= 9.8 Hz, H6), 3.68-3.80 (m, 2, H3, H1a), 3.76 and 3.86 [2 s, 6, (3,4-di-CH_3OPhCH_2)], 3.95 (d, 1, H7), 4.17 (br d, 1, $J_{1a,1e}$ = 13.2 Hz, H1e), 4.23-4.74 [m, 8, PhCH_2, (3,4-di-CH_3OPhCH_2)], 5.06 (s, 1, H10), 5.13 (d, 1, $J_{1',4}$ = 3.2 Hz, H1'), 6.81 [br s, 3, (3,4-di-CH_3O*Ph*CH_2)], 7.12-7.40 (m, 15, *Ph*CH_2). Anal. Calcd for $C_{42}H_{46}O_{10}$: C, 75.92; H, 6.98. Found: C, 76.00; H, 6.91.

Epoxide 19 and Cleavage to Tripyranoside 27. The identical procedure given above for the preparation of **15** was followed for the epoxidation of the unsaturated tripyranoside **8** with the following amounts: **8** (78.8 mg, 0.17 mmol), NBS (100 mg, 0.5 mmol), DME-water (3:1, 10 mL), for 29 h. TLC (F) showed only a trace of **8** (R_f 0.58) along with major (R_f 0.12) and minor (R_f 0.64 and 0.40) products. Treatment of this mixture with sodium hydride (30 mg) in 10 mL of dry DMF, as described for **15**, produced one product (R_f 0.64) containing a trace of the alkene **8** (R_f 0.58, ca. 10 mg recovered). Column chromatography (B) provided the epoxide **19** as an off-white semisolid (48.2 mg, 73%). To a solution of methyllithium (1.6 M in ether, 1.25 mL, 2 mmol), at 0 °C under argon was added a solution of methylmagnesium chloride (2.8 M in THF, 0.71 mL, 2 mmol). After 30 min at 20 °C, toluene (25 mL) was added to the white mixture and the temperature raised to 80 °C. After an additional 30 min, the epoxide (30 mg, 0.064 mmol), dissolved in 5 mL of toluene, was added to the hot white mixture. After 2 h, TLC (F) indicated the formation of a major product (R_f 0.04) along with traces of other material (R_f 0.26 and 0.04). The reaction mixture was cooled to 0 °C, poured onto water (100 mL), and extracted with ether (100 mL). The ether phase was washed with 5 M NH_4Cl (50 mL), dried ($MgSO_4$), filtered, and evaporated to yield a semisolid. Column chromatography (C) gave the starting material (7.0 mg) and **27a** (20.2 mg, 73%): ^{1}H NMR (200 MHz) δ 1.08 (d, J = 7.0 Hz, 3 H, C8CH_3), 1.34 (d, J = 7.2 Hz, 3 H, C2CH_3). O-Methylation with sodium hydride-MeI in DMF gave the tripyranoside **27b** as a pale yellow semisolid: mp ca. 100 °C; $[\alpha]_D^{25}$ -30.6° (*c* 0.34, $CHCl_4$); ^{1}H NMR (200 MHz) δ 1.10 (d, J = 7.2 Hz, 3 H, C8CH_3, 1.36 (d, J = 7.2 Hz, 3 H, C2CH_3), 2.08 (m, 1 H, H2), 2.42 (m, 1 H, H8), 2.47 (ddd, J = 10.5, 5.2, 3.2 Hz, 1 H, H4), 3.21 (br s, 1 H, H9), 3.41 and 3.53 (2 s, 6 H, OCH_3), 3.59 (dd, J = 12.0, 4.0 Hz, 1 H, H1a), 3.71 (t, J = 5.2 Hz, 1 H, H3), 3.73 (dd, J = 10.5, 8.5 Hz, 1 H, H6), 3.89 (dd, J = 12.0, 2.0 Hz, 1 H, H1e), 4.17 (dd, J = 10.5, 8.5 Hz, 1 H, H5), 4.25 (dd, J = 10.5, 5.0 Hz, 1 H, H7), 4.58 (AB q, J = 12.0 Hz, $\Delta\delta$ = 0.1, ppm, 2 H, Ph''CH_2), 4.65 (d, J = 3.2 Hz, 1 H, H1'), 4.69 (s, 1 H, H10), 4.81 (ABq, J = 11.5 Hz, $\Delta\delta$ = 0.06 ppm, 2 H, PhCH_4), and 7.30 (m, 10 H, *Ph*). Anal. Calcd for $C_{29}H_{38}O_7$: C, 69.87; H, 7.63. Found: C, 69.54; H, 7.41.

Tripyranoside 28. Epoxide **26** (125 mg, 0.180 mmol) was cleaved with dimethylmagnesium by using a similar procedure to that described above for **19** → **27a**. The alcohol **28** was obtained as a colorless syrup (120 mg, 92%): TLC R_f 0.18 (D); $[\alpha]_D^{19}$ +30.8° (*c* 1.17, $CHCl_3$); IR (neat) 3465, 3015, 2910, 1590, 1515, 1450, 1265, 1135, 775 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.10-1.18 (overlapping d and s, 6, C8CH_3, C2CH_3), 1.77 (d, 1, $J_{9,OH}$ = 7.0 Hz, OH, D_2O ex), 2.12 (m, 1, H4), 2.33 (m, 1, H8), 3.67-3.81 (m, 2, H9, H1a), 3.78 and 3.86 [2 s, 6, (3,4-di-CH_3PhCH_2)], 4.17 (dd, 1, $J_{1e,3}$ = 1.6 Hz, $J_{1e,1a}$ = 13.2 Hz, H1e), 4.24 (dd, 1, $J_{7,8}$ = 5.6 Hz, $J_{6,7}$ = 10.4 Hz, H7), 4.32-4.81 [m, 9, PhCH_2, H10, (3,4-di-CH_3OPhCH_2)], 5.12 (d, 1, $J_{1',4}$ = 3.3 Hz, H1'), 6.80 [br s, 3, (3,4-di-CH_3O*Ph*CH_2)], 7.21-7.43 (m, 15, *Ph*CH_2). Anal. Calcd for $C_{43}H_{50}O_{10}$: C, 70.94; H, 7.58. Found: C, 71.02; H, 7.69.

Registry No. 1, 17791-36-5; 2, 89731-21-5; 3, 52509-14-5; (*Z*)-4, 89731-22-6; (*E*)-4, 89747-98-8; 5, 89731-19-1; 6, 88392-83-0; 7a, 88392-84-1; (*E*)-7b, 110046-70-3; (*Z*)-7b, 110115-19-0; 8, 88392-86-3, 9a, 110046-71-4; 9b, 110046-72-5; 9c (diastereomer 1), 110046-73-6; 9c (diastereomer 2), 110115-23-6; 9d (diastereomer 1), 110046-74-7; 9d (diastereomer 2), 110115-24-7; 10 (diastereomer 1), 110046-75-8; 10 (diastereomer 2), 110115-25-8; 11, 71276-94-3; 12 (diastereomer 1), 110046-76-9; 12 (diastereomer 2), 110115-26-9; 13a, 110046-77-0; 13b, 110046-78-1; 14, 3169-98-0; 15, 3150-16-1; 19, 88392-87-4; 24, 110115-20-3; 25, 110115-21-4; 26, 110115-22-5; 27a, 110046-79-2; 27b, 88392-88-5; 28, 110046-80-5; OCCH=PPh_3, 2136-75-6; 3,4-dimethoxybenzyl alcohol, 93-03-8.

Complementary Routes to "Remote" Tertiary Alcohols of Streptovaricin A[1,2]

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This paper describes a model study connected with the "pyranosidic homologation" approach to the ansa chain of streptovaricin A. Of the nine contiguous chiral centers present in this array, the C14 tertiary alcohol is the only one that cannot be accommodated on the tripyranoside backbone. In the present study, the anomeric center of a dipyranoside model is transformed into the δ-lactone **2** and thence into the isopropenyl center in **9**. For both compounds **2** and **9**, reliance is placed upon the adjacent C7 oxygen to provide a stereocontrolling force. In the first set of reactions, the lactone is elaborated into a methyl ketone, **3b**, to which vinylmagnesium bromide adds with only modest stereoselectivity to give the mixture of tertiary alcohols **4** and **5**. In the second set of reactions, the double bond in **9** reacts with complete stereoselectivity to give (a) a single diol, **7**, upon hydroxylation and (b) a single epoxide, **13**. Processing of the latter leads to the complementary diol **6**. The sense of stereoselectivity in the various reactions follows an internally consistent pattern, which lends confidence to the configurational assignments that have been made.

In the accompanying papers,[5] we gave details for the preparation of tripyranose derivatives (e.g., I), which are being investigated as precursors for the ansamycin antibiotics. The retrosynthetic plan[6a] on which this approach is based led to structures Ia and Ib, which are capable of accommodating eight contiguous chiral centers. Structure Ia is an adequate chiron for the eight contiguous chiral centers present in the ansa chain of rifamycin S;[6a] however,

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(2) Pyranosidic Homologation part 11. For part 5, see ref 5a.

(3) Taken from the Ph.D. thesis of D.R.M., University of Maryland, 1986. present address: Department of Chemistry, Paul M. Gross Chemical Laboratory, Duke University, Durham, NC 27706.

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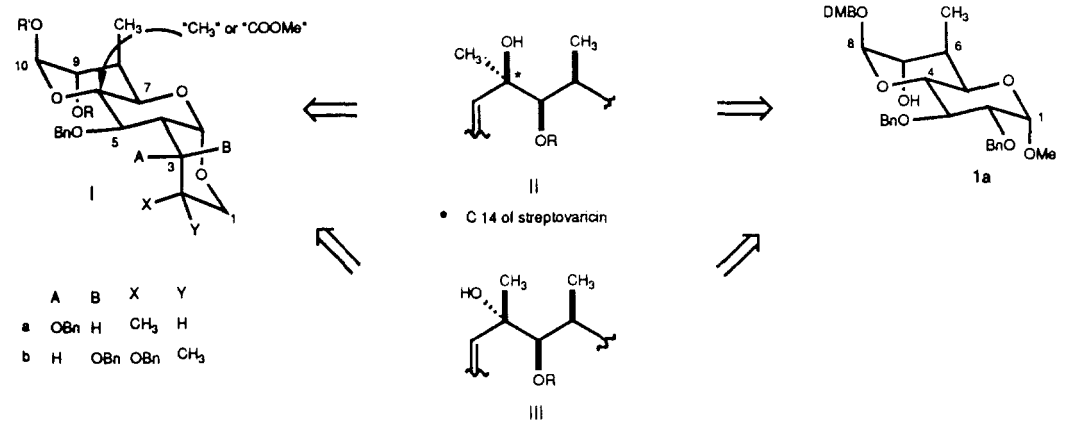
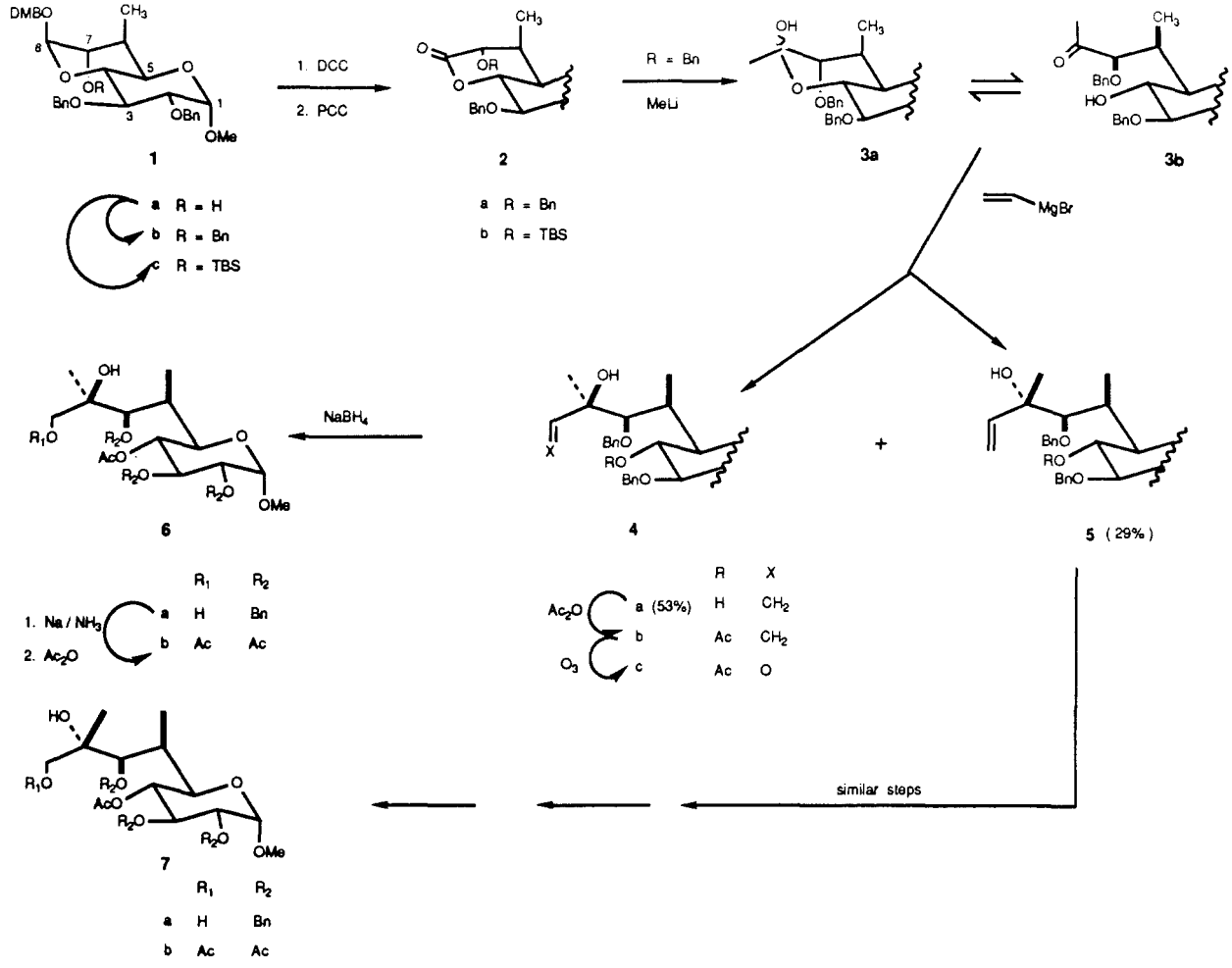
0022-3263/87/1952-4511$01.50/0

Scheme I



Scheme II



the ansa chain of streptovaricin A has nine contiguous chiral centers, and therefore, the correspondig chiron Ib needs to be extended to accommodate an alcohol, as in II, which would correspond to the C28 of streptovaricin A. The dipyranose 1[6b] has been prepared as a convenient model for the two upper rings of I, and in this paper, studies related to the tertiary alcohol at C8 will be described.

Stereocontrolled formation of the tertiary alcohol in II was recognized at the outset to be potentially troublesome, since the reaction would be occurring at the "upper" anomeric center (i.e., C10 or I or C8 of **1a**) at an "off-template" site Scheme I). In view of this element of uncertainty, a plan was desirable that would give one or other of the epimeric diols II or III, specifically, so that configurational assignments could be made on the basis of internally consistent reaction mechanisms, as well as upon detailed spectral comparisons. Our initial approach toward these targets sought to take advantage of the high stereoselectivities observed in (a) chelation-controlled addition to α-oxygenated ketones[7,8] and (b) in the ster-

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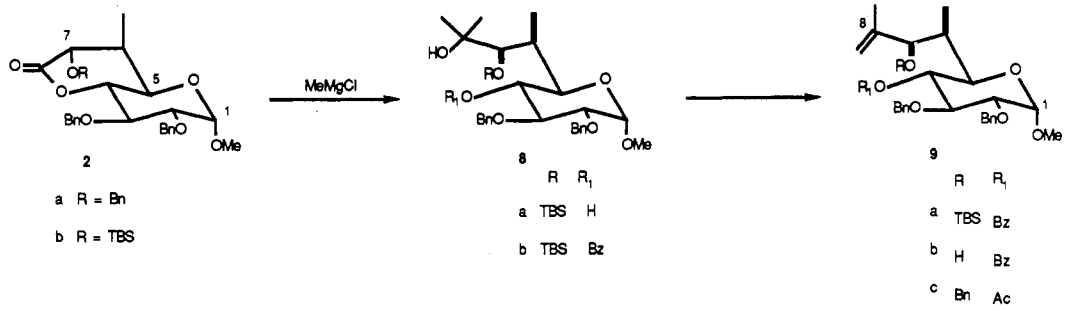
Scheme III



eoelectronically controlled oxidations of allylic alcohols.[9,10]

First Approach (Scheme II). The first approach to the desired syn-diol residue of II was based on Cram[7a] addition of a hydroxymethyl carbanion equivalent to the methyl ketone **3b**. The substrate was prepared from the model dipyranoside **1a**[6b] by protecting the C7-OH either as the benzyl (**1b**) or the silylated (**1c**) ether, followed by oxidative cleavage of the dimethoxybenzyl glycoside by treatment with DDQ.[11] The resulting hemiacetal mixture was oxidized directly with pyridinium chlorochromate to give lactones **2a** or **2b**, respectively.

Addition of 1 equiv of methyllithium to lactone **2a** afforded the desired ketone **3b** (as its hemiketal **3a**), which upon reaction with vinylmagnesium bromide gave a 5:2 mixture of epimers. These were assigned as **4a** and **5**, respectively, on the basis of the assumption that the major product would result from the chelating effect[7,8] of the Grignard reagent with the α-benzyloxy group. The compounds were separated and processed individually. The major isomer **4a** was acetylated, and ozonolysis of the product **4b** led to the aldehyde **4c**, which was reduced to a diol assigned as **6a**. Debenzylation under Birch conditions,[12] followed by acetylation, afforded the pentaacetate **6b**. Similar treatment of the minor compound **5** yielded a tribenzyl derivative, **7a**, and thence a pentaacetate, **7b**, which was distinctly identifiable from the analogue **6b**.

Second Approach (Scheme III). The foregoing results assured us that epimeric alcohols such as II and III (Scheme I) could be readily differentiated. The alternative route was therefore examined in the hope that a self-consistent and corroboratory set of results would be forthcoming and, also, that greater stereoselectivity could be achieved, leading to one or other isomer. This route required that C8 of **1** be converted into an isopropenyl center (as in **9**), and for this, our starting material was again the lactone **2**. Thus, addition of 2 equiv of methylmagnesium chloride to **2b** gave the diol **8a**, which was selectively benzoylated at the C4-OH. Dehydration of the benzoate **8b** by treatment with thionyl chloride gave alkene **9a**. Desilylation then afforded the allylic alcohol **9b** in 45% overall yield from **1a**. By a similar sequence of reaction, the O7-benzylated lactone **2a** was transformed into the alkene acetylated analogue **9c**.

Osmium tetraoxide hydroxylation[13] of olefin **9c** provided immediate access to the previously obtained diol **7a** whose C8 configuration was independently assignable on the basis of the empirical set of rules developed by Kishi and coworkers.[10] Their studies had shown that the relative configuration of the preexisting alkoxyl group and the adjacent, newly introduced hydroxyl group of the major product was in all cases anti.

In view of this promising development, we focused our efforts on obtaining the C8 epimeric alcohol **6** in order to enable comparisons to be made (Scheme IV). The plan was to hydrolyze the epoxide obtained from **9c**. Unfortunately, epoxidation with *m*-chloroperbenzoic acid was unselective, giving a 55:45 mixture of epoxide diastereomers **10**, which proved to be inseparable in several chromatographic systems. In spite of these problems, the mixture provided a convenient opportunity for evaluating the prospects of acid-catalyzed epoxide opening. Accordingly, treatment of **10** under a variety of protic and aprotic acid conditions gave furanoaldehydes **12**, resulting from participation of the pyranose ring oxygen (as in **11**) in the opening of the epoxide. Such RO5 participation[14,15] to form a furan is not unprecedented whenever there is an oxygen substituent γ to a potential electrophilic site; however, we are not aware of any instance involving the ring oxygen that led effectively to the *opening* of the pyranoside ring.[16]

This development dictated that an alternative process would be needed to avoid the participation of O5. This could conceivably be achieved by use of a more competitive neighboring group participator, and in this context, the acid-catalyzed opening of epoxyurethanes seemed promising. An extensive body of work shows that opening of such derivatives proceeds via intramolecular assistance of the phenylurethane group, leading to inversion at the proximate α-position.[17]

The allylic alcohol **9b**, described above, was an ideal substrate for this study. Hydroxylation, as in the case of

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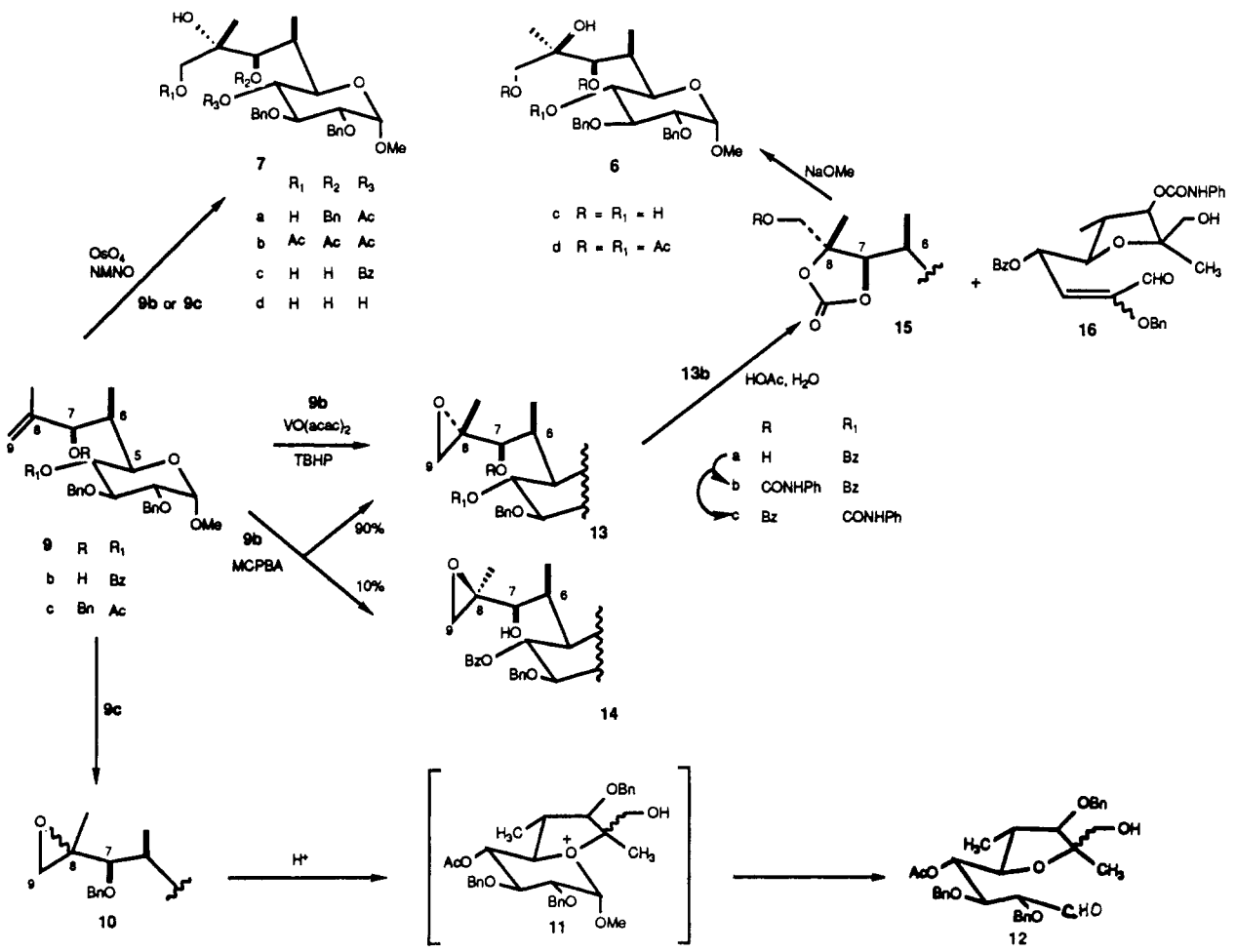
Scheme IV



corresponding benzyl derivative **9c**, was highly selective, providing a single product that was presumed to be the triol **7c**. Removal of the benzoate ester gave the tetrol **7d**, which was correlated with the previously described pentaacetate **7b** (Scheme II) by protecting group adjustments.

For the complementary route to the epimeric series **6**, the free hydroxy group should induce greater selectivity in the epoxidation product[9] and in addition should allow the phenylurethane to be put in place. Indeed, vanadium-mediated epoxidation of **9b** resulted in a single compound, whose stereochemistry was tentatively assigned as **13a**, since precedents indicate that the anti product should be favored.[9a,b]

From the reaction of *m*-chloroperbenzoic acid with **9b**, an 8:1 mixture was obtained, and since the major component was identical with the previously described epoxide **13a**, the minor component was assigned as **14**. Treatment of the major epoxide with phenyl isocyanate in pyridine afforded the desired phenylurethane derivative **13b**, in addition to a small amount of the regioisomer **13c**, arising from benzoate migration. Hydrolysis of compound **13b** in aqueous acetic acid gave a 3:1 mixture of the desired carbonate **15** and the furan **16** arising from ring oxygen (O5) participation. (The use of mineral or Lewis acids resulted in greater proportions of **16**.) Base hydrolysis of the carbonate **15** then afforded the tetrol **6c**, which was also correlated with previously obtained pentaacetate **6b** (Scheme II) by protecting group adjustments.

Thus, both pathways starting from the common allylic alcohol **9b** were complementary. Reaction models, precedents, and mechanistic studies combine to predict that the stereochemistry of the tertiary centers should be as shown for **6** and **7**, with the former possessing the required orientation for the C14-OH of streptovaricin A.

Experimental Section

For the general experimental procedures, see ref 5a. The numbering sequences used for reporting NMR data are indicated in the various schemes.

Methyl 2,3,7-Tri-*O*-benzyl-6-deoxy-6-*C*-methyl-L-*threo*-α-D-*gluco*-octopyranosiduronic Acid δ-Lactone (2a). The alcohol **1a** (633 mg, 0.91 mmol) was benzylated (see the General Procedures[5]), and the product **1b** (690 mg, 96%) was obtained as a colorless syrup after purification. The material was dissolved in a mixture of methylene chloride (25 mL), *p*-dioxane (0.5 mL), and water (0.05 mL). 2-3-Dichloro-5-6-dicyano-1,4-benzoquinone (DDQ; 220 mg, 0.97 mmol) was added and the reaction mixture stirred for 4 h at room temperature. TLC indicated the presence of a less polar product (R_f 0.2, solvent system F). Excess reagent was decomposed by adding 3,4-dimethoxybenzyl alcohol and stirring for 30 min. The reaction mixture was filtered through Celite and the filtrate concentrated in vacuo to give a brown oil, which was oxidized over 16 h with pyridinium chlorochromate (see the General Procedures). Flash chromatography gave **2a** (350 mg, 63% from **1b**) as a clear syrup: TLC R_f 0.61 (C); $[\alpha]^{25}_D$ +30.7° (*c* 1.30, $CHCl_3$); IR (neat) 1760 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.02 (d, 3 H, *J* = 7.2 Hz, CH_3-6), 2.33 (m, 1 H, H-6), 3.71 (s, 3 H, OCH_3), 3.44 (dd, 1 H, $J_{1,2}$ = 3.6, $J_{2,3}$ = 9.3 Hz, H-2), 3.64 (d, 1 H, *J* = 7.2 Hz, H-7), 3.99 (m, 3 H, H-3, H-4, H-5), 4.59 (d, 1 H, *J* = 3.6 Hz, H-1), 4.66 (AB q, 2 H, *J* = 12.0 Hz, Δδ = 0.24 ppm, $PhCH_2$), 4.83 (AB q, 2 H, *J* = 11.0 Hz, Δδ = 0.30 ppm, $PhCH_2$), 4.88 (AB q, 2 H, *J* = 10.8 Hz, Δδ = 0.02 ppm, $PhCH_2$), 7.35 (m, 15 H, $PhCH_2$ × 3). Anal. Calcd for $C_{31}H_{34}O_7$: C, 71.80; H, 6.61. Found C, 72.05; H, 6.73.

Methyl 2,3,7-Tri-*O*-benzyl-6-deoxy-6-methyl-L-*threo*-α-D-*gluco*-nonopyranosid-8-ulose (3a). Methyllithium (0.10 mL

of a 1.4 M solution in ether, 0.13 mmol) was added to a solution of lactone **2a** (68 mg, 0.13 mmol) in anhydrous ether (3 mL) at −78 °C under an argon atmosphere. The reaction was warmed to −60 °C, recooled to −78 °C, and quenched with saturated ammonium chloride solution. The mixture was extracted with ether (3 × 15 mL), and the combined ethereal phases were dried (Na_2SO_4), filtered, and evaporated in vacuo. Flash chromatography, with solvent system F, of the crude product afforded unreacted lactone **2a** (8 mg, 12%, R_f 0.45) and the tertiary alcohol (6 mg, 8%, R_f 0.20) and hemiketal mixture **3a** (51 mg, 72%): TLC R_f 0.30 (F); IR (neat) 3430, 1710 (m) cm^{-1}; selected resonances from the ^1H NMR (300 MHz, $CDCl_3$) δ 1.10 and 1.11 (2 d, J = 7.0 Hz, CH_3-6), 1.36 and 2.17 (2 s, CH_3-8), 3.32 and 3.36 (2 s, OCH_3). Anal. Calcd for $C_{32}H_{38}O_7$: C, 71.89; H, 7.16. Found C, 72.07; H, 7.30.

Methyl 2,3,7-Tri-*O*-benzyl-6,9,10-tridoexy-6,8-di-*C*-methyl-D-*xylo*-α-D-*gluco*-dec-9-eno-1,5-pyranoside (4a) and Its L-*arabino*-α-D-*gluco* Analogue (5). Vinylmagnesium bromide (0.15 mL of a 1.0 m solution in tetrahydrofuran, 0.15 mmol) was added at −78 °C to a solution of **3a** (43 mg, 0.081 mmol) in tetrahydrofuran (2 mL) and the reaction mixture warmed to 0 °C and quenched by the addition of saturated ammonium chloride solution (5 mL). The mixture was extracted with ether (3 × 10 mL), and the combined organics were dried (Na_2SO_4), filtered, and concentrated in vacuo. Flash chromatography afforded two compounds, **4a** (24 mg, 53%) and **5** (13 mg, 29%). Compound **4a** showed the following physical characterstics: clear gum; TLC R_f 0.45 (B); IR (neat) 3430 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.01 (d, 3 H, J = 7.2 Hz, CH_3-6), 1.24 (s, 3 H, CH_3-8), 2.19 (s, 1 H, 8-OH), 2.27 (m, 1 H, H-6), 3.27 (d, 1 H, J = 3.0 Hz, 4-OH), 3.38 (m, 1 H, overlapped by s at 3.39, 1 H, H-7), 3.39 (s, 3 H, OCH_3), 3.51 (m, 3 H, H-2, H-4, H-5), 3.81 (t, 1 H, J = 8.7 Hz, H-3), 4.53 (AB q, 2 H, J = 11.7 Hz, Δδ = 0.29 ppm, PhCH_2), 4.68 (d, 1 H, J = 2.7 Hz, H-1), 4.77 (AB q, 2 H, J = 11.4 Hz, Δδ = 0.06 ppm, PhCH_2), 4.89 (AB q, 2 H, J = 11.1 Hz, Δδ = 0.07 ppm, PhCH_2), 5.13 (dd, 1 H, J_{gem} = 2.1, J_{cis} = 10.5 Hz, H-10-cis), 5.26 (dd, H, J_{gem} = 2.1, J_{trans} = 17.7 Hz, H-10-trans), 6.03 (dd, 1 H, J_{cis} = 10.5, J_{trans} = 17.7 Hz, H-9), 7.34 (m, 15 H, *Ph*CH_2 × 3). Anal. Calcd for $C_{34}H_{42}O_7$: C, 72.57; H, 7.52. Found: C, 72.57; H, 7.59.

For **5**: TLC R_f 0.38 (B); IR (neat) 3430 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.09 (d, 3 H, J = 7.2 Hz, CH_3-6), 1.26 (s, 3 H, CH_3-8), 2.42 (m, 1 H, H-6), 2.98 (d, 1 H, J = 3.0 Hz, 4-OH), 3.38 (m, 1 H, H-7), 3.36 (s, 3 H, OCH_3), 3.50 (m, 3 H, H-2, H-4, H-5), 3.81 (t, 1 H, J = 9.0 Hz, H-3), 4.51 (AB q, 2 H, J = 10.8 Hz, Δδ = 0.32 ppm, PhCH_2), 4.65 (d, 1 H, J = 3.9 Hz, H-1), 4.75 (AB q, 2 H, J = 12.3 Hz, Δδ = 0.06 ppm, PhCH_2), 4.89 (AB q, 2 H, J = 10.2 Hz, Δδ = 0.12 ppm, PhCH_2), 5.06 (dd, 1 H, J_{gem} = 2.0, J_{cis} = 10.8 Hz, H-10-cis), 5.24 (dd, 1 H, J_{gem} = 2.0, J_{trans} = 17.2 Hz, H-10-trans), 6.00 (dd, 1 H, J_{cis} = 10.8, J_{trans} = 17.2 Hz, H-9), 7.34 (m, 15 H, *Ph*CH_2 × 3).

Methyl 2,3,4,7,9-Penta-*O*-acetyl-6-deoxy-6,8-di-*C*-methyl-α-D-*xylo*-nono-1,5-pyranoside (6b). (a) The major adduct from the previous reaction **4a** (20 mg, 0.036 mmol) was acetylated (see the General Procedures). A solution of the resulting acetate **4b** (15 mg, 0.025 mmol) in methylene chloride (1 mL) was treated with a saturated solution of ozone in methanol at −78 °C, and the reaction was warmed to room temperature and monitored by TLC (B). After 0.5 h, dimethyl sulfide (0.05 mL) was added and the reaction mixture stirred for an additional 0.5 h. The volatiles were removed in vacuo, the crude aldehyde **4c** was dissolved in methanol (1 mL), and sodium borohydride (2 mg, 0.05 mmol) was added at 0 °C. After 10 min at 0 °C, acetic acid (0.02 mL) was added and the reaction mixture stirred for an additional 10 min at 0 °C. The volatiles were removed in vacuo to give a yellow gum, which after flash chromatography afforded diol **6a** (8 mg, 53% from **4b**), TLC R_f 0.17 (D). Sodium (5 mg, 0.2 mmol) was added at −78 °C to a solution of diol **6a** (8 mg, 0.013 mmol) and liquid ammonia (2 mL) in dry dimethoxyethane (1 mL). The reaction mixture was warmed to −33 °C and stirring continued until the blue color had persisted for 20 min. The reaction was quenched by careful addition of solid ammonium chloride and the mixture allowed to warm to room temperature. The remaining solvent was removed in vacuo, and the crude residue, after acetylation (see the General Procedures), gave the pentaacetate **6b** (5 mg, 75% from **6a**): TLC R_f 0.26 (D); $[\alpha]^{25}_D$ 112° (*c* 0.90, $CHCl_3$); IR (neat) 3480 , 1725 (br) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.15 (s, 3 H, CH_3-8), 1.16 (d, 3 H, J = 7.5 Hz, CH_3-6), 1.98, 1.99, 2.03, 2.04, 2.09 (all s, 15 H, CH_3CO_2 × 5), 2.10 (m, 1 H, H-6), 3.36 (s, 3 H, OCH_3), 3.69 (dd, 1 H, $J_{4,5}$ = 9.6, $J_{5,6}$ = 3.3 Hz, H-5), 3.90 (br s, 2 H, CH_2-9), 4.75 (dd, 1 H, $J_{1,2}$ = 3.3, $J_{2,3}$ = 9.6 Hz, H-2), 4.81 (d, 1 H, J = 3.3 Hz, H-1), 5.25 (t, 1 H, J = 9.6 Hz, H-4), 5.29 (d, 1 H, J = 1.0 Hz, H-7), 5.40 (t, 1 H, J = 9.6 Hz, H-3). Anal. Calcd for $C_{22}H_{34}O_{13}$: C, 52.17; H, 6.77. Found: C, 52.12; H, 6.62.

(b) For the purpose of correlation, compound **6c** obtained from the epoxide **13** via **15** (12 mg, 0.026 mmol) was subjected to the identical two-step procedure described above for **6a**. The product obtained (7 mg, 54%) was identical with pentaacetate **6b** (TLC, IR, ^1H NMR), as described in part (a).

Methyl 2,3,4,7,9-Penta-*O*-acetyl-6-deoxy-6,8-di-*C*-methyl-α-L-*arabino*-nono-1,5-pyranoside (7b). (a) The minor compound **5** obtained from the vinyl magnesium bromide addition to **3a** was treated in a similar way (acetylation, ozonolysis, reduction) to that described for the major adduct **4a**. The product **7a** (27 mg, 0.044 mmol) was subjected to Birch reaction conditions and acetylation (see the General Procedures) to give pentaacetate **7b** (22 mg, 98%): TLC R_f 0.28 (D); $[\alpha]^{25}_D$ +115° (*c* 0.61, $CHCl_3$); IR (neat) 3500, 1720 (br) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.07 (d, 3 H, J = 7.5 Hz, CH_3-6), 1.14 (s, 3 H, CH_3-8), 1.98, 1.99, 2.01, 2.03, 2.11 (all s, 15 H, CH_3CO_2 × 5), 2.31 (m, 1 H, H-6), 2.44 (br s, 1 H, OH), 3.37 (s, 3 H, OCH_3), 3.80 (dd, 1 H, $J_{4,5}$ = 8.1, $J_{5,6}$ = 2.5 Hz, H-5), 3.87 (AB q, 2 H, J = 12.0 Hz, Δδ = 0.31 ppm, CH_2-9), 4.79 (m, 2 H, H-1, H-2), 5.20 (t, 1 H, J = 8.1 Hz, H-4), 5.29 (br s, 1 H, H-7), 5.40 (t, 1 H, J = 8.1 Hz, H-3). Anal. Calcd for $C_{22}H_{34}O_{13}$: C, 52.17; H, 6.77. Found: C, 52.33; H, 6.79.

(b) For the purpose of correlation, treatment of **7d**, the hydroxylation product of allylic alcohol 9b, was subjected to the conditions described above for **7a** to give a compound that was identical with pentaacetate **7b** (TLC, IR, ^1H NMR), as described in part (a).

Methyl 2,3-Di-*O*-benzyl-6-deoxy-6-*C*-methyl-7-*O*-(*tert*-butyldimethylsilyl)-L-*threo*-α-D-*gluco*-octopyranosiduronic Acid δ-Lactone (2b). The alcohol **1a** (730 mg, 1.05 mmol) was silylated, as described in the General Procedures, and transformed to lactone **2b** (450 mg, 81%) according to the procedure described for the benzylated analogue **1b**. For **2b**: TLC R_f 0.50 (D); $[\alpha]^{25}_D$ −15.1° (*c* 1.13, $CHCl_3$); IR (neat) 1760 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.02 and 0.11 [2 s, 3 H each, $Si(CH_3)_2$], 0.82 [s, 9 H, $SiC(CH_3)_3$], 1.01 (d, 3 H, J = 7.8 Hz, CH_3-6), 2.15 (m, 1 H, H-6), 3.27 (s, 3 H, OCH_3), 3.37 (dd, 1 H, $J_{1,2}$ = 3.0, $J_{2,3}$ = 8.4 Hz, H-2), 3.84 (d, 1 H, J = 6.9 Hz, H-7), 3.92 (m, 2 H, H-3, H-5), 3.98 (dd, J = 7.0, 8.0 Hz, H-4), 4.52 (d, 1 H, J = 3.0 Hz, H-1), 4.64 (AB q, 2 H, J = 12.3 Hz, Δδ = 0.11 ppm, PhCH_2), 4.79 (AB q, 2 H, J = 10.8 Hz, Δδ = 0.03 ppm, PhCH_2), 7.22 (m, 10 H, *Ph*CH_2 × 2). A portion of lactone **2b** (440 mg, 0.81 mmol) was dissolved in dry tetrahydrofuran (10 mL) under an argon atmosphere, and methylmagnesium chloride (0.72 mL, 2.8 M solution in tetrahydrofuran, 2.01 mmol) was added at 0 °C. The reaction mixture was warmed to room temperature and stirred for an additional 1 h. The solution was recooled to 0 °C, quenched with saturated ammonium chloride solution (20 mL), and extracted with ether (4 × 30 mL). The ethereal solution was dried (Na_2SO_4), filtered, and evaporated in vacuo. Flash chromatography of the yellow syrup gave diol **5a** (436 mg, 94%) as a clear gum: TLC R_f 0.33 (B); $[\alpha]^{25}_D$ +30° (*c* 0.83, $CHCl_3$); IR (neat) 3420 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.01 and 0.06 [2 s, 3 H each, $Si(CH_3)_2$], 0.76 [s, 9 H, $SiC(CH_3)_3$], 0.85 (d, 3 H, J = 7.2 Hz, CH_3-6), 0.95 and 1.06 (2 s, 3 H each, CH_3-8 × 2), 1.97 (s, 1 H, 8-OH), 2.23 (m, 1 H, H-6), 2.94 (d, 1 H, J = 1.2 Hz, 4-OH), 3.22 (s, 3 H, OCH_3), 3.33 (m, 3 H, H-2, H-4, H-5), 3.48 (d, 1 H, J = 1.8 Hz, H-7), 3.63 (dd, 1 H, J = 7.0, 8.6 Hz, H-3), 4.39 (d, 1 H, J = 3.9 Hz, H-1), 4.61 (AB q, 2 H, J = 12.6 Hz, Δδ = 0.08 ppm, PhCH_2), 4.74 (AB q, 2 H, J = 12.3 Hz, Δδ = 0.11 ppm, PhCH_2), 7.21 (m, 10 H, *Ph*CH_2 × 2). Anal. Calcd for $C_{32}H_{50}O_7Si$: C, 66.86; H, 8.77. Found: C, 66.79; H, 8.54.

Methyl 4-*O*-Benzoyl-2,3-di-*O*-benzyl-6,8,9-trideoxy-6,8-di-*C*-methyl-7-*O*-(*tert*-butyldimethylsilyl)-L-*threo*-α-D-*gluco*-non-8-eno-1,5-pyranoside (9b). Benzoyl chloride (0.26 mL, 2.21 mmol) was added at 0 °C to a solution of the diol **8a** (420 mg, 0.73 mmol) in dry pyridine (5 mL). The reaction mixture was heated to 40 °C and stirred for 16 h at this temperature. Excess reagent was decomposed by the addition of methanol (0.05

mL), and the solution was diluted with methylene chloride (50 mL) and washed successively with 5% hydrochloric acid (2 × 10 mL), saturated sodium bicarbonate (10 mL), and sodium chloride solutions (10 mL). The organic phase was dried over anhydrous sodium sulfate, filtered, and evaporated in vacuo. The residue was dissolved in methylene chloride and filtered through a short column of silica gel. Removal of the solvent in vacuo gave the crude benzoate **8b** as a clear syrup. Thionyl chloride (0.08 mL, 1.10 mmol) was added at 0 °C to a solution of crude tertiary alcohol **8b** in dry pyridine (2 mL). After 5 min at 0 °C, the reaction was quenched with methanol (0.02 mL), and the solution was diluted with methylene chloride (50 mL) and washed successively with 5% hydrochloric acid (2 × 10 mL), saturated sodium bicarbonate (10 mL), and sodium chloride solutions (10 mL). The organic phase was dried (Na_2SO_4), filtered, and evaporated in vacuo to give the crude olefin **9a** as a yellow oil. The material was dissolved in methanol and *dl*-camphorsulfonic acid was added to achieve a pH of 3. The reaction mixture was stirred at room temperature for 20 h and then neutralized by addition of sodium bicarbonate. The solvent was removed in vacuo and the residue taken up in ethyl acetate and filtered. The filtrate was evaporated in vacuo to give a yellow syrup, which yielded after flash chromatography allylic alcohol **9b** (275 mg, 69% from **8a**): TLC R_f 0.30 (B); $[\alpha]^{25}_D$ −37.7 (*c* 1.26, $CHCl_3$); IR (neat) 3550, 1720, 1650, 845 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.94 (d, 3 H, J = 7.2 Hz, CH_3-6), 1.49 (br s, 3 H, CH_3-8), 1.81 (m, 1 H, H-6), 2.94 (s, 1 H, OH), 3.43 (s, 3 H, OCH_3), 3.67 (dd, 1 H, $J_{1,2}$ = 2.7, $J_{2,3}$ = 9.0 Hz, H-2), 3.97 (dd, 1 H, $J_{5,6}$ = 1.4, $J_{4,5}$ = 9.3 Hz, H-5), 4.05 (t, 1 H, J = 9.1 Hz, H-3), 4.58 (br s, 1 H, =C*H*), 4.64 (d, 1 H, J = 2.7 Hz, H-1), 4.64 (br s, 1 H, H-7), 4.73 (AB q, 2 H, J = 11.7 Hz, $\Delta\delta$ = 0.18 ppm, PhCH_2), 4.76 (AB q, 2 H, J = 11.7 Hz, $\Delta\delta$ = 0.13 ppm, PhCH_2), 5.05 (br s, 1 H, =C*H*), 5.46 (t, 1 H, J = 9.5 Hz, H-4), 7.22 (m, 10 H, *Ph*CH_2 × 2), 7.42, 7.57, 7.98 (t, t, d, J = 7 Hz, 2 H, 1 H, 2 H, respectively, *Ph*CO_2). Anal. Calcd for $C_{33}H_{38}O_7$: C, 72.51; H, 7.01. Found: C, 72.56; H, 6.97.

Methyl 4-*O*-Acetyl-2,3,7-tri-*O*-benzyl-6,8,9-trideoxy-6,8-di-*C*-methyl-L-*threo*-α-D-*gluco*-non-8-eno-1,5-pyranoside (9c). The δ-lactone **2a** was converted into the corresponding olefin **9c** (91%) as described above for the preparation of **9a**, except for the use of the acetyl rather than benzoyl protecting groups: TLC R_f 0.32 (B); $[\alpha]^{25}_D$ +23.5 (*c* 1.19, $CHCl_3$); IR (neat) 1740, 905 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.01 (d, 3 H, J = 6.9 Hz, CH_3-6), 1.68 (br s, 3 H, CH_3-8), 1.69 (s, 3 H, CH_3CO_2), 1.93 (m, 1 H, H-6), 3.33 (s, 3 H, OCH_3), 3.50 (dd, 1 H, $J_{1,2}$ = 3.0, $J_{2,3}$ = 9.6 Hz, H-2), 3.61 (d, 1 H, J = 7.8 Hz, H-7), 3.73 (dd, 1 H, $J_{4,5}$ = 9.6, $J_{5,6}$ = 3.0 Hz, H-5), 3.78 (t, 1 H, J = 9.6 Hz, H-3), 4.36 (AB q, 2 H, J = 12.3 Hz, $\Delta\delta$ = 0.31 ppm, PhCH_2), 4.54 (d, 1 H, J = 3.0 Hz, H-1), 4.65 (AB q, 2 H, J = 12.3 Hz, $\Delta\delta$ = 0.15 ppm, PhCH_2), 4.74 (AB q, 2 H, J = 12.3 Hz, $\Delta\delta$ = 0.21 ppm, PhCH_2), 4.88 and 5.10 (both br s, 1 H each, CH_2-9), 4.97 (t, 1 H, J = 9.6 Hz, H-4), 7.28 (m, 15 H, *Ph*CH_2 × 3). Anal. Calcd for $C_{35}H_{42}O_7$: C, 73.15; H, 7.37. Found: C, 73.33; H, 7.47.

Methyl 4-*O*-Acetyl-8,9-anhydro-2,3,7-tri-*O*-benzyl-6-deoxy-6,8-di-*C*-methyl-D-*xylo*- and -L-*arabino*-α-D-*gluco*-nono-1,5-pyranoside (10). *m*-Chloroperoxybenzoic acid (26 mg, 85% technical grade, 0.12 mmol) was added to a solution of olefin **9c** (30 mg, 0.052 mmol) in dry methylene chloride (2 mL). The reaction mixture was stirred at room temperature for 10 h, diluted with methylene chloride (5 mL), and washed successively with 10% sodium thiosulfate (2 mL) and saturated sodium bicarbonate solutions (2 × 2 mL). The organic phase was dried (Na_2SO_4), filtered, and concentrated in vacuo. Flash chromatography of the residue afforded an inseparable mixture **10** (20 mg, 66%) as a clear syrup: TLC R_f 0.20 (B); IR (neat) 1740 cm^{-1}; selected resonances from the ^1H NMR (300 MHz, $CDCl_3$) δ 1.01 and 1.05 (2 d, respective ratio 55:45, J = 7.5 Hz, CH_3-6), 1.26 and 1.33 (2 s, respective ratio 55:45, CH_3-8), 1.71 and 1.83 (2 s, respective ratio 45:55, CH_3CO_2), 1.97 (m, H-6), 2.62 and 2.66 (2 AB q, J = 4.5, 3.9 Hz, $\Delta\delta$ = 0.25, 0.09 ppm, respectively, CH_2-9), 2.92 (d, J = 7.0 Hz, H-7 of one epimer), 3.34 (s, OCH_3), 3.48 (m, H-2), 3.80 (m, H-3, H-5, H-7 of other epimer), 4.36–4.77 (m, PhC*H* × 4), 4.84–4.98 (m, PhC*H* × 2, H-4), 7.27 (m, *Ph*CH_2). Anal. Calcd for $C_{35}H_{42}O_8$: C, 71.17; H, 7.17. Found: C, 70.93; H, 7.20.

4-*O*-Acetyl-5,8-anhydro-2,3,7-tri-*O*-benzyl-6-deoxy-6,8-di-*C*-methyl-D-*xylo*- and -L-*arabino*-α-D-*gluco*-nonaldose (12). Aqueous perchloric acid (0.1 mL of a 1% solution) was added to a solution of mixture **10** (15 mg, 0.025 mmol) in acetonitrile (1 mL). The reaction mixture was stirred at room temperature for 1.5 h, neutralized by the addition of saturated sodium bicarbonate solution, diluted with a saturated solution of sodium chloride (5 mL), and extracted with ether (4 × 5 mL). The combined organics were washed with saturated sodium chloride solution (1 × 5 mL), dried (Na_2SO_4), filtered, and evaporated in vacuo. Flash chromatography of the crude syrup afforded **12** (9 mg, 62%) as a clear gum: TLC R_f 0.10 (B); IR (neat) 3450, 1715 (br) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.95 and 1.00 (2 d, J = 6.5 Hz, respective ratio 45:55, CH_3-6), 1.03 and 1.19 (2 s, respective ratio 45:55, CH_3-8), 2.32 (m, H-6), 3.20–3.88 (m, H-2, H-5, H-7, CH_2-9), 4.04 and 4.11 (2 dd, respective ratio 45:55, $J_{2,3}$ = 5.7, $J_{3,4}$ = 3.0 Hz, H-3), 4.38–4.72 (m, PhCH_2), 5.18 and 5.27 (2 dd, respective ratio 45:55, $J_{3,4}$ = 5.7, $J_{4,5}$ = 8.7 Hz, H-4), 7.25 (m, *Ph*CH_2), 9.68 and 9.69 (2 s, respective ratio 55:45, C*H*O). Anal. Calcd for $C_{34}H_{40}O_8$: C, 70.81; H, 6.99. Found: C, 70.83; H, 6.97.

Methyl 8,9-Anhydro-4-*O*-benzoyl-2,3-tri-*O*-benzyl-6-deoxy-6,8-di-*C*-methyl-D-*arabino*-α-D-*gluco*-nono-1,5-pyranoside (13a). (a) *tert*-Butyl hydroperoxide (0.025 mL of ~2.5 M solution in 1,2-dichloroethane, 0.062 mmol) was added to a solution of vanadyl acetylacetonate (2 mg, 0.008 mmol) and allylic alcohol **9b** (22 mg, 0.039 mmol) in dry benzene (2 mL). The reaction was stirred at room temperature until the bright red coloration had changed to greenish-yellow (0.5 h), diluted with ethyl acetate (20 mL), and washed sequentially with 1 M sodium bisulfite (5 mL) and saturated sodium chloride (5 mL) solutions. The organic phase was dried (Na_2SO_4), filtered, and evaporated in vacuo to give a yellow oil. Flash chromatography afforded a single compound **13a** (20 mg, 88%) as a clear gum: TLC R_f 0.20 (C); $[\alpha]^{25}_D$ −33 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 0.98 (d, 3 H, J = 7.2 Hz, CH_3-6), 1.16 (s, 3 H, CH_3-8), 1.91 (m, 1 H, H-6), 2.42 (s, 1 H, OH), 2.74 (AB q, 2 H, J = 5.7 Hz, $\Delta\delta$ = 0.41 ppm, CH_2-9), 3.43 (s, 3 H, OCH_3), 3.65 (dd, 1 H, $J_{1,2}$ = 3.0, $J_{2,3}$ = 9.6 Hz, H-2), 3.94 (dd, 1 H, $J_{4,5}$ = 9.8, $J_{5,6}$ = 4.2 Hz, H-5), 4.04 (t, 1 H, J = 9.6 Hz, H-3), 4.28 (br s, 1 H, H-7), 4.65 (d, 1 H, J = 3.0 Hz, H-1), 4.71 (AB q, 2 H, J = 11.4 Hz, $\Delta\delta$ = 0.19 ppm, PhCH_2), 4.75 (AB q, 2 H, J = 13.2 Hz, $\Delta\delta$ = 0.12 ppm, PhCH_2), 5.37 (dd, 1 H, $J_{3,4}$ = 9.6, $J_{4,5}$ = 9.8 Hz, H-4), 7.20 (m, 10 H, *Ph*CH_2 × 2), 7.44, 7.58, 7.98 (t, t, d, 2 H, 1 H, 2 H, respectively, J = 7.0 Hz, PhCO_2). Anal. Calcd for $C_{33}H_{38}O_8$: C, 70.44; H, 6.81. Found: C, 70.53; H, 6.65.

(b) The allylic alcohol **9b** (125 mg, 0.23 mmol) was treated under the conditions described above for the preparation of **10** except that the reaction was completed with 0.5 h. This procedure afforded an inseparable mixture of two compounds (16 mg, 92%), the ^1H NMR of which indicated an 8:1 ratio. The major compound was identical with **13a** (TLC, IR, ^1H NMR).

Methyl 2,3-Di-*O*-benzyl-6-deoxy-6,8-di-*C*-methyl-D-*xylo*-α-D-*gluco*-nono-1,5-pyranoside (6c). Phenyl isocyanate (0.08 mL, 0.80 mmol) was added to a solution of epoxy alcohol **13a** (110 mg, 0.20 mmol) in dry pyridine (2 mL) and the reaction mixture stirred at room temperature for 20 h. The reaction was quenched by the addition of water (0.05 mL), and the volatiles were removed in vacuo. The solid residue was taken up in chloroform and filtered, and the filtrate was concentrated in vacuo to give a 5:1 mixture of the isomers **13b** and **13c**. For **13b**: TLC R_f 0.30 (F); IR (neat) 3340, 1710 (br), 1600 (w) cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 1.07 (d, 3 H, J = 7.2 Hz, CH_3-6), 1.28 (s, 3 H, CH_3-8), 2.03 (m, 1 H, H-6), 2.65 (AB q, 2 H, J = 4.8 Hz, $\Delta\delta$ = 0.30 ppm, CH_2-9), 3.34 (s, 3 H, OCH_3), 3.63 (dd, 1 H, $J_{1,2}$ = 4.0, $J_{2,3}$ = 10.0 Hz, H-2), 3.82 (dd, 1 H, $J_{4,5}$ = 10.0, $J_{5,6}$ = 4.0 Hz, H-5), 4.01 (t, 1 H, J = 10.0 Hz, H-3), 4.45 (d, 1 H, J = 4.0 Hz, H-1), 4.62 (AB q, 2 H, J = 11.2 Hz, $\Delta\delta$ = 0.15 ppm, PhCH_2), 4.69 (AB q, 2 H, J = 10.5 Hz, $\Delta\delta$ = 0.20 ppm, PhCH_2), 5.46 (d, 1 H, J = 2.0 Hz, H-7), 5.53 (t, J = 10.0 Hz, H-4), 6.58 (br s, 1 H, NH), 7.25–7.98 (m, 20 H, *Ph*CH_2 × 2, *Ph*CO_2, *Ph*NH). For **13c**: TLC R_f 0.60 (F); IR (neat) 3350, 1712 (br) cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.52 (d, 3 H, J = 7.2 Hz, CH_3-6), 1.03 (s, 3 H, CH_3-8), 1.80 (m, 1 H, H-6), 2.16 (AB q, 2 H, J = 4.6 Hz, $\Delta\delta$ = 0.12 pm, CH_2-9), 3.32 (s, 3 H, OCH_3), 3.58 (dd, 1 H, $J_{1,2}$ = 4.0, $J_{2,3}$ = 8.8 Hz, H-2), 3.64 (dd, 1 H, $J_{4,5}$ = 8.8, $J_{5,6}$ = 3.8 Hz, H-5), 3.96 (t, 1 H, J = 8.8 Hz, H-3), 4.42 (d, 1 H, J = Hz, H-1), 4.68 (AB q, 2 H, J = 12.8 Hz, $\Delta\delta$ = 0.22 ppm, PhCH_2), 4.78 (AB q, 2 H, J = 12.0 Hz, $\Delta\delta$ = 0.18 ppm, PhCH_2) 5.50 (t, 1 H, J = 8.8 Hz, H-4), 5.58 (br s, 1 H, H-7), 7.20–7.90 (m, 20 H, *Ph*CH_2 × 2, *Ph*CO_2, *Ph*NH), 9.07

(br s, 1 H, NH). The crude mixture of carbamates was dissolved in an 80% solution of acetic acid in water (2 mL) and the reaction mixture stirred at 80 °C for 0.5 h. The volatiles were removed in vacuo, and the residue was subjected to flash chromatography. The major product was the cyclic carbonate **15** (18 mg, 16% from **13a**): colorless gum; TLC R_f 0.27 (H); IR (neat) 3430, 1790, 1720 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.13 (d, 3 H, J = 6.3 Hz, CH_3-6), 1.23 (s, 3 H, CH_3-8), 1.91 (m, 1 H, H-6), 2.70 (m, 1 H, OH), 3.42 (s, 3 H, OCH_3), 3.64 (dd, 1 H, $J_{1,2}$ = 4.2, $J_{2,3}$ = 9.0 Hz, H-2), 3.70 (m, 3 H, H-5, CH_2-9), 4.08 (t, 1 H, J = 9.0 Hz, H-3), 4.69 (AB q, 2 H, J = 10.8 Hz, $\Delta\delta$ = 0.07 ppm, PhCH_2), 4.71 (d, 1 H, J = 4.2 Hz, H-1), 4.72 (AB q, 2 H, J = 12.1 Hz, $\Delta\delta$ = 0.07 ppm, PhCH_2), 5.02 (s, 1 H, H-7), 5.14 (t, 1 H, J = 9.0 Hz, H-4), 7.20–7.94 (m, 15 H, PhCH$_2$ × 2, PhCO$_2$). The material was treated with a solution of sodium methoxide (0.10 mL of a 1.5 M solution, 0.15 mmol) in dry methanol. After it was stirred at room temperature for 4 h, the reaction mixture was neutralized with 2 N hydrochloric acid in methanol and the solvent evaporated in vacuo. The residue was triturated with ethyl acetate, filtered, and concentrated in vacuo, and the product **6c** (11 mg, 78%) was acetylated (see the General Procedures). The triacetate **6d** had the following physical characteristics: TLC R_f 0.12 (C); IR (neat) 3450, 1720, (br) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.10 (d, 3 H, J = 7.0 Hz, CH_3-6), 1.11 (s, 3 H, CH_3-8), 1.84, 1.89, and 2.06 (all s, 3 H each, CH_3CO_2 × 3), 2.08 (s, 1 H, OH), 3.29 (s, 3 H, OCH_3), 3.49 (m, 2 H, H-2, H-5), 3.80 (t, 1 H, J = 9.9 Hz, H-3), 3.86 (br s, 2 H, CH_2-9), 4.26 (d, 1 H, J = 3.3 Hz, H-1), 4.65 (AB q, 2 H, J = 11.7 Hz, $\Delta\delta$ = 0.16 ppm, PhCH_2), 4.70 (AB q, 2 H, J = 11.7 Hz, $\Delta\delta$ = 0.23 ppm, PhCH_2), 5.16 (dd, 1 H, $J_{3,4}$ = 9.9, $J_{4,5}$ = 10.8 Hz, H-4), 5.26 (br s, 1 H, H-7), 7.27 (m, 10 H, PhCH$_2$ × 2). Anal. Calcd for $C_{32}H_{42}O_{11}$: C, 63.77; H, 7.03. Found: C, 63.64; H, 7.21.

For **16** (5 mg, 5.0% from **13a**): colorless gum; TLC R_f 0.23 (H); IR (neat) 3400, 1705 (br), 1600 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$), δ 1.13 (d, 3 H, J = 7.2 Hz, CH_3-6), 1.30 (s, 3 H, CH_3-8), 2.26 (m, 1 H, OH) 2.42 (m, 1 H, H-6), 3.47 (d AB q, 2 H, $J_{9,OH}$ = 6.0, J_{gem} = 10.8 Hz, $\Delta\delta$ = 0.07 ppm, CH_2-9), 3.91 (dd, 1 H, $J_{4,5}$ = 3.9, $J_{5,6}$ = 9.3 Hz, H-5), 4.85 (d, 1 H, J = 7.2 Hz, H-7), 5.23 (AB q, 2 H, J = 10.8 Hz, $\Delta\delta$ = 0.14 ppm, PhCH_2), 6.02 (d, 1 H, J = 7.8 Hz, H-3), 6.16 (dd, 1 H, $J_{3,4}$ = 10.8, $J_{4,5}$ = 3.9 Hz, H-4), 6.91 (br s, 1 H, NH), 7.24–8.07 (m, 15 H, PhCH$_2$, PhCO$_2$, PhNH), 9.35 (s, 1 H, CHO).

Methyl 4-*O*-Acetyl-2,3,7-tri-*O*-benzyl-6-deoxy-6,8-di-*C*-methyl-L-*arabino*-α-D-*gluco*-nono-1,5-pyranoside (7a). *N*-Methylmorpholine *N*-oxide (0.02 mL, 60 wt % in water, 0.10 mmol) and osmium tetraoxide (0.6 mL, 2.5 wt % in *tert*-butyl alcohol, 0.006 mmol) were added to a solution of **9c** (31 mg, 0.054 mmol) in acetone (2 mL). The reaction mixture was stirred for 12 h at room temperature. Sodium bisulfite (0.02 mL of N solution) was added, and the mixture was stirred for an additional 0.5 h. Most of the solvent was evaporated in vacuo, and the residue was diluted with water (2 mL) and extracted with ethyl acetate (3 × 5 mL). The combined organic extracts were dried (Na_2SO_4), filtered, and concentrated in vacuo. Flash chromatography gave the diol **7a** (28 mg, 85%) as a clear gum: TLC R_f 0.25 (D); $[\alpha]^{25}_D$ +4.2 (*c* 0.51, $CHCl_3$); IR (neat) 3500, 1730 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$), δ 1.0 (s, 3 H, CH_3-8), 1.07 (d, 3 H, J = 7.5 Hz, CH_3-6), 1.65 (t, 1 H, J = 6.2 Hz, 9-OH), 1.85 (s, 3 H, CH_3CO_2), 2.41 (m, 1 H, H-6), 2.31 (s, 1 H, 8-OH), 3.19 (dd, 1 H, $J_{9a,OH}$ = 6.2, J_{gem} = 10.5 Hz, H-9a), 3.36 (s, 3 H, OCH_3), 3.55 (m, 3 H, H-2, H-7, H-9b), 3.63 (dd, 1 H, $J_{4,5}$ = 9.6, $J_{5,6}$ = 2.0 Hz, H-5), 3.84 (t, 1 H, J = 10.0 Hz, H-3), 4.49 (AB q, 2 H, J = 12.0 Hz, $\Delta\delta$ = 0.20 ppm, PhCH_2), 4.53 (d, 1 H, J = 3.3 Hz, H-1), 4.66 (AB q, 2 H, J = 10.0 Hz, $\Delta\delta$ = 0.14 ppm, PhCH_2), 4.73 (AB q, 2 H, J = 11.0 Hz, $\Delta\delta$ = 0.20 ppm, PhCH_2), 4.92 (t, 1 H, J = 10.0 Hz, H-4), 7.42 (m, 15 H, PhCH$_2$ × 3). Anal. Calcd for $C_{35}H_{44}O_9$: C, 69.06; H, 7.29. Found: C, 69.03; H, 7.37.

Methyl 2,3-Di-*O*-benzyl-6-deoxy-6,8-di-*C*-methyl-L-*arabino*-α-D-*gluco*-nono-1,5-pyranoside (7d). Allylic alcohol **9b** (72 mg, 0.13 mmol) was treated under similar hydroxylation conditions to those described for the preparation of **7a**. The reaction was completed within 2 h and afforded triol **7c** (65 mg, 85%). Triol **7d** (65 mg, 0.11 mmol) was debenzoylated by using sodium methoxide according to the procedure described for the preparation of **6a**, and the resulting tetrol **7d** was acetylated (see the General Procedures). The triacetate **7e** had the following physical properties: TLC R_f 0.14 (C); IR (neat) 3500, 1635 (br) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.01 (d, 3 H, J = 6.6 Hz, CH_3-6), 1.08 (s, 3 H, CH_3-8), 1.85, 1.87, and 2.08 (all s, 3 H each, CH_3CO_2 × 3), 2.19 (m, 1 H, H-6), 2.51 (s, 1 H, OH), 3.30 (s, 3 H, OCH_3), 3.52 (dd, 1 H, $J_{1,2}$ = 3.3, $J_{2,3}$ = 9.8 Hz, H-2), 3.55 (dd, 1 H, $J_{4,5}$ = 9.8, $J_{5,6}$ = 3.3 Hz, H-5), 3.80 (AB q, 2 H, J = 11.1 Hz, $\Delta\delta$ = 0.24 ppm, CH_2-9), 3.81 (t, 1 H, J = 9.8 Hz, H-3), 4.34 (d, 1 H, J = 3.3 Hz, H-1), 4.64 (AB q, 2 H, J = 12.0 Hz, $\Delta\delta$ = 0.13 ppm, PhCH_2), 4.67 (AB q, 2 H, J = 12.0 Hz, $\Delta\delta$ = 0.23 ppm, PhCH_2), 5.13 (t, 1 H, J = 9.8 Hz, H-4), 5.29 (br s, 1 H, H-7), 7.24 (m, 10 H, PhCH$_2$ × 2). Anal. Calcd for $C_{32}H_{42}O_{11}$: C, 63.77; H, 7.03. Found: C, 63.69; H, 7.29.

Registry No. **1a**, 110045-79-9; **1b**, 110045-80-2; **2a**, 110045-81-3; **2b**, 110045-90-4; **3a**, 110045-82-4; **4a**, 110045-83-5; **4b**, 110045-85-7; **4c**, 110045-86-8; **5**, 110045-84-6; **6a**, 110045-87-9; **6b**, 110045-88-0; **6c**, 110046-03-2; **6d**, 110046-04-3; **7a**, 110046-06-5; **7b**, 110045-89-1; **7c**, 110046-07-6; **7d**, 110046-08-7; **7e**, 110046-09-8; **8a**, 110045-91-5; **8b**, 110045-92-6; **9a**, 110045-93-7; **9b**, 110045-94-8; **9c**, 110045-95-9; **10** (isomer 1), 110045-96-0; **10** (isomer 2), 110045-97-1; **12** (isomer 1), 110045-98-2; **12** (isomer 2), 110046-10-1; **13a**, 110045-99-3; **13b**, 110046-00-9; **13c**, 110046-01-0; **15**, 110046-02-1; **16**, 110046-05-4; vinylmagnesium bromide, 1826-67-1.

Minor and Trace Sterols from Marine Invertebrates. 58.[1] Stereostructure and Synthesis of New Sponge Sterols Jaspisterol and Isojaspisterol

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Two new trace sterols, jaspisterol and isojaspisterol, were isolated from the Australian sponge *Jaspis stellifera*. The structures, geometry, and stereochemistry were determined by synthesis and spectroscopic methods. Jaspisterol (**26**) and isojaspisterol (**25**) correspond to further variations of the aplysterol side chain.

While studying the biosynthesis of marine sterols in the Australian sponge *Jaspis stellifera*, we encountered a new trace sterol fraction, which was highly radioactive when carbon-14-labeled epicodisterol (**1**) was fed to the sponge.[2] In order to interpret our incorporation results, the composition of this fraction had to be determined. We now

(1) For preceding paper, see: Cho, J.-H.; Djerassi, C. *J. Chem. Soc. Perkin Trans. 1* **1987**, 1307–1318.

(2) Cho, J.-H.; Thompson, J. E.; Stoilov, I. L.; Silva, C.; Djerassi, C., manuscript in preparation. 25% of the radioactivity accumulated in the jaspisterol fraction when carbon-14-labeled epicodisterol (**1**) was fed to the sponge, whereas no radioactivity was encountered when radiolabeled codisterol (**2**) was fed.

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