scientific discussions and encouragement.

Registry No. (*R,S*)-**3**, 90134-40-0; (*S*)-(+)-**3**, 90192-96-4; (*R*)-(−)-**3**, 90192-97-5; (*R,S*)-**4**, 69177-44-2; (*S*)-(+)-**4**, 65756-08-3; (*R*)-(−)-**4**, 90192-98-6; (*R,S*)-**5**, 82679-36-5; (*S*)-(+)-**5**, 82729-82-6; (*R*)-(−)-**5**, 90192-99-7; (*R,S*)-**6**, 90134-41-1; (*S*)-(+)-**6**, 90193-00-3; (*R*)-(−)-**6**, 90193-01-4; (*R,S*)-**7**, 90134-42-2; (*S*)-(+)-**7**, 90193-02-5; (*R*)-(−)-**7**, 90193-03-6; **8**, 928-90-5; **9**, 53293-00-8; (*R,S*)-**10**, 90134-43-3; (*S*)-(+)-**10**, 90193-04-7; (*R*)-(−)-**10**, 90193-05-8; (*R,S*)-**11**, 90134-44-4; (*R,S*)-**12**, 90134-45-5; (*S*)-(+)-**12**, 90242-06-1; (*R*)-(−)-**12**, 90193-06-9; **13**, 927-74-2; **14**, 78592-82-2; **15**, 90134-46-6; **16**, 90134-47-7; **18**, 90134-48-8; **19**, 90134-49-9; **20**, 90134-50-2; **21**, 90134-51-3; **23**, 1002-36-4; **24**, 63478-76-2; **25**, 90134-52-4; **26**, 90134-53-5; **27**, 90134-54-6; **28**, 90134-55-7; **29**, 90134-56-8; **30**, 90134-57-9; (*R,S*)-I, 90134-38-6; (*S*)-(+)-I, 90192-94-2; (*R*)-(−)-I, 90192-95-3; II, 86583-51-9; III, 90134-39-7; 1-butyne, 107-00-6; (*R,S*)-methyloxirane, 16033-71-9; (*S*)-(−)-methyloxirane, 16088-62-3; (*R*)-(+)-methyloxirane, 15448-47-2; 1-hexyne, 693-02-7.

Synthesis of Two Fragments of the 14-Membered Macrolide Antibiotic Oleandomycin from D-Glucose

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Methyl 3-*O*-benzyl-7-*O*-(*tert*-butyldimethylsilyl)-2,4-di-*C*-methyl-2,4,6-trideoxy-α-D-*galacto*-heptopyranoside and methyl 2,4-di-*C*-methyl-3-*O*-((2-methoxyethoxy)methyl)-2,4,6-trideoxy-α-D-*galacto*-hexopyranoside, protected forms of the C_3–C_8 and C_9–C_{13} fragments, respectively, of the medically important 14-membered macrolide antibiotic oleandomycin were synthesized from D-glucose. Catalytic hydrogenation of the intermediate 4-*C*-methylene derivatives in the presence of 10% palladium on barium sulfate proceeded with high stereoselectivity, affording mainly galacto isomers. The C_3 hydroxy groups of these chiral fragments were protected with different groups in view of the planned ultimate glycosylation reactions.

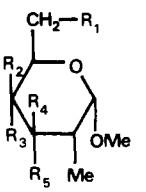
Considerable effort has been directed recently toward the total synthesis of the medically important macrolide antibiotics.[1] A recent paper[2] on the construction of the C_1–C_7 and C_8–C_{13} fragments of the aglycon of oleandomycin (**6**) prompts us to disclose results obtained in this field in our laboratories.

Our synthetic strategy for the construction of the major part of the aglycon of oleandomycin (**6**), from carbohydrate precursors, Scheme I, is based on an aldol condensation reaction between fragments **2** and **4** to create the C_8–C_9 bond of intermediate **5**. The stereochemical complication resulting from this reaction will be of no consequence since the expected diasterochemical aldol mixture (**5**) will have to be oxidized at C_9 to a ketone. This step is planned to be carried out after removal of the unwanted oxygen atom of **5** at C_7 as performed in the recently reported Woodward synthesis of erythromycin A.[3]

We describe here the synthesis of two carbohydrates (**1** and **3**) comprising seven of the 10 asymmetric centers of the aglycon of oleandomycin (**6**).[4] These carbohydrates, with the required different protecting groups on their C_3 oxygen atom, are precursors of fragments **2** and **4**, respectively.

Results and Discussion

Synthesis of the Protected Form of the C_3–C_8 Fragment of the Aglycon of Oleandomycin. Selective tosylation of diol **7**, prepared in 10 steps from D-glucose[5,6] afforded **8**. Treatment of **8** in dimethyl sulfoxide solution with 1.5 equiv of potassium cyanide allowed chain extension and preparation of **9**. Reaction of **9** in dry toluene at room temperature with diisobutylaluminum hydride followed by lithium aluminum hydride reduction afforded



7, $R_1 = R_3 = OH$; $R_2 = R_4 = H$; $R_5 = OBn$
8, $R_1 = OTs$; $R_2 = R_4 = H$; $R_3 = OH$; $R_5 = OBn$
9, $R_1 = CN$; $R_2 = R_4 = H$; $R_3 = OH$; $R_5 = OBn$
10, $R_1 = CH_2OH$; $R_2 = R_4 = H$; $R_3 = OH$; $R_5 = OBn$
11, $R_1 = CH_2OSi\text{-}t\text{-}BuMe_2$; $R_2 = R_4 = H$; $R_3 = OH$; $R_5 = OBn$
12, $R_1 = CH_2OSi\text{-}t\text{-}BuMe_2$; $R_4 = H$; $R_2,R_3 = O$; $R_5 = OBn$
13, $R_1 = CH_2OSi\text{-}t\text{-}BuMe_2$; $R_5 = H$; $R_2,R_3 = O$; $R_4 = OBn$
14, $R_1 = CH_2OSi\text{-}t\text{-}BuMe_2$; $R_5 = H$; $R_2,R_3 = CH_2$; $R_4 = OBn$
15, $R_1 = CH_2OSi\text{-}t\text{-}BuMe_2$; $R_2 = R_5 = H$; $R_3 = Me$; $R_4 = OBn$
18, $R_1 = Br$; $R_2 = R_4 = H$; $R_3 = OBz$; $R_5 = OMEM$
19, $R_1 = R_2 = R_4 = H$; $R_3 = OBz$; $R_5 = OMEM$
20, $R_1 = R_2 = R_4 = H$; $R_3 = OH$; $R_5 = OMEM$
21, $R_1 = R_4 = H$; $R_2,R_3 = O$; $R_5 = OMEM$
22, $R_1 = R_5 = H$; $R_2,R_3 = O$; $R_4 = OMEM$
23, $R_1 = R_5 = H$; $R_2,R_3 = CH_2$; $R_4 = OMEM$
24, $R_1 = R_2 = R_5 = H$; $R_3 = Me$; $R_4 = OMEM$

the diol **10**. Selective protection of the primary hydroxy group of **10** by treatment with *tert*-butyldimethylsilyl chloride furnished **11**. Oxidation of **11** by pyridinium chlorochromate[7] gave the highly unstable ketone **12**. Isomerization of the axially oriented C_3 substituent of **12** was performed by sodium methoxide treatment,[5] leading

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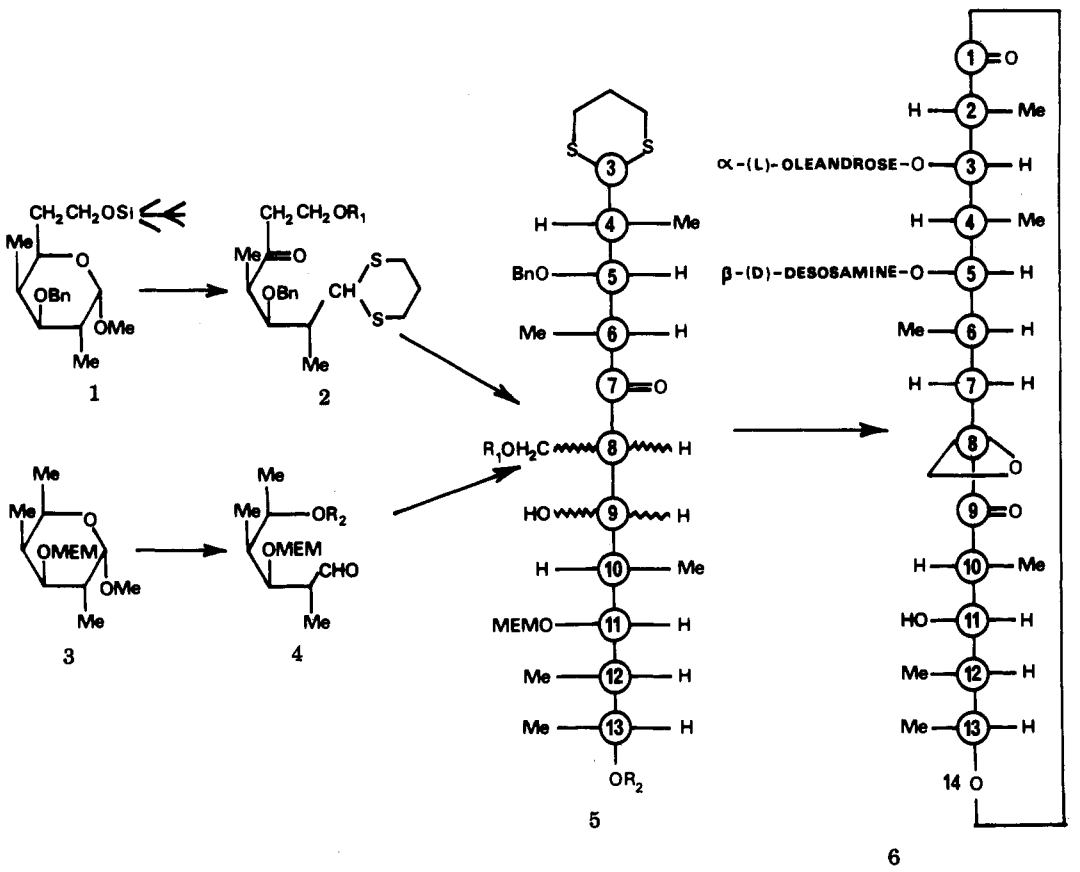
0022-3263/84/1949-2338$01.50/0

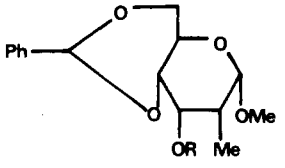
Scheme I



to **13**. Reaction of **13** with methylenetriphenylphosphorane furnished the unsaturated carbohydrate **14**. Catalytic hydrogenation of the latter proceeded[6] in the presence of 10% palladium on barium sulfate with high stereoselectivity, affording methyl 3-*O*-benzyl-7-*O*-(*tert*-butyldimethylsilyl)-2,4-di-*C*-methyl-2,4,6-trideoxy-α-D-*galacto*-heptopyranoside (**1**) in 80% yield and its C_4 epimer **15**.

The stereochemistry at C_4 of the major reduction product of **14** was easily established on the basis of the double of doublets type ^1H NMR signal of H_3 ($J_{3,4}$ = 5 Hz and $J_{3,2}$ = 11 Hz). This conclusion was consistent with a very high field ^{13}C NMR signal (5.4 ppm) observed in the spectrum of **1** and attributed to its highly hindered axially disposed C_4 methyl group.

Synthesis of the Protected Form of the C_9–C_{13} Fragment of the Aglycon of Oleandomycin. In the synthesis of the C_9–C_{13} fragment of the aglycon of oleandomycin (**6**), *N*-bromosuccinimide-induced opening of a 4,6-*O*-benzylidene system was planned. Thus, protection of the C_3 oxygen atom of **16** with a (2-methoxyethoxy)-



16, R = H
17, R = $CH_2OCH_2CH_2OMe$ (MEM)

methyl (MEM) group was attempted since this group is also known for its stability under basic conditions. Treatment of methyl 4,6-*O*-benzylidene-2-deoxy-2-*C*-methyl-α-D-allopyranoside (**16**) with (2-methoxyethoxy)-methyl chloride[8] in refluxing ether afforded **17**. Reaction of **17** with *N*-bromosuccinimide gave **18**. Catalytic hydrogenation of **18** in the presence of 10% Pd/C furnished the 2,6-dideoxy derivative **19**. Hydrolysis of the benzoate group of **19** proceeded smoothly, leading to **20**. Transformation of **20** into **23** via the intermediates **21** and **22** was accomplished as described above for the preparation of **14** from **11**. Catalytic hydrogenation of the unsaturated derivative **23** was attempted in the presence of 10% palladium on barium sulfate in different solvents (benzene, ethyl acetate, methanol). The highest yield of the target methyl 2,4-di-*C*-methyl-3-*O*-((2-methoxyethoxy)-methyl)-2,4,6-trideoxy-α-D-galactopyranoside (**3**) was obtained with benzene as solvent. The stereoselectivity of the reduction in favor of the galacto isomer was 77%, 75%, and 60%, respectively, in benzene, ethyl acetate, and methanol. Compound **24**, the C_4 epimer of **3** was also isolated from the reaction mixture by chromatography.

The stereochemistry at C_4 of the major reduction product of **23** was determined on the basis of the doublet of doublets type ^1H NMR signal of H_3 ($J_{3,4}$ = 5 Hz and $J_{3,2}$ = 11 Hz).

Experimental Section

General Methods. Melting points were determined with a Büchi apparatus and are uncorrected. A Perkin-Elmer Model 141 MC polarimeter and 1-dm tubes were used for measurement of specific rotations. ^1H NMR spectra were recorded in chloroform-*d* solution at 60 MHz with a Varian T-60 or at 250 MHz with a Cameca spectrometer; ^{13}C NMR spectra were recorded in chloroform-*d* solution at 22.63 MHz with a Bruker HX 90E

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spectrometer; chemical shifts are given in ppm and tetramethylsilane was the internal standard (δ 0.00). Microanalyses were performed by the Service Cental de Microanalyse du C. N.R.S. Kieselgel G (type 60, Merck) activated at 120 °C was the support for TLC. The term "standard workup" means that the organic layer was washed with water, dried over Na_2SO_4, and filtered and the solvent was removed at reduced pressure.

Methyl 3-*O*-Benzyl-2-deoxy-2-*C*-methyl-6-*O*-tosyl-α-D-allopyranoside (8). To a solution of **7** (4 g, 14.1 mmol) in dry pyridine (40 mL) was added *p*-toluenesulfonyl chloride (5.37 g, 28.2 mmol) in dry pyridine (5 mL) and the mixture was kept for 1 day at room temperature. After addition of crushed ice and a saturated aqueous solution (200 mL) of sodium hydrogen carbonate, the mixture was extracted with ethyl acetate. Evaporation of the organic layer afforded a crude product which was chromatographed on Kieselgel G, giving pure **8** (4.3 g, 70%) as a syrup: $[\alpha]_D^{22}$ +83° (*c* 1, chloroform) mass spectrum, *m/z* 436 ($M^{+\cdot}$); ^1H NMR δ 7.78 and 7.30 (2 d, 4 H, *J* = 7 Hz, SO_2PhMe), 7.33 (m, 5 H, Ph), 4.85 and 4.54 (2d, 2 H, J_{gem} = 12 Hz, CH_2Ph), 4.42 (d, 1 H, $J_{1,2}$ = 4 Hz, H-1), 4.29 (dd, 1 H, $J_{6',6}$ = 11 Hz, $J_{6',5}$ = 2.5 Hz, H-6'), 4.21 (dd, 1 H, $J_{6,6'}$ = 11 Hz, $J_{6,5}$ = 5 Hz, H-6), 3.80 (m, 1 H, H-5), 3.71 (t, 1 H, $J_{3,2} = J_{3,4}$ = 4 Hz, H-3), 3.43 (m, 1 H, H-4), 2.41 (s, 3 H, SO_2PhMe), 1.91 (m, 1 H, H-2) and 1.07 (d, 3 H, *J* = 7 Hz, Me-2).

Anal. Calcd for $C_{22}H_{28}O_7S$: C, 60.55; H, 6.42; O, 25.69; S, 7.34. Found: C, 60.35; H, 6.45; O, 25.84; S, 7.27.

Methyl 3-*O*-Benzyl-6-cyano-2,6-dideoxy-2-*C*-methyl-α-D-allopyranoside (9). To a solution of **8** (2.6 g, 5.9 mmol) in dimethyl sulfoxide (25 mL) at 85 °C was added potassium cyanide (576 mg, 8.8 mmol). The mixture was stirred for 1 h, then cooled to room temperature, and diluted with a saturated aqueous solution (250 mL) of sodium hydrogen carbonate. Extraction with ethyl acetate gave a crude product which was chromatographed on Kieselgel G. Pure **9** (1.3 g, 76%) was obtained. A sample of **9** was recrystallized from a mixture of dichloromethane–hexane: mp 93–95 °C; $[\alpha]_D^{22}$ +122° (*c* 0.88, chloroform); mass spectrum, *m/z* 291 ($M^{+\cdot}$); ^1H NMR δ 7.31 (m, 5 H, Ph), 4.92 and 4.51 (2 d, 2 H, J_{gem} = 12 Hz, CH_2Ph), 4.50 (d, 1 H, $J_{1,2}$ = 4 Hz, H-1), 3.95 (m, 1 H, H-5), 3.75 (t, 1 H, $J_{3,2} = J_{3,4}$ = 3.5 Hz, H-3), 3.42 (s, 3 H, OMe), 3.33 (dd, 1 H, $J_{4,5}$ = 11 Hz, $J_{4,3}$ = 3.5 Hz, H-4), 2.80 (dd, 1 H, $J_{6',6}$ = 17 Hz, $J_{6',5}$ = 3.5 Hz, H-6'), 2.56 (dd, 1 H, $J_{6,6'}$ = 17 Hz, $J_{6,5}$ = 7.5 Hz, H-6), 2.01 (m, 1 H, H-2) and 1.15 (d, 3 H, *J* = 7 Hz, Me-2).

Anal. Calcd for $C_{16}H_{21}NO_4$: C, 65.98; H, 7.22; N, 4.81; O, 21.99. Found: C, 65.80; H, 7.14; N, 5.03; O, 21.66.

Methyl 3-*O*-Benzyl-7-*O*-(*tert*-butyldimethylsilyl)-2,6-dideoxy-2-*C*-methyl-α-D-*allo*-heptopyranoside (11). To a solution of **9** (1.3 g, 4.47 mmol) in dry toluene (20 mL) and in a nitrogen atmosphere was added at room temperature dropwise diisobutylaluminum hydride (1.27 g, 8.94 mmol) in 20% hexane solution. The mixture was stirred for 2 h and then diluted with toluene (50 mL) and the excess of reagent was destroyed by a saturated aqueous solution (100 mL) of ammonium chloride. After filtration, the organic layer was dried and evaporated to yield a syrup (1.2 g) which was dissolved in dry ether (100 mL). To this solution was added lithium aluminum hydride (0.85 g, 22.4 mmol) and the mixture was heated under reflux overnight. After dilution with ether the excess of lithium aluminum hydride was destroyed by dropwise addition of water. Evaporation of the organic layer gave a syrupy product which was chromatographed on Kieselgel H, affording syrupy diol **10** (1.1 g). To a solution of **10** (390 mg, 1.3 mmol) in *N,N*-dimethylformamide (5 mL) was added imidazole (177 mg, 2.6 mmol) and the mixture was stirred for 15 min. To this solution was added *tert*-butyldimethylsilyl chloride (195 mg, 1.3 mmol) and the mixture was stirred for another 3 h. Then additional quantities of *tert*-butyldimethylsilyl chloride (450 mg, 3 mmol) and imidazole (400 mg, 6 mmol) were added to the solution. After 7 h, the mixture was diluted with a saturated aqueous solution (50 mL) of sodium hydrogen carbonate and extracted with toluene. Evaporation of the organic layer gave **11** (320 mg, 52%) as a syrupy product. Preparative thin-layer chromatography afforded pure syrupy **11**: $[\alpha]_D^{20}$ +95° (*c* 0.83, chloroform); mass spectrum, *m/z* 410 ($M^{+\cdot}$); ^1H NMR δ 7.36 (m, 5 H, Ph), 4.86 and 4.71 (2 d, 2 H, J_{gem} = 12 Hz, CH_2Ph), 4.41 (d, 1 H, $J_{1,2}$ = 4 Hz, H-1), 3.90 (m, 1 H, H-5), 3.82 (m, 1 H, H-7'), 3.75 (m, 1 H, H-7), 3.71 (t, 1 H, $J_{3,4} = J_{3,2}$ = 3.5 Hz, H-3), 3.36 (s, 3 H, OMe), 3.33 (dd, 1 H, $J_{4,5}$ = 9 Hz, $J_{4,3}$ = 3.5 Hz, H-4), 2.02 (m, 1 H, H-6'), 1.92 (m, 1 H, H-2), 1.66 (m, 1 H, H-6), 1.04 (d, 3 H, *J* = 7 Hz, Me-2), 0.92 (s, 9 H, *t*-Bu) and 0.13 (s, 6 H, $SiMe_2$).

Anal. Calcd for $C_{22}H_{38}O_5Si$: C, 64.39; H, 9.27. Found: C, 64.31; H, 9.31.

Methyl 3-*O*-Benzyl-7-*O*-(*tert*-butyldimethylsilyl)-2,6-dideoxy-2-*C*-methyl-α-D-*ribo*-4-heptulose (12). To a solution of **11** (329 mg, 0.8 mmol in boiling benzene (20 mL) was added pyridinium chlorochromate (517 mg, 2.4 mmol). The mixture was refluxed for 45 min with azeotropic distillation. After filtration the solution was evaporated, giving chromatographically homogeneous **12** (268 mg, 82%) as a syrupy product: ^1H NMR 7.31 (s, 5 H, Ph), 4.46 (d, 1 H, $J_{1,2}$ = 4 Hz, H-1), 4.26 (m, 1 H, H-5), 4.49 and 4.16 (2 d, 2 H, J_{gem} = 11 Hz, CH_2Ph), 3.88 (d, 1 H, $J_{3,2}$ = 5 Hz, H-3), 3.53 (m, 2 H, H-7,7'), 3.22 (s, 3 H, OH), 2.45 (m, 1 H, H-2), 1.75 (m, 2 H, H-6,6'), 0.91 (d, 3 H, *J* = 7 Hz, Me-2) 0.86 (s, 9 H, *t*-Bu) and 0.13 (s, 6 H, $SiMe_2$).

Methyl 3-*O*-Benzyl-7-*O*-(*tert*-butyldimethylsilyl)-2,6-dideoxy-2-*C*-methyl-α-D-*xylo*-4-heptulose (13). Compound **12** (268 mg, 0.65 mmol) was dissolved in a solution of methanol (20 mL) containing sodium methoxide (1 g). The mixture was stirred at room temperature for 30 min, and then neutralized by filtration through Amberlite IRC 50 (H^+). Evaporation of the solution gave **13** (260 mg, 97%) as a syrup: ^1H NMR δ 7.30 (m, 5 H, Ph), 4.64 (d, 1 H, $J_{1,2}$ = 4 Hz, H-1), 4.92 and 4.43 (2 d, 2 H, J_{gem} = 11 Hz, CH_2Ph), 4.37 (dd, 1 H, $J_{5,6}$ = 9 Hz, $J_{5,6'}$ = 5 Hz, H-5), 4.02 (d, 1 H, $J_{3,2}$ = 11 Hz, H-3), 3.72 (m, 2 H, H-7,7'), 3.42 (s, 3 H, OMe), 2.28 (m, 1 H, H-6'), 2.10 (m, 1 H, H-2), 1.70 (m, 1 H, H-6), 1.10 (d, 3 H, *J* = 7 Hz, Me-2), 0.91 (s, 9 H, *t*-Bu) and 0.13 (s, 6 H, $SiMe_2$).

Methyl 3-*O*-Benzyl-7-*O*-(*tert*-butyldimethylsilyl)-2-*C*-methyl-4-*C*-methylene-2,4,6-trideoxy-α-D-*xylo*-heptopyranoside (14). To methylenetriphenylphosphorane (280 mg, 1 mmol) in dry ether (3 mL) was added in a nitrogen atmosphere at room temperature butyllithium in 15% hexane solution (0.6 mL, 1 mmol). The mixture was stirred for 30 min. To this mixture was then added **13** (260 mg, 0.63 mmol) in dry ether (4 mL). After 2 h the mixture was diluted with hexane (20 mL). Filtration and evaporation of the solution gave **14** (97 mg, 40%). A sample of **14** was purified by preparative thin-layer chromatography on Kieselguhr G: $[\alpha]_D^{20}$ +165° (*c* 0.69, chloroform); mass spectrum, *m/z* 406 ($M^{+\cdot}$); ^1H NMR δ 7.31 (m, 5 H, Ph), 5.18 and 4.95 (2 s, 2 H, H-4',4''), 4.59 (d, 1 H, $J_{1,2}$ = 3.5 Hz, H-1), 4.69 and 4.44 (2 d, 2 H, J_{gem} = 11 Hz, CH_2Ph), 4.31 (dd, 1 H, $J_{5,6}$ = 10 Hz, $J_{5,6'}$ = 4 Hz, H-5), 3.91 (d, 1 H, $J_{3,2}$ = 11 Hz, H-3), 3.80 (m, 2 H, H-7,7'), 3.36 (s, 3 H, OMe), 1.91 (m, 3 H, H-2, 6,6'), 1.03 (d, 1 H, *J* = 7 Hz, Me-2), 0.90 (s, 9 H, *t*-Bu) and 0.13 (s, 6 H, $SiMe_2$).

Anal. Calcd for $C_{23}H_{38}O_4Si$: C, 67.98; H, 9.36. Found: C, 67.91; H, 9.29.

Methyl 3-*O*-Benzyl-7-*O*-(*tert*-butyldimethylsilyl)-2,4-di-*C*-methyl-2,4,6-trideoxy-α-D-*galacto*-heptopyranoside (1). A solution of **14** (39 mg, 0.096 mmol) in ethyl acetate (8 mL) was hydrogenated overnight at atmospheric pressure in the presence of 10% palladium on barium sulfate (12 mg). The catalyst was filtered off and the solvent was evaporated furnishing a mixture of two products (36 mg, 92%) which were separated by high-pressure liquid chromatography (Perkin-Elmer LC 75). Compound **1** (28 mg, 80%) was a syrup: $[\alpha]_D^{20}$ +135.7° (*c* 0.49, chloroform); mass spectrum, *m/z* 408 ($M^{+\cdot}$); ^1H NMR δ 7.31 (m, 5 H, Ph), 4.50 (d, 1 H, $J_{1,2}$ = 4 Hz, H-1), 4.59 and 4.34 (2 d, 2 H, J_{gem} = 11 Hz, CH_2Ph), 3.95 (m, 1 H, H-5), 3.70 (m, 2 H, H-7,7'), 3.55 (dd, 1 H, $J_{3,2}$ = 11 Hz, $J_{3,4}$ = 5 Hz, H-3), 3.28 (s, 3 H, OMe), 2.04 (m, 1 H, H-4), 1.96 (m, 1 H, H-2), 1.77 (m, 1 H, H-6'), 1.58 (m, 1 H, H-6), 1.00 (d, 3 H, *J* = 7 Hz, Me-2), 0.92 (d, 3 H, *J* = 7 Hz, Me-4), 0.90 (s, 9 H, *t*-Bu) and 0.13 (s, 6 H, $SiMe_2$); ^{13}C NMR δ 128.4–127.9–127.7 (Ph), 102.4 (C-1), 79.4 (C-3), 70.2 (CH_2Ph), 66.4 (C-5), 60.1 (C-7), 54.9 (OMe), 36.1–35.1–34.7 (C-2,4,6), 13.0 (Me-2) and 5.4 (Me-4).

Anal. Calcd for $C_{23}H_{40}O_4Si$: C, 67.65; H, 9.80. Found: C, 66.97; H, 9.61.

Compound **15** was contaminated by about 15% of **1**: mass spectrum, *m/z* 408 ($M^{+\cdot}$); ^1H NMR δ 7.38 (m, 5 H, Ph), 4.55 (d, 1 H, $J_{1,2}$ = 4 Hz, H-1), 4.64 and 4.57 (2 d, 2 H, J_{gem} = 11 Hz, CH_2Ph), 3.77 (m, 2 H, H-7,7'), 3.59 (m, 1 H, H-5), 3.34 (s, 3 H, OMe), 3.21 (t, $J_{3,2} = J_{3,4}$ = 11 Hz, H-3), 1.90 (m, 1 H, H-2), 1.57 (m, 3 H, H-4,6,6'), 1.08 (d, 3 H, *J* = 7 Hz, Me-2), 1.01 (d, 3 H,

J = 7 Hz, Me-4), 0.90 (s, 9 H, t-Bu) and 0.13 (s, 6 H, SiMe).

Methyl 4,6-*O*-Benzylidene-2-deoxy-2-*C*-methyl-3-*O*-((2-methoxyethoxy)methyl)-α-D-allopyranoside (17). To a solution of **16** (2.1 g, 7.5 mmol) in dry ether (80 mL) in a nitrogen atmosphere was added sodium hydride (0.27 g, 11.2 mmol). The mixture was boiled under reflux for 30 min, then freshly distilled (2-methoxyethoxy)methyl chloride (4.7 g, 37.5 mmol) was added to it. After 3 h of reflux, triethylamine (3.7 g, 37.5 mmol) was added to the mixture. After filtration the solution was diluted with water (300 mL) and extracted with dichloromethane. Standard workup gave syrupy **17** which was chromatographed on Kieselgel G. Pure syrupy **17** (2.26 g, 82%) was obtained: $[\alpha]^{20}_D$ +38° (c 0.6, chloroform); mass spectrum, m/z 368 ($M^{+\cdot}$); ^{1}H NMR δ 7.46–7.32 (m, 5 H, Ph) 5.47 (s, 1 H, H-7), 5.04 and 4.81 (2 d, 2 H, J_{gem} = 7 Hz, OCH_2O), 4.47 (d, 1 H, $J_{1,2}$ = 4 Hz, H-1), 4.31 (dd, 1 H, $J_{6',6}$ = 10 Hz, $J_{6',5}$ = 5 Hz, H-6′), 4.18 (td, 1 H, $J_{5,6}$ = $J_{5,4}$ = 10 Hz, $J_{5,6'}$ = 5 Hz, H-5), 4.09 (t, 1 H, $J_{3,4}$ = $J_{3,2}$ = 3 Hz, H-3), 3.81, 3.70 and 3.36 (2 m, 4 H, OCH_2CH_2O), 3.69 (t, 1 H, $J_{6,6'}$ = $J_{6,5}$ = 10 Hz, H-6), 3.64 (dd, 1 H $J_{4,5}$ 10 Hz, $J_{4,3}$ 3 Hz, H-4), 3.39 (s, 3 H, OMe), 3.31 (s, 3 H, OMe), 2.05 (m, 1 H H-2) and 1.08 (d, 3 H J = 7 Hz, Me-2).

Anal. Calcd for $C_{19}H_{28}O_7$: C, 61.96; H, 7.61; O, 30.43. Found: C, 62.02; H, 7.57; O, 30.18.

Methyl 4-*O*-Benzoyl-6-bromo-2,6-dideoxy-2-*C*-methyl-3-*O*-((2-methoxyethoxy)methyl)-α-D-allopyranoside (18). To a solution of **17** (1.6 g, 4.3 mmol) in dry carbon tetrachloride (80 mL) were added N-bromosuccinimide (0.84 g, 4.7 mmol) and barium carbonate (2.5 g, 12.7 mmol). The mixture was boiled under reflux for 40 min and, after cooling, filtered. The filtrate was diluted with dichloromethane (50 mL), washed successively with water and aqueous sodium hydrogen carbonate, dried, and evaporated. A syrupy residue of **18** (1.8 g, 94%) was obtained. A sample of **18** was purified by preparative chromatography on Kieselgel: $[\alpha]^{20}_D$ +69.8° (c 1.07, chloroform); mass spectrum, m/z 446 ($M^{+\cdot}$); ^{1}H NMR δ 8.02–7.44 (m, 5 H, Ph), 5.01 (dd, 1 H, $J_{4,5}$ = 10 Hz, $J_{4,3}$ = 3.5 Hz, H-4), 4.79 and 4.71 (2 d, 2 H, J_{gem} = 7 Hz, OCH_2O), 4.60 (d, 1 H, $J_{1,2}$ = 4 Hz, H-1), 4.45 (m, 1 H, H-5), 4.17 (t, 1 H, $J_{3,2}$ = $J_{3,4}$ = 3.5 Hz, H-3), 3.71–3.50 (m, 6 H, H-6,6′ and OCH_2CH_2O), 3.47 (s, 3 H, OMe), 3.26 (s, 3 H, OMe), 2.15 (m, 1 H, H-2) and 1.09 (d, 3 H, J = 7 Hz, Me-2).

Anal. Calcd for $C_{19}H_{27}BrO_7$: C, 51.02; H, 6.04; Br, 17.88; O, 25.06. Found: C, 50.92; H, 6.16; Br, 17.60; O, 25.25.

Methyl 4-*O*-Benzoyl-2,6-dideoxy-2-*C*-methyl-3-*O*-((2-methoxyethoxy)methyl)-α-D-allopyranoside (19). A solution of **18** (180 mg, 0.4 mmol) in methanol (30 mL) was hydrogenated at atmospheric pressure for 23 h in the presence of 10% Pd/C (90 mg) and triethylamine (0.2 mL, 1.4 mmol). The catalyst was filtered off and the solvent was evaporated furnishing a syrupy product which was purified by preparative chromatography on Kiselgel. Pure syrupy **19** was obtained (109 mg, 73%): $[\alpha]^{20}_D$ +72° (c 0.65, chloroform); mass spectrum, m/z 368 ($M^{+\cdot}$); ^{1}H NMR δ 7.81–7.21 (m, 5 H, Ph), 4.78–4.65 (m, 3 H, OCH_2O and H-4), 4.33–4.26 (m, 2 H, H-1,5), 3.95 (t, 1 H, $J_{3,2}$ = $J_{3,4}$ = 2.5 Hz, H-3), 3.70–3.46 (m, 4 H, OCH_2CH_2O), 3.36 (s, 3 H, OMe), 3.20 (s, 3 H, OMe), 2.06 (m, 1 H, H-2), 1.20 (d, 3 H, J = 7 Hz, Me-5) and 1.06 (d, 3 H, J = 7 Hz, Me-2).

Anal. Calcd for $C_{19}H_{28}O_7$: C, 61.96; H, 7.61; O, 30.43. Found: C, 61.89; H, 7.72; O, 30.28.

Methyl 2,6-Dideoxy-2-*C*-methyl-3-*O*-((2-methoxyethoxy)methyl)-α-D-allopyranoside (20). A solution of **19** (109 mg, 0.29 mmol) in absolute methanol (12 mL) was treated with 1 M sodium methoxide (0.2 mL) at room temperature. After 24 h, the mixture was neutralized with Amberlite IRC 50 (H^+). Evaporation of the solvent gave **20** (67 mg, 88%).

Methyl 2,6-Dideoxy-2-*C*-methyl-3-*O*-((2-methoxyethoxy)methyl)-α-D-*ribo*-4-hexulose (21). To a solution of **20** (300 mg, 1.1 mmol) in boiling benzene was added pyridinium chlorochromate (711 mg, 3.3 mmol). The mixture was refluxed for 1 h with azeotropic distillation. After filtration the solution was evaporated giving **21** (230 mg, 80%) as a syrup: mass spectrum, m/z 262 ($M^{+\cdot}$); ^{1}H NMR δ 4.85 (m, 3 H, OCH_2O and H-1), 4.55 (d, 1 H, $J_{3,2}$ = 6 Hz, H-3), 4.37 (m, 1 H, H-5), 3.75–3.56 (m, 4 H, OCH_2CH_2O), 3.45 (s, 3 H, OMe), 3.40 (s, 3 H, OMe), 2.81 (m, 1 H, H-2), 1.32 (d, 3 H, J = 7 Hz, Me-5) and 1.01 (d, 3 H, J = 7 Hz, Me-2).

Methyl 2,6-Dideoxy-2-*C*-methyl-3-*O*-((2-methoxyethoxy)methyl)-α-D-*xylo*-4-hexulose (22). Compound **21** (230 mg, 0.87 mmol) was dissolved in a solution of methanol (45 mL) containing sodium methoxide (2 g). The mixture was stirred at room temperature for 1.5 h and then neutralized by filtration through Amberlite IRC 50(H^+). Evaporation of the solvent gave **22** (223 mg 97%) as a syrup: ^{1}H NMR δ 4.83 (m, 2 H, OCH_2O), 4.65 (d, 1 H, $J_{1,2}$ = 3.5 Hz, H-1), 4.37 (d, 1 H, $J_{3,2}$ = 12 Hz, H-3), 3.92 (m, 1 H, H-5), 3.81, 3.69 and 3.56 (3 m, 4 H, OCH_2CH_2O), 3.46 (s, 3 H, OMe), 3.39 (s, 3 H, OMe), 1.27 (d, 3 H, J = 7 Hz, Me-5) and 1.11 (d, 3 H, J = 7 Hz, Me-2).

Methyl 2-*C*-Methyl-4-*C*-methylene-3-*O*-((2-methoxyethoxy)methyl)-2,4,6-trideoxy-α-D-xylopyranoside (23). To methylenetriphenylphosphorane (280 mg, 1 mmol) in dry ether (2.5 mL) was added in a nitrogen atmosphere at room temperature butyllithium in 15% hexane solution (0.6 mL, 1 mmol). The mixture was stirred for 30 min. To this mixture was then added **22** (180 mg, 0.68 mmol) in dry ether (5 mL). After 2.5 h, the mixture was diluted with hexane (20 mL). Filtration and evaporation of the filtrate gave **23** (74 mg, 42%). A sample of **23** was purified by preparative thin-layer chromatography on Kieselgel G: $[\alpha]^{20}_D$ +248° (c 1.2, chloroform); ^{1}H NMR δ 5.04 and 4.92 (2 s, 2 H, H-4′,4″), 4.77 (s, 2 H, OCH_2O), 4.58 (d, 1 H, $J_{1,2}$ = 3.5 Hz, H-1), 4.22 (m, 1 H, H-5), 4.18 (d, 1 H, $J_{3,2}$ = 11 Hz, H-3), 3.86, 3.62 and 3.55 (3 m, 4 H, OCH_2CH_2O), 3.39 (s, 3 H, OMe), 3.36 (s, 3 H, OMe), 1.48 (m, 1 H, H-2), 1.34 (d, 3 H, J = 7 Hz, Me-5) and 1.04 (d, 3 H, J = 7 Hz, Me-2).

Methyl 2,4-Di-*C*-methyl-3-*O*-((2-methoxyethoxy)methyl)-2,4,6-trideoxy-α-D-galactopyranoside (3) and Methyl 2,4-Di-*C*-methyl-3-*O*-((2-methoxyethoxy)methyl)-2,4,6-trideoxy-α-D-glucopyranoside (24). Method A. A solution of **23** (24 mg, 0.09 mmol) in benzene (8 mL) was hydrogenated overnight at atmospheric pressure in the presence of 10% palladium on barium sulfate (24 mg). The catalyst was filtered off and the solvent was evaporated, furnishing a mixture (^{1}H NMR 250 MHz) of two products (22 mg, 93%) which were separated by preparative chromatography on Kieselgel (type G 1500, 250 μm, S. Schüll). Compound **3** (17 mg, 77%) was a syrup: $[\alpha]^{20}_D$ +215° (c 0.85, chloroform); mass spectrum, m/z 262 ($M^{+\cdot}$); ^{1}H NMR δ 4.77 and 4.67 (2 d, 2 H, J_{gem} = 7 Hz, OCH_2O), 4.48 (d, 1 H, $J_{1,2}$ = 4 Hz, H-1), 3.95 (m, 1 H, H-5), 3.75 (dd, 1 H, $J_{3,2}$ = 11 Hz, $J_{3,4}$ = 5 Hz, H-3), 3.67–3.50 (2 m, 4 H, OCH_2CH_2O), 3.33 (s, 3 H, OMe), 3.26 (s, 3 H, OMe), 1.91 (m, 2 H, H-2,4), 1.12 (d, 3 H, J = 7 Hz, Me-5), 0.95 (d, 3 H, J = 7 Hz, Me-2) and 0.90 (d, 3 H, J = 7 Hz, Me-4).

Anal. Calcd for $C_{13}H_{26}O_5$: C, 59.54; H, 9.92; O, 30.53. Found: C, 59.52; H, 9.96; O, 30.41.

Compound **24** (2.5 mg, 11%) was a syrup: mass spectrum, m/z 262 ($M^{+\cdot}$); ^{1}H NMR δ 4.80 (s, 2 H, OCH_2O), 4.53 (d, 1 H, $J_{1,2}$ = 3.5 Hz, H-1), 3.78 (m, 3 H, H-5 and CH_2O), 3.57 (m, 2 H, CH_2O), 3.40 (s, 3 H, OMe), 3.32 (s, 3 H, OMe), 3.25 (t, 1 H, $J_{3,4}$ = $J_{3,2}$ = 10 Hz, H-3), 1.80 (m, 1 H, H-2), 1.37 (m, 1 H, H-4), 1.21 (d, 3 H, J = 7 Hz, Me-5), 1.00 (d, 3 H, J = 7 Hz, Me-2) and 0.96 (d, 3 H, J = 7 Hz, Me-4).

Anal. Calcd for $C_{13}H_{26}O_5$: C, 59.54; H, 9.92; O, 30.53. Found: C, 59.11; H, 9.68; O, 31.03.

Method B. A solution of **23** (24 mg, 0.09 mmol) in ethyl acetate (15 mL) was hydrogenated as in Method A, giving **3** (16 mg, 75%) and **24** (4 mg, 19%).

Method C. A solution of **23** (24 mg, 0.09 mmol) in methanol (10 mL) was hydrogenated as in Method A, giving **3** (13 mg, 60%) and **24** (10 mg, 40%).

Registry No. 1, 90132-64-2; 3, 90132-73-3; 7, 90132-56-2; 8, 90132-57-3; 9, 90132-58-4; 10, 90132-59-5; 11, 90132-60-8; 12, 90132-61-9; 13, 90132-62-0; 14, 90132-63-1; 15, 90132-65-3; 16, 75879-81-1; 17, 90132-66-4; 18, 90132-67-5; 19, 90132-68-6; 20, 90132-69-7; 21, 90132-70-0; 22, 90132-71-1; 23, 90132-72-2; 24, 90192-85-1; oleandomycin, 3922-90-5; D-glucose, 50-99-7; methylenetriphenylphosphorane, 3487-44-3.