (17). To a stirred solution of **16** (580 mg, 1.5 mmol) in 80% aqueous MeCN (60 mL) were added $CaCO_3$ (1.54 g, 15 mmol) and MeI (9.6 mL, 154 mmol). The mixture was stirred for 22 h at room temperature, diluted with ethyl acetate, and filtered through a short column of Celite. The filtrate was concentrated and the residue was purified by flash chromatography (30–40% ethyl acetate/hexane) to give **17** (403 mg, 92%): $[\alpha]^{25}_D$ −53.07° (c = 0.6, $CHCl_3$); IR ($CHCl_3$) 3540, 1700, 1375, 1365, 1220, 1075, 915 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.34 (3 H, s, Me), 1.39 (3 H, s, Me), 1.62 (2 H, m), 2.31 (2 H, br t, J = 7.3 Hz), 2.52 (1 H, dd, J = 16.4 and 4.6 Hz), 2.62 (1 H, dd, J = 11.0 and 6.8 Hz), 2.66 (1 H, dd, J = 11.0 and 8.1 Hz), 3.37 (3 H, s, OMe), 3.52 (1 H, m), 3.53 (1 H, dd, J = 8.3 and 6.8 Hz), 3.74 (1 H, br s, OH), 4.17 (1 H, dd, J = 8.3 and 6.1 Hz), 4.23 (1 H, m), 4.46 (1 H, quintet, J = 6.4 Hz), 5.08 (1 H, br d, J = 9.8 Hz), 5.09 (1 H, br d, J = 17.6 Hz), 5.76 (1 H, ddt, J = 17.6, 9.8, and 7.1 Hz); CIMS (isobutane) m/z 287 (MH^+), 269 ($MH^+ - H_2O$).

(2*S*,4*S*,6*S*,8*S*)-1,2-*O*-Isopropylidene-8-methoxy-10-undecene-1,2,4,6-tetrol (18). To a stirred solution of **17** (610 mg, 2.13 mmol) and LiI (1.8 g, 12.3 mmol) in dry ether (60 mL) at −100 °C was added $LiAlH_4$ (0.78 g, 21 mmol). The reaction mixture was stirred for 1.5 h at −100 °C under nitrogen and then warmed gradually to −70 °C. Excess $LiAlH_4$ was decomposed by addition of ethyl acetate (5 mL) and 1 N NaOH. The mixture was then stirred at room temperature until the precipitates aggregated. The organic layer was separated and extracted with ethyl acetate. The extract was washed with brine, dried ($MgSO_4$), and evaporated. The residue was purified by flash chromatography (10–15% acetone/CH_2Cl_2) to give **18** (518 mg, 85%): $[\alpha]^{25}_D$ +38.12° (c = 1.0, $CHCl_3$); IR ($CHCl_3$) 3460, 1618, 1425, 1380, 1190, 920 cm1−1; ^1H NMR (400 MHz, benzene-d_6) δ 1.31 (3 H, s, Me), 1.39 (3 H, s, Me), 1.28 (1 H, dt, J = 13.0 and 2.4 Hz), 1.34 (3 H, ddd, J = 14.4, 3.9, and 2.7 Hz), 1.54 (1 H, ddd, J = 14.4, 5.1, and 3.9 Hz), 1.63 (1 H, td, J = 9.8 and 2.4 Hz), 1.66 (1 H, td, J = 9.8 and 2.0 Hz), 1.78 (1 H, dt, J = 13.0 and 7.8 Hz), 2.12 (2 H, dd, J = 6.8 and 5.6 Hz), 2.96 (3 H, s, OMe), 3.22 (1 H, m), 3.46 (1 H, t, J = 7.8 Hz), 3.91 (1 H, dd, J = 8.1 and 5.9 Hz), 3.92 (1 H, m), 4.02 (1 H, m), 4.11 (1 H, br s, OH), 4.14 (1 H, br s, OH), 4.20 (1 H, tt, J = 7.6 and 5.6 Hz), 5.02 (1 H, br d, J = 17.0 Hz), 5.02 (1 H, br d, J = 10.3 Hz), 5.70 (1 H, ddt, J = 17.0, 10.3, and 7.1 Hz); CIMS (isobutane) m/z 289 (MH^+); high-resolution EIMS m/z 273.1741 (M^+ − Me), calcd for $C_{14}H_{25}O_5$, mmu error 4.1.

(2*S*,4*S*,6*S*,8*S*)-1,2-*O*-Isopropylidene-4,6,8-trimethoxy-10-undecene-1,2-diol (19). To a stirred solution of **18** (684 mg, 2.37 mmol) in dry THF (20 mL) at 0 °C were added excess KH and MeI (2.0 mL), and the reaction mixture was stirred for 1 h. The excess KH was decomposed by addition of MeOH (1.5 mL), and the mixture was extracted with ethyl acetate. The extract was washed with water and brine, dried ($MgSO_4$), and evaporated. The oily residue was purified by flash chromatography (17% ethyl acetate/hexane) to give **19** (698 mg, 93%): $[\alpha]^{25}_D$ +33.67° (c = 1.0, $CHCl_3$); IR ($CHCl_3$) 1635, 1240, 1080, 915 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.35 (3 H, s, Me), 1.41 (3 H, s, Me), 1.58 (1 H, ddd, J = 14.2, 6.4, and 5.1 Hz), 1.64 (2 H, m), 1.73 (1 H, ddd, J = 14.2, 6.4, and 5.9 Hz), 1.82 (1 H, m), 1.92 (1 H, dt, J = 14.2 and 6.1 Hz), 2.31 (2 H, br t, J = 5.9 Hz), 3.29 (3 H, s, OMe), 3.30 (3 H, s, OMe), 3.33 (3 H, s, OMe), 3.36 (1 H, m), 3.41 (1 H, quintet, J = 5.9 Hz), 3.43 (1 H, quintet, J = 5.7 Hz), 3.52 (1 H, t, J = 7.8 Hz), 4.07 (1 H, dd, J = 7.8 and 5.9 Hz), 4.22 (1 H, quintet, J = 6.4 Hz), 5.08 (1 H, br d, J = 10.0 Hz), 5.09 (1 H, br d, J = 17.1 Hz), 5.82 (1 H, ddt, J = 17.1, 10.0, and 7.1 Hz); CIMS (isobutane) m/z 317 (MH^+), 285 (MH^+ − MeOH), 253 (MH^+ − 2MeOH), 221 (MH^+ − 3MeOH). Anal. Calcd for $C_{17}H_{32}O_5$: C, 64.53; H, 10.19. Found: C, 64.93; H, 10.45.

(4*S*,6*S*,8*S*,10*S*)-10,11-Epoxy-4,6,8-trimethoxy-1-undecene (6). A solution of **19** (690 mg, 2.18 mmol) in MeOH (35 mL) and 5% HCl–MeOH (0.5 mL) was allowed to stand for 18 h at room temperature. After removal of the solvent the residue was purified by flash chromatography (2% MeOH/ethyl acetate) to give a diol (553 mg, 92%). To a stirred solution of the diol (552 mg, 2.0 mmol) in pyridine (6 mL) at 0 °C was added p-toluenesulfonyl chloride (1.14 g, 6.0 mmol). The mixture was stirred for 2 h and extracted with ether. The extract was washed with water and brine, dried ($MgSO_4$), and evaporated in vacuo. Flash chromatography (40–50% ethyl acetate/hexane) gave a monotosylate (523 mg, 61%).

To a stirred solution of the tosylate (523 mg, 1.22 mmol) in ether (20 mL) and MeOH (4 mL) at 0 °C was added t-BuOK (192 mg, 1.71 mmol). The mixture was stirred for 30 min and extracted with ether. The extract was washed with water and brine, dried ($MgSO_4$), and evaporated. The oily residue was purified by flash chromatography (30% ethyl acetate/hexane) to give **6** (279 mg, 88%): $[\alpha]^{25}_D$ +20.70° (c = 0.6, $CHCl_3$); IR ($CHCl_3$) 1635, 1080, 915 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.56–1.92 (6 H), 2.31 (2 H, br t, J = 5.9 Hz), 2.49 (1 H, dd, J = 5.1 and 2.7 Hz), 2.78 (1 H, t, J = 4.9 Hz), 3.04 (1 H, m), 3.29 (3 H, s, OMe), 3.34 (6 H, s, OMe × 2), 3.37 (1 H, m), 3.44 (1 H, quintet, J = 6.1 Hz), 3.50 (1 H, quintet, J = 6.1 Hz), 5.09 (1 H, br d, J = 10.3 Hz), 5.10 (1 H, br d, J = 17.1 Hz), 5.82 (1 H, ddt, J = 17.1, 10.3, and 7.1 Hz); CIMS (isobutane) m/z 259 (MH^+), 227 (MH^+ − MeOH), 195 (MH^+ − 2MeOH). Anal. Calcd for $C_{14}H_{26}O_4$: C, 65.09; H, 10.14. Found: C, 65.39; H, 10.33.

(4*S*,6*S*,8*S*,10*S*)-4,6,8-Trimethoxy-12-(trimethylenedithio)-1-heptadecen-10-ol (20). To a stirred solution of **8** (263 mg, 1.38 mmol) in dry THF (5 mL) at −30 °C under nitrogen was added 1.6 M n-butyllithium in hexane (1.1 mL, 1.76 mmol.) The solution was stirred at −30 °C for 2 h and then a solution of **6** (77 mg, 0.29 mmol) in dry THF (3 ml) was added. The reaction vessel was closed under positive pressure of nitrogen and stored at −20 °C for 22 h. The reaction mixture was quenched with aqueous NH_4Cl and extracted with ethyl acetate. The extract was washed with water and brine, dried ($MgSO_4$), and evaporated. Flash chromatography (30% ethyl acetate/hexane) gave **20** (82 mg, 60%): $[\alpha]^{25}_D$ +32.9° (c = 1.0, $CHCl_3$); IR ($CHCl_3$) 3450, 1630, 1080 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.89 (3 H, t, J = 6.6 Hz), 1.28–2.20 (18 H), 2.30 (2 H, br t, J = 6.8 Hz), 2.74–3.00 (4 H), 3.29 (3 H, s, OMe), 3.32 (3 H, s, OMe), 3.34 (3 H, s, OMe), 3.35 (1 H, m), 3.42 (1 H, quintet, J = 6.1 Hz), 3.53 (1 H, quintet, J = 6.1 Hz), 3.78 (1 H, s, OH), 4.10 (1 H, m), 5.08 (1 H, br d, J = 10.0 Hz), 5.09 (1 H, br d, J = 17.3 Hz), 5.81 (1 H, ddt, J = 17.3, 10.0, and 7.3 Hz); CIMS (isobutane) m/z 449 (MH^+), 431 ($MH^+ - H_2O$), 417 (MH^+ − MeOH), 399 ($MH^+ - H_2O$ − MeOH), 385 (MH^+ − 2MeOH), 353 (MH^+ − 3MeOH).

(4*S*,6*S*,8*S*,10*S*)-12-Oxo-4,6,8-trimethoxy-1-heptadecen-10-ol (21). To a stirred solution of **20** (20 mg, 0.046 mmol) in 80% aqueous MeCN (3 mL) were added $CaCO_3$ (46 mg, 0.46 mmol) and MeI (0.3 mL, 4.8 mmol). The mixture was stirred for 15 h at room temperature, diluted with ethyl acetate, and filtered through a short column of Celite. The filtrate was concentrated and the residue was purified by flash chromatography (30% ethyl acetate/hexane) to give **21** (12 mg, 72%): $[\alpha]^{25}_D$ +46.7° (c = 0.72, $CHCl_3$); IR ($CHCl_3$) 1700, 1630, 1080, 915 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.89 (3 H, t, J = 6.8 Hz), 1.29 (4 H, m), 1.51–1.70 (7 H), 1.81 (2 H, m), 2.30 (2 H, br t, J = 6.5 Hz), 2.44 (2 H, t, J = 7.1 Hz), 2.51 (1 H, dd, J = 16.8 and 4.4 Hz), 2.61 (1 H, dd, J = 16.6 and 8.1 Hz), 3.29 (3 H, s, OMe), 3.33 (3 H, s, OMe), 3.34 (3 H, s, OMe), 3.35 (1 H, m), 3.40 (1 H, m), 3.57 (1 H, m), 3.72 (1 H, d, J = 1.9 Hz, OH), 4.22 (1 H, m), 5.08 (1 H, br d, J = 10.3 Hz), 5.09 (1 H, br d, J = 17.1 Hz), 5.80 (1 H, ddt, J = 17.1, 10.3, and 7.1 Hz); CIMS (isobutane) m/z 359 (MH^+), 341 ($MH^+ - H_2O$).

(4*S*,6*S*,8*R*,10*R*,12*R*)-4,6,8-Trimethoxy-1-heptadecene-10,12-diol (22). To a stirred solution of **21** (8 mg, 0.022 mmol) in dry THF (1 mL) and dry MeOH (0.25 mL) at −70 °C was added diethylmethoxyborane (0.01 mL, 0.1 mmol). After stirring for 15 min $NaBH_4$ (1.7 mg, 0.045 mmol) was added, and the solution was stirred at −70 °C for 3 h. The reaction mixture was quenched with acetic acid (2 drops) and extracted with ethyl acetate. The extract was washed with aqueous $NaHCO_3$ and brine, dried ($MgSO_4$), and evaporated. Flash chromatography (40% ethyl acetate/hexane) gave **22** (6.3 mg, 79%): $[\alpha]^{25}_D$ +65.8° (c = 0.53, $CHCl_3$); IR ($CHCl_3$) 3450, 1630 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.89 (3 H, t, J = 6.8 Hz, Me), 1.24–1.70 (14 H), 1.83 (2 H, m), 2.32 (2 H, m), 3.29 (3 H, s, OMe), 3.34 (3 H, s, OMe), 3.35 (3 H, s, OMe), 3.34 (1 H, m), 3.40 (1 H, m), 3.59 (1 H, m), 3.82 (1 H, br s, OH), 3.86 (1 H, m), 4.05 (1 H, m), 4.22 (1 H, br s, OH), 5.09 (1 H, br d, J = 10.5 Hz), 5.10 (1 H, br d, J = 17.6 Hz), 5.80 (1 H, ddt, J = 17.6, 10.5, and 7.1 Hz); CIMS (isobutane) m/z 361

(MH$^+$), 343 (MH$^+$ - H_2O), 329 (MH$^+$ - MeOH), 297 (MH$^+$ - 2MeOH).

(4*S*,6*S*,8*R*,10*R*,12*R*)-4,6,8,10,12-Pentamethoxy-1-heptadecene (1). To a stirred solution of **22** (5.7 mg, 0.016 mmol) in dry THF (2 mL) at 0 °C were added excess KH and MeI (0.5 mL). After stirring for 30 min the reaction mixture was quenched with MeOH (0.5 mL) and extracted with ether. The extract was washed with water and brine, dried ($MgSO_4$), and evaporated. Flash chromatography (10% ethyl acetate/hexane) gave **1** (5.5 mg, 90%): $[\alpha]^{25}_D$ +7.57° (*c* = 0.78, $CHCl_3$). The spectroscopic data were identical with those of natural **1**.

(4*S*,6*S*,8*S*,10*S*,14*R*)-4,6,8,14-Tetramethoxy-12-(trimethylenedithio)-1-nonadecen-10-ol (23). The procedure described for **20** was employed with **6** (93 mg, 0.36 mmol) and **9** (208 mg, 0.83 mmol). Flash chromatography (25% ethyl acetate/hexane) gave **23** (107 mg, 58%): $[\alpha]^{25}_D$ +4.0° (*c* = 0.46, $CHCl_3$); IR ($CHCl_3$) 3450, 1630, 1085, 915 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (3 H, t, *J* = 6.6 Hz), 1.31 (6 H), 1.52 (4 H, m), 1.61 (1 H, m), 1.66 (1 H, m), 1.79 (3 H), 1.92 (1 H, m), 2.04 (2 H, m), 2.15 (1 H, dd, *J* = 15.1 and 7.6 Hz), 2.31 (2 H, br t, *J* = 7.8 Hz), 2.76 (1 H, ddd, *J* = 14.7, 6.8, and 3.1 Hz), 2.79 (1 H, ddd, *J* = 14.7, 6.6, 3.0 Hz), 2.91 (1 H, ddd, *J* = 14.7, 9.5, and 2.9 Hz), 3.01 (1 H, ddd, *J* = 14.7, 9.8, and 2.9 Hz), 3.28 (3 H, s, OMe), 3.30 (3 H, s, OMe), 3.33 (3 H, s, OMe), 3.34 (3 H, s, OMe), 3.37 (1 H, quintet, *J* = 6.8 Hz), 3.43 (1 H, quintet, *J* = 6.1 Hz), 3.52 (1 H, m), 3.54 (1 H, quintet, *J* = 6.0 Hz), 3.77 (1 H, s, OH), 4.12 (1 H, br t, *J* = 8.1 Hz), 5.08 (1 H, br d, *J* = 10.0 Hz), 5.10 (1 H, br d, *J* = 17.1 Hz), 5.82 (1 H, ddt, *J* = 17.1, 10.0, and 7.1 Hz); CIMS (isobutane) *m*/*z* 507 (MH$^+$). 489 (MH$^+$ - H_2O), 475 (MH$^+$ - MeOH), 443 (MH$^+$ - 2MeOH), 411 (MH$^+$ - 3MeOH). Anal. Calcd for $C_{26}H_{50}O_5S_2$: C, 61.62; H, 9.95. Found: C, 61.31; H, 10.06.

(4*S*,6*S*,8*S*,10*S*,14*R*)-12-Oxo-4,6,8,14-tetramethoxy-1-nonadecen-10-ol (24). The procedure described for **21** was followed with **23** (100 mg, 0.198 mmol), $CaCO_3$ (198 mg, 1.98 mmol), and MeI (1.2 mL, 19.8 mmol). Flash chromatography (50% ethyl acetate/hexane) gave **24** (66 mg, 80%): $[\alpha]^{25}_D$ +41.9° (*c* = 0.42, $CHCl_3$); IR ($CHCl_3$) 3450, 1700, 1085, 915 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (3 H, t, *J* = 7.1 Hz), 1.30 (6 H), 1.41–1.72 (6 H), 1.81 (2 H, m), 2.31 (2 H, br t, *J* = 6.4 Hz), 2.48 (1 H, dd, *J* = 15.9 and 4.9 Hz), 2.56 (1 H, dd, *J* = 16.6 and 4.4 Hz), 2.68 (1 H, dd, *J* = 16.6 and 8.1 Hz), 2.71 (1 H, dd, *J* = 15.9 and 7.6 Hz), 3.29 (3 H, s, OMe), 3.31 (3 H, s, OMe), 3.33 (6 H, s, OMe × 2), 3.35 (1 H, m), 3.40 (1 H, m), 3.58 (1 H, m), 3.68 (1 H, m), 3.73 (1 H, d, *J* = 2.0 Hz, OH), 4.24 (1 H, m), 5.09 (1 H, br d, *J* = 10.0 Hz), 5.10 (1 H, br d, *J* = 16.9 Hz), 5.81 (1 H, ddt, *J* = 16.9, 10.0, and 7.1 Hz); CIMS (isobutane) *m*/*z* 417 (MH$^+$), 399 (MH$^+$ - H_2O).

(4*S*,6*S*,8*S*,10*R*,12*R*,14*R*)-4,6,8,14-Tetramethoxy-1-nonadecene-10,12-diol (25). The procedure described for **22** was employed with **24** (61 mg, 0.145 mmol), diethylmethoxyborane (0.58 mL, 0.58 mmol), and $NaBH_4$ (11 mg, 0.29 mmol). Flash chromatography (65% ethyl acetate/hexane) gave **25** (55 mg, 91%): $[\alpha]^{25}_D$ +16.62° (*c* = 0.55, $CHCl_3$); IR ($CHCl_3$) 3450, 1635, 1080, 9.15 cm^{-1}; ^{1}H NMR (400 MHz, benzene-d_6) δ 0.90 (3 H, t, *J* = 6.8 Hz), 1.16–1.32 (6 H), 1.38–1.48 (4 H), 1.66 (2 H, m), 1.70–1.82 (3 H), 1.96 (3 H, m), 2.28 (2 H, br t, *J* = 6.4 Hz), 3.05 (3 H, s, OMe), 3.15 (6 H, s, OMe × 2), 3.18 (3 H, s, OMe), 3.32 (1 H, quintet, *J* = 5.4 Hz), 3.34 (1 H, quintet, *J* = 5.4 Hz), 3.57 (1 H, quintet, *J* = 5.2 Hz), 3.70 (1 H, quintet, *J* = 6.4 Hz), 4.07 (1 H, tt, *J* = 9.5 and 2.5 Hz), 4.16 (1 H, tt, *J* = 9.3 and 2.5 Hz), 4.35 (2 H, br s, OH), 5.08 (1 H, br d, *J* = 10.3 Hz), 5.10 (1 H, br d, *J* = 17.1 Hz), 5.87 (1 H, ddt, *J* = 17.1, 10.3, and 7.1 Hz); CIMS (isobutane) *m*/*z* 419 (MH$^+$), 401 (MH$^+$ - H_2O), 387 (MH$^+$ - MeOH), 355 (MH$^+$ - 2MeOH), 323 (MH$^+$ - 3MeOH). Anal. Calcd for $C_{23}H_{46}O_6$: C, 65.99; H, 11.08. Found: C, 66.42; H, 11.37.

(4*S*,6*S*,8*S*,10*R*,12*R*,14*R*)-4,6,8,10,12,14-Hexamethoxy-1-nonadecene (2). The procedure for **1** was followed with **25** (45 mg) and flash chromatography (30% ethyl acetate/hexane) gave **2** (44 mg, 91%): $[\alpha]^{25}_D$ +6.26° (*c* = 0.82, $CHCl_3$). The spectroscopic data were identical with those of natural **2**.

(4*S*,6*S*,8*R*,10*R*)-4,6,8-Trimethoxy-1-pentadecen-10-ol (26). To a stirred suspension of CuI (1.5 g, 7.9 mmol) in dry ether (10 mL) at −20 °C under nitrogen was added 1.6 M *n*-butyllithium in hexane (9.9 mL, 15.84 mmol). After stirring for 30 min, a solution of **6** (409 mg, 1.58 mmol) in dry ether (5 mL) was added, and the mixture was stirred at −20 °C for 1 h. The reaction mixture was quenched with aqueous NH_4Cl and extracted with ethyl acetate. The extract was washed with aqueous NH_4Cl, water, and brine, dried ($MgSO_4$), and evaporated. Flash chromatography (30% ethyl acetate/hexane) gave **26** (434 mg, 87%): $[\alpha]^{25}_D$ +62.6° (*c* = 0.83, $CHCl_3$); IR ($CHCl_3$) 3450, 1630 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (3 H, t, *J* = 6.8 Hz), 1.26–1.68 (12 H), 1.81 (1 H, dd, *J* = 8.3 and 4.7 Hz), 1.85 (1 H, dd, *J* = 8.1 and 4.9 Hz), 2.31 (2 H, br t, *J* = 6.1 Hz), 3.29 (3 H, s, OMe), 3.34 (3 H, s, OMe), 3.36 (3 H, s, OMe), 3.32 (1 H, m), 3.40 (1 H, m), 3.55 (1 H, d, *J* = 1.7 Hz, OH), 3.57 (1 H, m), 3.77 (1 H, m), 5.10 (1 H, br d, *J* = 10.3 Hz), 5.11 (1 H, br d, *J* = 17.1 Hz), 5.81 (1 H, ddt, *J* = 17.1, 10.3, and 7.1 Hz): CIMS (isobutane) *m*/*z* 317 (MH$^+$), 299 (MH$^+$ - H_2O), 285 (MH$^+$ - MeOH), 267 (MH$^+$ - H_2O - MeOH), 253 (MH$^+$ - 2MeOH), 221 (MH$^+$ - 3MeOH).

(4*S*,6*S*,8*R*,10*R*)-4,6,8,10-Tetramethoxy-1-pentadecene (27). The procedure for **1** was employed with **26** (434 mg) and the crude product was purified by flash chromatography (15% ethyl acetate/hexane) to give **27** (435 mg, 96%): $[\alpha]^{25}_D$ +9.47° (*c* = 0.52, $CHCl_3$); IR ($CHCl_3$) 1635, 1090 cm^{-1}; ^{1}H NMR (400 Hz, benzene-d_6) δ 0.91 (3 H, t, *J* = 6.8 Hz), 1.30 (4 H), 1.44 (2 H, m), 1.57 (2 H, m), 1.62–1.77 (3 H), 1.93–2.03 (3 H), 2.32 (2 H, m), 3.17 (3 H, s, OMe), 3.20 (3 H, s, OMe), 3.21 (3 H, s, OMe), 3.22 (3 H, s, OMe), 3.38 (2 H, m), 3.59 (2 H, quintet, *J* = 6.1 Hz), 5.08 (1 H, br d, *J* = 10.3 Hz), 5.09 (1 H, br d, *J* = 17.3 Hz), 5.91 (1 H, ddt, *J* = 17.3, 10.3, and 7.1 Hz): CIMS (isobutane) *m*/*z* 331 (MH$^+$), 229 (MH$^+$ - MeOH), 197 (MH$^+$ - 2MeOH), 165 (MH$^+$ - 3MeOH), 133 (MH$^+$ - 4MeOH). Anal. Calcd for $C_{19}H_{38}O_4$: C, 69.05; H, 11.59. Found: C, 68.87; H, 11.83.

(3*R*,5*R*,7*R*,9*R*)-3,5,7,9-Tetramethoxytetradecanal (28). To a stirred solution of **27** (430 mg, 1.33 mmol) in dioxane–water (3:1) (40 mL) was added OsO_4 (20 mg). After being stirred for 30 min, $NaIO_4$ (850 mg, 3.98 mmol) was added to the solution. The reaction mixture was stirred for 2.5 h and extracted with ethyl acetate. The extract was washed with water and brine, dried ($MgSO_4$), and evaporated. Flash chromatography (35% ethyl acetate/hexane) gave **28** (382 mg, 82%): $[\alpha]^{25}_D$ −32.48° (*c* = 0.73, $CHCl_3$); IR ($CHCl_3$) 1720 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (3 H, t, *J* = 7.3 Hz), 1.30 (6 H), 1.49 (3 H, m), 1.60 (1 H, ddd, *J* = 13.9, 6.6, and 4.8 Hz), 1.69 (1 H, ddd, *J* = 14.3, 6.6, and 4.8 Hz), 1.78–1.91 (3 H, m), 2.63 (2 H, m), 3.29 (3 H, s, OMe), 3.30 (3 H, s, OMe), 3.31 (3 H, s, OMe), 3.35 (3 H, s, OMe), 3.23–3.46 (3 H), 3.88 (1 H, quintet, *J* = 5.9 Hz), 9.81 (1 H, *t*, *J* = 2.2 Hz); CIMS (isobutane) *m*/*z* 333 (MH$^+$), 301 (MH$^+$ - MeOH), 269 (MH$^+$ - 2MeOH), 237 (MH$^+$ - 3MeOH), 205 (MH$^+$ - 4MeOH).

2-[(2*R*,4*R*,6*R*,8*R*)-2,4,6,8-Tetramethoxytridecyl]-1,3-dithiane (7). To a stirred solution of **28** (382 mg, 1.15 mmol) in CH_2Cl_2 (30 mL) at 0 °C were added 1,3-propanedithiol (0.35 mL, 3.45 mmol) and BF_3·OEt_2 (3 drops). After stirring for 17 h at room temperature, 2,2-dimethoxypropane (1.5 mL) was added to the solution, and the mixture was stirred for 30 min. The reaction mixture was quenched with triethylamine (0.3 mL) and the solvent was evaporated. Flash chromatography (20% ethyl acetate/hexane) gave **7** (474 mg, 98%): $[\alpha]^{25}_D$ −16.49° (*c* = 0.75, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (3 H, t, *J* = 6.8 Hz), 1.31 (6 H), 1.46–1.62 (5 H), 1.78–1.96 (6 H), 2.13 (1 H, m), 2.80–2.96 (4 H), 3.26 (1 H, m), 3.30 (3 H, s, OMe), 3.31 (3 H, s, OMe), 3.32 (3 H, s, OMe), 3.36 (3 H, s, OMe), 3.38 (2 H, m), 3.63 (1 H, quintet, *J* = 5.6 Hz), 4.21 (1 H, dd, *J* = 7.6 and 6.8 Hz); CIMS (isobutane) *m*/*z* 423 (MH$^+$), 391 (MH$^+$ - MeOH), 359 (MH$^+$ - 2MeOH), 327 (MH$^+$ - 3MeOH), 295 (MH$^+$ - 4MeOH). Anal. Calcd for $C_{21}H_{42}O_4S_2$: C, 59.69; H, 10.02. Found: C, 60.02; H, 10.27.

(4*S*,6*S*,8*S*,10*S*,14*R*,16*R*,18*R*,20*R*)-4,6,8,14,16,18,20-Heptamethoxy-12-(trimethylenedithio)-1-pentacosen-10-ol (29). The procedure described for **20** was employed with **6** (433 mg, 1.68 mmol) and **7** (473 mg, 1.12 mmol), and the crude product was purified by flash chromatography (40% ethyl acetate/hexane) to give **29** (485 mg, 64%): $[\alpha]^{25}_D$ −8.48° (*c* = 0.83, $CHCl_3$); IR ($CHCl_3$) 3450, 1635, 1085, 915 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (3 H, t, *J* = 7.1 Hz), 1.31 (6 H), 1.50–1.72 (9 H), 1.76–2.02 (7 H), 2.02 (1 H, br d, *J* = 15.1 Hz), 2.16 (1 H, dd, *J* = 15.1 and 7.3 Hz), 2.22 (1 H, br d, *J* = 15.1 Hz), 2.32 (3 H, m), 2.77–3.02 (4 H), 3.29 (3 H, s, OMe), 3.30 (3 H, s, OMe), 3.32 (6 H, s, OMe × 2), 3.33 (3 H, s, OMe), 3.34 (6 H, s, OMe × 2), 3.24–3.45 (5 H), 3.54 (1 H, quintet, *J* = 6.1 Hz), 3.69 (1 H, m), 3.77 (1 H, s, OH), 4.15 (1 H, m), 5.08 (1 H, br d, *J* = 10.0 Hz), 5.09 (1 H, br d, *J* = 17.1 Hz), 5.82 (1 H, ddt, *J* = 17.1, 10.0, and 7.1 Hz); CIMS

(isobutane) m/z 681 (MH^+), 649 (MH^+ - MeOH), 631 (MH^+ - MeOH - H_2O), 617 (MH^+ - 2MeOH), 599 (MH^+ - 2MeOH - H_2O), 585 (MH^+ - 3MeOH), 567 (MH^+ - 3MeOH - H_2O), 553 (MH^+ - 4MeOH), 535 (MH^+ - 4MeOH - H_2O).

(4*S*,6*S*,8*S*,10*S*,14*R*,16*R*,18*R*,20*R*)-4,6,8,14,16,18,20-Heptamethoxy-12-oxo-1-pentacosen-10-ol (30). The procedure described for **21** was followed with **29** (416 mg, 0.612 mmol), $CaCO_3$ (612 mg, 6.12 mmol), and MeI (3.8 mL, 61.2 mmol). Flash chromatography (90% ethyl acetate/hexane) gave **30** (348 mg, 96%): $[\alpha]^{25}_D$ +18.52° (c = 1.0, $CHCl_3$); IR ($CHCl_3$) 3450, 1700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.89 (3 H, t J = 6.7 Hz), 1.30 (6 H), 1.48–1.86 (14 H), 2.30 (2 H, t, J = 6.2 Hz), 2.55 (1 H, dd, J = 16.6 and 4.1 Hz), 2.61 (1 H, dd, J = 16.1 and 5.4 Hz), 2.67 (1 H, dd, J = 16.6 and 6.6 Hz), 2.73 (1 H, dd, J = 16.1 and 7.1 Hz), 3.28 (3 H, s, OMe), 3.29 (3 H, s, OMe), 3.30 (3 H, s, OMe), 3.31 (6 H, s, OMe × 2), 3.33 (6 H, s, OMe × 2), 3.24–3.42 (5 H), 3.57 (1 H, quintet, J = 5.4 Hz), 3.74 (1 H, br s, OH), 3.83 (1 H, quintet, J = 5.8 Hz), 4.24 (1 H, m), 5.08 (1 H, br d, J = 10.3 Hz), 5.09 (1 H, br d, J = 17.1 Hz), 5.80 (1 H, ddt, J = 17.1, 10.3, and 7.1 Hz); CIMS (isobutane) m/z 591 (MH^+), 573 (MH^+ - H_2O).

(4*S*,6*S*,8*S*,10*S*,12*R*,14*R*,16*R*,18*R*,20*R*)-4,6,8,14,16,18,20-Heptamethoxy-1-pentacosene-10,12-diol (31). The procedure described for **22** was employed with **30** (20.4 mg, 0.035 mmol), diethylmethoxyborane (0.138 mL), and $NaBH_4$ (2.6 mg , 0.069 mmol). Flash chromatography (1% MeOH/ethyl acetate) gave **31** (20 mg, 98%): $[\alpha]^{25}_D$ +3.04° (c = 1.0, $CHCl_3$); IR ($CHCl_3$) 3450, 1630, 1080 cm^{-1}; ^1H NMR (400 MHz, benzene-d_6) δ 0.91 (3 H, t, J = 6.8 Hz), 1.30 (4 H), 1.38–1.85 (14 H), 1.86–2.06 (6 H), 2.26 (2 H, t, J = 6.4 Hz), 3.13 (3 H, s, OMe), 3.14 (3 H, s, OMe), 3.16 (3 H, s, OMe), 3.17 (3 H, s, OMe), 3.21 (3 H, s, OMe), 3.22 (3 H, s, OMe), 3.23 (3 H, s, OMe), 3.33 (2 H, m), 3.54 (1 H, quintet, J = 5.1 Hz), 3.59 (1 H, quintet, J = 5.4 Hz), 3.63 (1 H, quintet, J = 5.9 Hz), 3.66 (1 H, quintet, J = 6.1 Hz), 3.71 (1 H, quintet, J = 5.9 Hz), 4.12 (2 H, m), 4.37 (2 H, br s, OH × 2), 5.07 (1 H, br d, J = 10.3 Hz), 5.08 (1 H, br d, J = 17.1 Hz), 5.85 (1 H, ddt, J = 17.1, 10.3, and 7.1 Hz); CIMS (isobutane) m/z 593 (MH^+), 575 (MH^+ - H_2O), 561 (MH^+ - MeOH), 529 (MH^+ - 2MeOH), 497 (MH^+ - 3MeOH).

(4*S*,6*S*,8*S*,10*S*,12*R*,14*R*,16*R*,18*R*,20*R*)-4,6,8,10,12,14,16,-18,20-Nonamethoxy-1-pentacosene (4). The procedure for **1** was employed with **31** (150 mg, 0.253 mmol) and the product was purified by flash chromatography (60% ethyl acetate/hexane) to give **4** (138mg, 88%): $[\alpha]^{25}_D$ +4.45° (c = 1.0, $CHCl_3$). The spectroscopic data were identical with those of natural **4**.

(3*R*,5*R*,7*R*,9*R*,11*R*,13*R*,15*R*,17*R*,19*R*)-3,5,7,9,11,13,15,-17,19-Nonamethoxy-1-tetracosanal (32). The procedure described for **28** was followed with **4** (42 mg, 0.068 mmol), OsO_4 (2 mg), and $NaIO_4$ (58 mg, 0.272 mmol). Flash chromatography (ethyl acetate) gave **32** (35 mg, 83%): $[\alpha]^{25}_D$ -21.33° (c = 1.0, $CHCl_3$); IR ($CHCl_3$) 1720 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.89 (3 H, t, J = 7.3 Hz), 1.30 (8 H), 1.50 (2 H, m), 1.54–1.73 (8 H), 1.76–1.92 (8 H), 2.63 (2 H, br d, J = 7.0 Hz), 3.27 (2 H, m), 3.29 (3 H, s, OMe), 3.30 (9 H, s, OMe × 3), 3.31 (12 H, s, OMe × 4), 3.34 (3 H, s, OMe), 3.40 (6 H, quintet, J = 5.9 Hz), 3.87 (1 H, quintet, J = 5.9 Hz), 9.80 (1 H, t, J = 2.2 Hz).

(5*S*,7*S*,9*S*,11*S*,13*R*,15*R*,17*R*,19*R*)-5,7,9,11,13,15,17,19-Octamethoxy-2-tetracosenal (33). A solution of **32** (90 mg, 0.145 mmol) and p-toluenesulfonic acid (550 mg, 0.289 mmol) in benzene (10 mL) was heated at 60 °C for 1 h. After cooling, the reaction mixture was extracted with ethyl acetate. The extract was washed with aqueous $NaHCO_3$, water, and brine, dried ($MgSO_4$), and evaporated. Flash chromatography (70% ethyl acetate/hexane) gave **33** (64 mg, 60%): $[\alpha]^{25}_D$ -4.24° (c = 0.38, $CHCl_3$): IR ($CHCl_3$) 1685 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.90 (3 H, t, J = 7.0 Hz), 1.30 (6 H), 1.46–1.66 (9 H), 1.78–1.84 (7 H), 2.51 (1 H, m), 2.67 (1 H, m), 3.30 (3 H, s, OMe), 3.31 (18 H, s, OMe × 6), 3.36 (3 H, s, OMe), 3.41 (7 H, quintet, J = 5.9 Hz), 3.55 (1 H, quintet, J = 5.9 Hz), 6.19 (1 H, dd, J = 15.8 and 8.1 Hz), 6.90 (1 H, dt, J = 15.8 and 7.3 Hz), 9.53 (1 H, d, J = 8.1 Hz).

(3*R*,5*R*,7*R*,9*R*,11*R*,13*R*,15*R*,17*R*)-3,5,7,9,11,13,15,17-Octamethoxydocosanal (34). To a solution of **33** (65 mg, 0.109 mmol) in dry ether (10 mL) was added $LiAlH_4$ (20 mg, 0.54 mmol). After being stirred for 5 min, the reaction mixture was quenched with 1 N NaOH and stirred until precipitates aggregated. The ether layer was separated and evaporated. Flash chromatography (1% MeOH/ethyl acetate) gave an allylic alcohol (57 mg, 88%).

The allylic alcohol (53 mg, 0.109 mmol) was subjected to OsO_4–$NaIO_4$ oxidation in the same manner as described for **28**. Flash chromatography (85% ethyl acetate/hexane) gave **34** (42 mg, 82%): $[\alpha]^{25}_D$ -21.17° (c = 0.33, $CHCl_3$); IR ($CHCl_3$) 1720 cm^{-1}; ^1H NMR (400 MHz, benzene-d_6) δ 0.92 (3 H, t, J = 7.3 Hz), 1.31 (4 H), 1.43 (2 H, m), 1.57 (2 H, m), 1.66 (2 H, m), 1.70–1.92 (6 H), 1.93–2.12 (6 H), 2.27 (1 H, ddd, J = 16.1, 5.1, and 1.7 Hz), 2.34 (1 H, ddd, J = 16.1, 6.2, and 2.6 Hz), 3.07 (3 H, s, OMe), 3.14 (3 H, s, OMe), 3.22 (3 H, s, OMe),3.23 (3 H, s, OMe), 3.25 (3 H, s, OMe), 3.26 (3 H, s, OMe), 3.27 (6 H, s, OMe × 2), 3.36 (1 H, quintet, J = 5.5 Hz), 3.50 (1 H, quintet, J = 5.9 Hz), 3.58 (1 H, quintet, J = 5.5 Hz), 3.61–3.70 (3 H, m), 3.75 (1 H, quintet, J = 5.9 Hz), 9.54 (1 H, t, J = 2.2 Hz); CIMS (isobutane) m/z 567 (MH^+), 535 (MH^+ - MeOH), 503 (MH^+ - 2MeOH), 471 (MH^+ - 3MeOH), 439 (MH^+ - 4MeOH), 407 (MH^+ - 5MeOH).

(4*S*,6*S*,8*S*,10*S*,12*R*,14*R*,16*R*,18*R*)-4,6,8,10,12,14,16,18-Octamethoxy-1-tricosene (3). To a stirred solution of **34** (17 mg, 0.03 mmol) in dry THF (2 mL) at -78 °C under nitrogen was added a solution of methylenetriphenylphosphorane in dry THF (0.5 mL) prepared from methyltriphenylphosphonium bromide (571 mg, 1.6 mmol) and 1.6 M n-butyllithium (1.0 mL, 1.6 mmol) in dry THF (4 mL). After being stirred at -78 °C for 30 min, the reaction mixture was warmed to room temperature during 1 h and extracted with ethyl acetate. The extract was washed with water and brine, dried ($MgSO_4$), and evaporated. Flash chromatography (50% ethyl acetate/hexane) gave **3** (12 mg, 82%): $[\alpha]^{25}_D$ +5.22° (c = 1.0, $CHCl_3$). The spectroscopic data were identical with those of natural **3**.

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Supplementary Material Available: ^1H NMR spectra of compounds **1–4**, **6–7**, and **19–34** and ^{13}C NMR spectra of **1** and **2** (24 pages). Ordering information is given on any current masthead page.