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A CHIRAL SYNTHESIS OF 3,5,7-TRI-*O*-BENZYL-1,4,6-TRIDEOXY-4,6-DI-*C*-METHYL-*keto*-L-*ido*-2-HEPTULOSE, A SYNTHETIC SEGMENT OF THE C-1–C-6 PORTION OF ERYTHRONOLIDE A*

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ABSTRACT

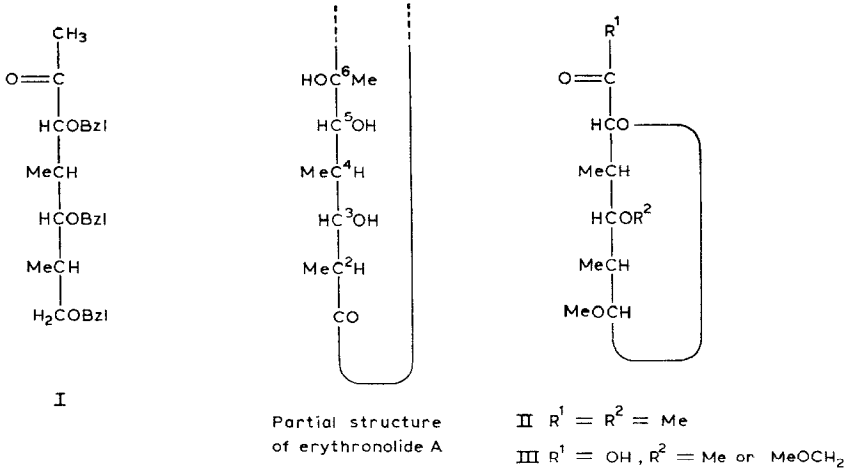
3,6-Dideoxy-1,2-*O*-isopropylidene-3-*C*-methyl-α-D-glucofuranose (**9**) was prepared from methyl 4,6-*O*-benzylidene-3-deoxy-3-*C*-methyl-α-D-glucopyranoside *via* 3-deoxy-1,2-*O*-isopropylidene-3-*C*-methyl-α-D-glucofuranose (**5**) in 61% yield. The key intermediates, 3,5,6-trideoxy-1,2-*O*-isopropylidene-3-*C*-methyl-5-*C*-methylene-α-D-*xylo*-hexofuranose (**13**) and 3,5-dideoxy-1,2-*O*-isopropylidene-3-*C*-methyl-5-*C*-methylene-α-D-*xylo*-hexofuranose (**21**) were prepared from **9** and **5**, respectively. Hydroboration of **13**, followed by treatment with alkaline hydrogen peroxide, afforded a 4:1 mixture of 3,5-dideoxy-1,2-*O*-isopropylidene-3,5-di-*C*-methyl-β-L-idofuranose (**14**) and the α-D-*gluco* epimer (**15**) in 85% yield. Homogeneous hydrogenation of **21** with chlorotris(triphenylphosphine)rhodium(I) gave a 6.4:1 mixture of **15** and **14**. Homogeneous hydrogenation of 1,6-anhydro-3,5-dideoxy-3-*C*-methyl-5-*C*-methylene-β-D-*xylo*-hexofuranose, prepared from **21**, afforded exclusively the 1,6-anhydro compound **17**, which could be derived from **14**. Both **14** and **17** were converted into the diethyl dithioacetal, from which the title compound was synthesized, in 4 steps, in 50% yield.

INTRODUCTION

Considerable effort has recently been directed toward the chiral synthesis of the macrolide antibiotics[1]. In regard to the 16-membered macrolide antibiotics, the chiral syntheses of macrocyclic lactone antibiotic A26771B (ref. 2), carbomycin B (ref. 3), and tylonolide[4], the aglycon of tylosin, have been completed. On the other hand, a novel and ingenious approach to the 14-membered macrolide erythronolide A, the aglycon of erythromycin A, by the use of carbohydrates has already been reported by Hanessian *et al.*[1a,b]. However, a practical chiral synthesis of this macrolide has not thus far been achieved.

During the course of our synthetic studies of erythronolide A, using carbo-

*Dedicated to Professor Sumio Umezawa on the occasion of his 73rd birthday and the 25th anniversary of the Microbial Chemistry Research Foundation.



I

Partial structure of erythronolide A

II $R^1 = R^2 = Me$

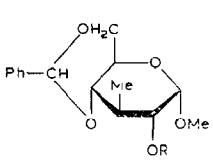
III $R^1 = OH$, $R^2 = Me$ or $MeOCH_2$

hydrates, we found it necessary to prepare effectively the synthetic segment of the C-1–C-6 portion of the macrolide, which is practically viable and also well suited for a stereoselective coupling-reaction with a second synthetic, chiral segment. As a synthetic precursor representing the C-1–C-6 portion of erythronolide A or B, the sugar derivative[5] **II** or **III** had been synthesized from the 2-deoxy-2-*C*-methyl-D-altrose derivative.[1a] We now describe the chiral synthesis of the acyclic precursor (I), starting from the readily available[1f] 3-deoxy-3-*C*-methyl-D-glucose derivative (**1**). The synthetic plan was devised by considering that the key intermediate **13** (or **21**) (whose absolute stereochemistry at C-2, C-3, and C-4 correlates to that at C-3, C-4, and C-5, respectively, of I) is obtainable from **1**, and that formation of a new chiral center (corresponding to C-6, the last asymmetric carbon atom in I) on C-5 of the intermediate should be possible by addition of appropriate reagents to its unsaturated portion.

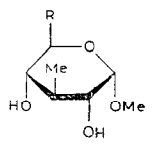
RESULTS AND DISCUSSION

The starting material, methyl 4,6-*O*-benzylidene-3-deoxy-3-*C*-methyl-α-D-glucopyranoside[1f] (**1**) could be obtained on a large scale from methyl 4,6-*O*-benzylidene-3-deoxy-3-*C*-methyl-α-D-altropyranoside[1f,6]. Methyl 3,6-dideoxy-3-*C*-methyl-α-D-glucopyranoside (**3**) was prepared in 40% overall yield from **1** *via* its 2-*O*-acetyl derivative (**2**)* by the procedure reported[1f,g], including the bromination with *N*-bromosuccinimide (NBS) and subsequent reduction with lithium aluminum hydride. Acetolysis of **3**, followed by hydrolysis, yielded the free sugar, which was subjected to isopropylidenation with acetone and iron(III) chloride[8], to afford 3,6-dideoxy-1,2-*O*-isopropylidene-3-*C*-methyl-α-D-glucofuranose (**9**) in 49% yield, and its pyra-

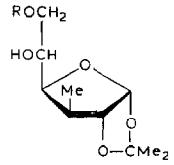
*A direct, NBS bromination of **1** (on a scale of more than 10 g), instead of acetate **2**, afforded methyl 4-*O*-benzoyl-6-bromo-3,6-dideoxy-3-*C*-methyl-α-D-glucopyranoside (66%), accompanied by a considerable proportion (33%) of methyl 4-*O*-benzoyl-3-deoxy-3-*C*-methyl-α-D-glucopyranoside.



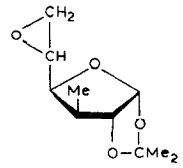
1 R = H
2 R = Ac



3 R = Me
4 R = CH_2OH



5 R = H
6 R = Ts
7 R = Ac



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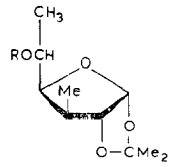
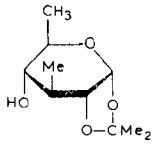


9 R = H
10 R = Bzl



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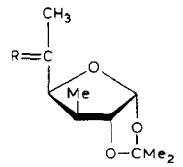
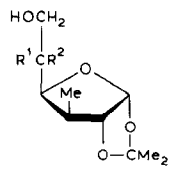
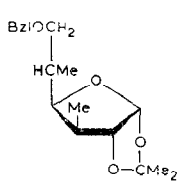


12 R = O
13 R = CH_2



14 R^1 = H, R^2 = Me
15 R^1 = Me, R^2 = H



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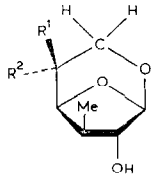
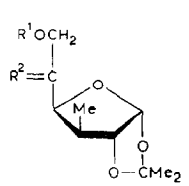
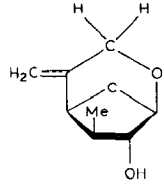


17 R^1 = Me, R^2 = H
18 R^1 = H, R^2 = Me



19 R^1 = Ac, R^2 = O
20 R^1 = Ac, R^2 = CH_2
21 R^1 = H, R^2 = CH_2



22

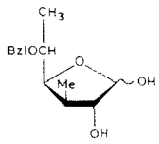
Bzl = $PhCH_2$
Ts = $SO_2C_6H_4$-Me-*p*

nose isomer (**11**) in 3% yield. The overall yield of this synthetic route from **1** to **9**, *via* **3**, was unsatisfactory, because attempts to improve the yield in the last step were all unsuccessful, and so the following, alternative process was undertaken in order to improve the yield of **9** from **1**.

Debenzylidenation of **1** with methanolic hydrogen chloride gave methyl 3-deoxy-3-*C*-methyl-α-D-glucopyranoside (**4**) in 94% yield, and acetolysis of **4**, followed by hydrolysis, afforded 3-deoxy-3-*C*-methyl-D-glucose in 86% yield. Treatment of this free sugar with acetone and iron(III) chloride, followed by selective hydrolysis of the resulting 1,2:5,6-diisopropylidene acetal with 90% aqueous acetic acid, gave 3-deoxy-1,2-*O*-isopropylidene-3-*C*-methyl-α-D-glucofuranose[4] (**5**) in 95% yield. Selective 6-*O*-tosylation of **5** with 2 equimolar proportions of tosyl chloride in pyridine, followed by treatment of the 6-tosylate (**6**) with sodium methoxide in chloroform, afforded the 5,6-anhydro derivative (**8**), which was then converted into **9** by reduction with lithium aluminum hydride (in 79% yield from **5**).

Jones oxidation of **9** gave ketone **12** in 84% yield. The key intermediate **13** was prepared, in 94% yield, by Wittig condensation of **12** with 3 equimolar proportions

of methylenetriphenylphosphorane in Me_2SO[9]. Hydroboration of **13** with 1.3 equimolar proportions of borane–dimethyl sulfide (BMe_2S)[10], and treatment of the product with alkaline hydrogen peroxide provided 3,5-dideoxy-1,2-*O*-isopropylidene-3,5-di-*C*-methyl-*β*-L-idofuranose (**14**) and its *α*-D-*gluco* epimer (**15**) in 68 and 17% yield, respectively, after column-chromatographic separation. The presence of the desired (5*S*) configuration in the major product (**14**) was determined by transformation of **14** into a product that proved identical with 1-*O*-benzyl-2,4,7-trideoxy-2,4-di-*C*-methyl-D-*glycero*-L-*ido*-heptitol (**37**). The reference compound **37** was synthesized from **9**, *via* the key intermediates **24**, **29**, and **30**, by the following procedure.



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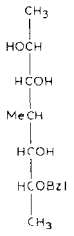

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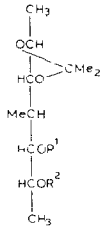
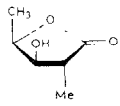


25 R^1 = H, R^2 = Bzl
26 R^1 = Ac, R^2 = Bzl
27 R^1 = Ac, R^2 = Ms



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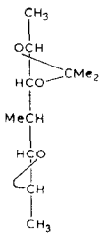

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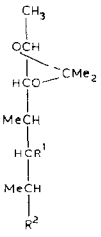
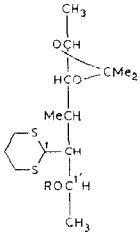
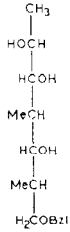


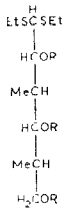
30 R^1 = OH, R^2 = 
31 R^1 = OAc, R^2 = 
32 R^1 = OAc, R^2 = CHO
33 R^1 = OH, R^2 = CH_2OH
34 R^1 = OH, R^2 = CH_2OBzl



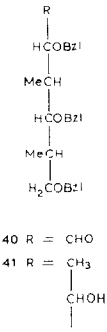
35 R = H
36 R = Ac



37



38 R = H
39 R = OBzl



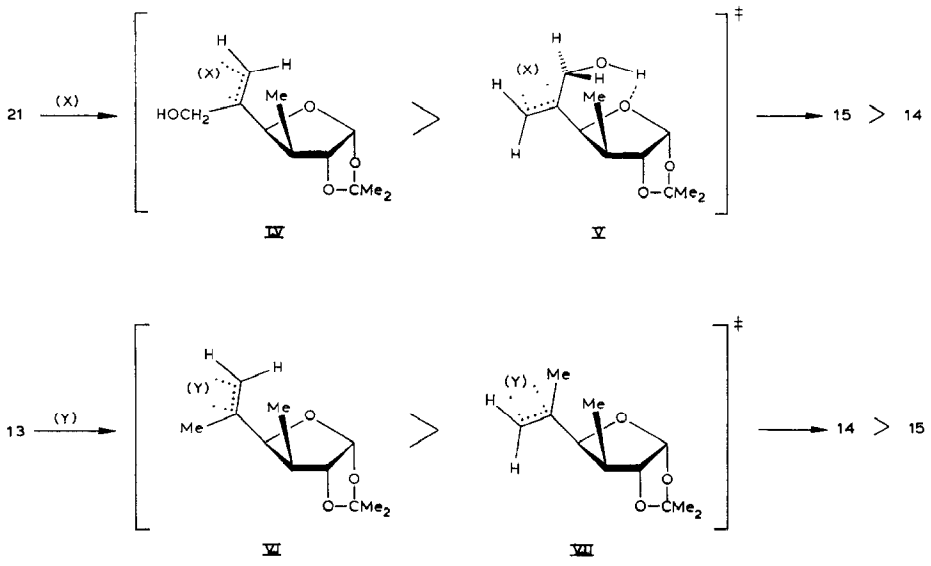
40 R = CHO
41 R = CH_3

The 6-*O*-benzyl derivative (**10**), prepared from **9** in 85% yield, was hydrolyzed. The resulting, free sugar (**23**) was then subjected to Grignard condensation with 10 equimolar proportions of methylmagnesium iodide, to afford the "Cram product", 2-*O*-benzyl-1,4,7-trideoxy-4-*C*-methyl-D-*glycero*-L-*gulo*-heptitol (**24**), as the sole addition-product (in 82% yield). The (6*R*) configuration of **24** was confirmed by the fact that it was transformed into the 1,4-lactone (**28**) by a procedure previously reported[1g], and the relative configuration of **28** was, by ^{1}H-n.m.r. analysis, proved to be identical with that of (2*S*,3*S*,4*S*)-3-hydroxy-2-methyl-4-pentanolide[1g,11]. The

5,6-*O*-isopropylidene derivative (**25**) of **24** was prepared in 95% yield by the use of 2,2-dimethoxypropane (DMP) and *p*-toluenesulfonic acid in DMF; it was then acetylated with acetic anhydride and 4-(dimethylamino)pyridine (DMAP), to afford **26** in 97% yield. Hydrogenolysis of **26** with hydrogen (palladium black), followed by mesylation, yielded the mesylate **27**, which was immediately treated with sodium methoxide to give the epoxide **29** in 82% yield.

Reaction of **29** with 10 equivalents of 2-lithio-1,3-dithiane in oxolane (THF) at 5° furnished a 1:3.1 mixture of two positionally isomeric, dithiane derivatives. The isomers were separated by chromatography on a column of silica gel, and the minor (22% yield) and the major isomer (68% yield) were assigned the structures **30** and **35**, respectively, on the basis of the coupling features of the acetoxymethine protons in the ^{1}H-n.m.r. spectra of their acetates (**31** and **36**). It is noteworthy that the regioselectivity of the nucleophilic addition of 2-lithio-1,3-dithiane to a *trans*-2,3-epoxide having the *threo* configuration at C-3 and C-4, such as **29**, is the reverse of that reported in the case of *trans*-2,3-epoxides having the *erythro* configuration at C-3 and C-4, such as 2,3-anhydro-1,4,7-trideoxy-5,6-*O*-isopropylidene-4-*C*-methyl-L-*glycero*-D-*galacto*-heptitol[18].

Treatment of the minor acetate **31** with a 1:1 mixture of mercury(II) chloride and red mercury(II) oxide afforded the aldehyde **32**, and this was subjected to reduction with lithium aluminum hydride. The product (**33**) was then selectively 6-*O*-benzylated, and the ether hydrolyzed, to provide **37** in 70% overall yield from **31**. On the other hand, hydrolysis of the 6-*O*-benzyl derivative (**16**) prepared from **14**, followed by Grignard condensation with an excess of methylmagnesium iodide gave a single condensation product that was identical in all respects with the aforesaid, reference sample of **37**. Furthermore, treatment of **14** and **15** with 70% trifluoroacetic



Scheme 1

acid (TFA) respectively afforded the 1,6-anhydro compounds, **17** (29%) and **18** (33%). The ^{1}H-n.m.r. spectra of **17** and **18** showed signals in conformity with the structures depicted (see Experimental section). An alternative route from **5** to **14**, *via* the second, synthetic intermediate (**21**), was examined. Selective acetylation of **5** with a 1.05 equimolar proportion of acetic anhydride and a 0.1 equimolar proportion of DMAP in pyridine afforded acetate **7** in 85% yield, and Jones oxidation of **7** gave the crystalline ketone (**19**) in 90% yield; this was treated with methylenetriphenylphosphorane in ether to provide **20** in 52% yield. Hydrolysis of **20** with methanolic sodium hydroxide afforded the intermediate **21** in 95% yield, and homogeneous hydrogenation of **21** with a 0.4 equimolar proportion of chlorotris(triphenylphosphine)rhodium(I) in benzene with hydrogen at atmospheric pressure gave a 6.4:1 mixture of **15** and **14**. This preponderance of **15** in the hydrogenation of **21**, and the aforementioned 4:1 excess of **14** in the hydroboration of **13**, reveal that, in these reactions, the transition states **IV** and **VI** are more stable than **V** and **VII**, respectively (see Scheme 1). This result prompted us to examine the homogeneous hydrogenation of the 1,6-anhydro compound **22**, whose rigid conformation in the ground state may be similar to that of the less-stable, transition state (**V**). Compound **22** was then prepared by treatment of **21** with 70% TFA, and was subjected to hydrogenation by the procedure described in the case of **21**, to afford exclusively the anticipated 1,6-anhydride (**17**) in 80% yield.

The dithioacetalation of **14** or **17** with ethanethiol and boron trifluoride etherate afforded **38** in 95% yield. The tri-*O*-benzyl derivative **39**, prepared from **38** in 74% yield, was then cleaved in the usual way to aldehyde **40**, in 88% yield. Grignard condensation of **40** with an excess of methylmagnesium iodide gave the alcohol (**41**) in 90% yield as a 7:1 mixture of the C-2 epimers. Oxidation of **41** with pyridinium chlorochromate and molecular sieve 3A powder[12] proceeded effectively, and afforded the title compound (**I**) in 86% yield.

EXPERIMENTAL

General. — Melting points were determined on a Yanaco MP-83 micro hot-stage, and are uncorrected. Specific rotations were measured with a Carl Zeiss photoelectric polarimeter, using a 0.2-dm tube, for solutions in chloroform, unless stated otherwise. T.l.c. was conducted on t.l.c. plates (Merck, 60F-254, 0.25 mm), and column chromatography was performed on silica gel Wakogel G-200. In general, evaporations were conducted under diminished pressure below 30°. ^{1}H-N.m.r. spectra were recorded with either a Varian EM-390 or a Bruker WM 250 spectrometer for solutions in $CDCl_3$, using Me_4Si as the internal standard.

Methyl 2-O-acetyl-4,6-O-benzylidene-3-deoxy-3-C-methyl-α-D-glucopyranoside (**2**). — To a stirred, ice-cooled solution of **1** (98.7 g, 352 mmol) in pyridine (495 mL) were successively added acetic anhydride (39.7 mL, 1.2 equiv.) and DMAP (4.30 g, 0.1 equiv.). After being kept at room temperature for 1.5 h, the mixture was poured into ice–water. The precipitate was collected by filtration, washed with water, and

dried, to afford pale-yellow crystals of **2** (89.3 g, 79%). An analytical sample was obtained by chromatography on a column of silica gel with 30:1 benzene–ethyl acetate, and subsequent recrystallization from acetone–petroleum ether: m.p. 113–114.5°, $[\alpha]_D^{19}$ +93° (*c* 1.40); ν_{max}^{KBr} 1740 cm^{-1}; ^{1}H-n.m.r.: δ 1.06 (d, 3 H, *J* 7.0 Hz, Me-3), 2.13 (s, 3 H, OAc), 3.41 (s, 3 H, OMe), 4.62 (dd, 1 H, $J_{1,2}$ 4.0, $J_{2,3}$ 12.0 Hz, H-2), 4.79 (d, 1 H, H-1), and 5.50 (s, 1 H, =C*H*Ph).

Anal. Calc. for $C_{17}H_{22}O_6$: C, 63.34; H, 6.88. Found: C, 63.20; H, 6.78.

*Methyl 3,6-dideoxy-3-*C*-methyl-α-*D*-glucopyranoside* (**3**). — A mixture of **2** (49.6 g, 154 mmol), NBS (38.0 g, 185 mmol), and CCl_4 (750 mL) containing $BaCO_3$ (45.6 g, 0.20 mol) was stirred for 23 h at 80°. The solids were filtered off, and washed with chloroform, and the filtrate and washings were combined, successively washed with saturated aqueous $Na_2S_2O_3$, $NaHCO_3$, and NaCl solutions, dried, and evaporated, to give a red–brown, crude syrup (67.3 g) of methyl 2-*O*-acetyl-4-*O*-benzoyl-6-bromo-3-deoxy-3-*C*-methyl-α-D-glucopyranoside. The crude syrup (22.9 g) was dissolved in dry THF (213 mL), and the solution cooled in an ice bath. Powdered $LiAlH_4$ (8.0 g) was slowly added to the stirred solution, and the mixture was stirred for 2 h at 75°, cooled in an ice bath, and $Na_2SO_4 \cdot 10\ H_2O$ slowly added, to decompose unchanged $LiAlH_4$. The mixture was filtered through Celite, the filter cake was washed with ethyl acetate (2 L), the filtrate and washings were combined, and evaporated, and the oily residue (11.9 g) was chromatographed on silica gel (190 g) with 1:3 benzene–ethyl acetate, to afford practically pure, syrupy **3** (4.7 g, 51% from **2**), which spontaneously crystallized. Recrystallization from ethyl acetate–hexane gave a pure sample: colorless needles, m.p. 51.5–52.5°, $[\alpha]_D^{19}$ +155° (*c* 0.71, MeOH); ^{1}H-n.m.r.: δ 1.15 (d, 3 H, *J* 6.5 Hz, Me-3), 1.25 (d, 3 H, *J* 6.5 Hz, 3 H-6), 2.84 (dd, $J_{3,4} = J_{4,5}$ = 11.0 Hz, H-4), 3.54 (dd, 1 H, $J_{1,2}$ 4.0, $J_{2,3}$ 6.0 Hz, H-2), and 4.55 (d, 1 H, H-1).

Anal. Calc. for $C_8H_{16}O_4$: C, 54.53; H, 9.15. Found: C, 54.44; H, 8.95.

*3,6-Dideoxy-1,2-*O*-isopropylidene-3-*C*-methyl-α-*D*-glucofuranose* (**9**). — (*a*) *Preparation from* **3**. To a solution of **3** (15.0 g, 85 mmol) in acetic anhydride (450 mL) was slowly added a mixture of conc. H_2SO_4 (4.5 mL) and acetic anhydride (86 mL) under ice-cooling. After being kept at room temperature for 1.5 h, the mixture was poured into cold water (1 L), the acid neutralized with solid $NaHCO_3$, and the solution extracted with chloroform. The extract was dried, and evaporated, to afford crude 1,2,4-tri-*O*-acetyl-3,6-dideoxy-3-*C*-methyl-D-glucopyranose (22.6 g) as a brown syrup. To a solution of the crude acetate (22.6 g) in methanol (227 mL) was added dropwise a solution of NaOH (18.8 g) in methanol (150 mL) under ice-cooling. After being kept at room temperature for 3 h, the base was neutralized (pH 8) with CO_2 gas, and the solution evaporated. The residual solid was extracted with acetone (3 × 120 mL) and the extracts were combined, and evaporated, to give yellow, solid 3,6-dideoxy-3-*C*-methyl-D-glucose (11.5 g). To a solution of this crude, free sugar (0.54 g) in dry acetone (13.6 mL) was added a solution of anhydrous iron(III) chloride (0.16 g) in dry acetone (2.7 mL) under ice-cooling, and the mixture was stirred for 5.5 h at room temperature, cooled in ice, and the acid neutralized (pH 7) with cold, aqueous, 10% K_2CO_3 solution. The insoluble matter was filtered off

(Celite), the filtrate was concentrated to remove acetone, and the concentrate was extracted with chloroform. The extract was washed with saturated, aqueous NaCl solution, dried, evaporated, and the residual syrup chromatographed on silica gel (50 g) with 10:1 chloroform–acetone, to afford **9** (0.33 g, 49%) and its pyranose isomer **11** (22 mg, 3.2%):

Compound **9**, a colorless syrup; $[\alpha]_D^{25}$ −42° (*c* 1.0); ^{1}H-n.m.r.: δ 0.95 (d, 3 H, *J* 7.5 Hz, Me-3), 1.31 and 1.52 (each s, each 3 H, CMe_2), 1.32 (d, 3 H, *J* 6.0 Hz, 3 H-6), 2.42 (dq, 1 H, $J_{3,4}$ 3.5 Hz, H-3), 4.30 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-2), and 5.74 (d, 1 H, H-1).

Anal. Calc. for $C_{10}H_{18}O_4$: C, 59.38; H, 8.97. Found: C, 59.23; H, 8.72.

Compound **11**, a crystalline solid; ^{1}H-n.m.r.: δ 1.09 (d, 3 H, *J* 7.3 Hz, Me-3), 1.35 (d, 3 H, *J* 6.0 Hz, 3 H-6), 1.35 and 1.59 (each s, each 3 H, CMe_2), 1.9–2.4 (m, 2 H, H-3 and OH-4), 3.0–3.3 (m, 1 H, H-4), 3.75 (dq, 1 H, $J_{4,5} = J_{5,6} = 6.0$ Hz, H-5), 4.11 (dd, 1 H, $J_{1,2}$ 5.0, $J_{2,3}$ 3.0 Hz, H-2), and 5.46 (d, 1 H, H-1).

(*b*) *Preparation from* **5**. To a solution of **5** (4.6 g, 21.1 mmol) in dry pyridine (46 mL) was added a solution of tosyl chloride (8.0 g, 42.2 mmol) in dry pyridine (32 mL) under ice-cooling. After being kept for 2.5 h at room temperature, the mixture was poured into ice–water (150 mL), extracted with chloroform, and the extract washed successively with saturated aqueous $KHSO_4$, $NaHCO_3$, and NaCl solutions, dried, and evaporated, to afford a brown syrup (8.6 g) of crude 6-tosylate (**6**). To a solution of the syrup (7.9 g) in dry chloroform (79 mL) was added 2.09M sodium methoxide in methanol (12 mL) under ice-cooling. After being kept for 0.5 h at room temperature, the resulting, pale-yellow suspension was poured into ice water (200 mL), and extracted with chloroform. The extract was washed with saturated, aqueous NaCl solution, dried, and evaporated, to give crude **8** (4.0 g, 95% from **5**) as a yellow syrup: ^{1}H-n.m.r.: δ 1.01 (d, 3 H, *J* 7.5 Hz, Me-3), 1.28 and 1.28 (each s, each 3 H, CMe_2), 2.48 (dq, 1 H, $J_{3,4}$ 4.5 Hz, H-3), 2.35–3.1 (m, 3 H, H-5,6,6′), 3.85 (dd, 1 H, $J_{4,5}$ 6.0 Hz, H-4), 4.34 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-2), and 5.80 (d, 1 H, H-1). To a solution of crude **8** (4.0 g) in dry THF (40 mL) was slowly added a suspension of $LiAlH_4$ (0.92 g, 24 mmol) in THF (40 mL) under ice-cooling. After being stirred for 2 h at room temperature, ethyl acetate (50 mL) and then water (30 mL) were added to the cooled mixture, and stirring was continued for 2 h at room temperature. The resulting suspension was filtered through Celite, the filter cake was washed with ethyl acetate, and the filtrate and washings were combined, washed with saturated, aqueous NaCl solution, dried, and evaporated to a pale-yellow syrup (4.9 g). The syrup was chromatographed on silica gel (120 g) with 2:1 benzene–ethyl acetate, to afford **9** (3.4 g, 79% from **5**).

*Methyl 3-deoxy-3-*C*-methyl-*α*-*D*-glucopyranoside* (**4**). — To a suspension of **1** (0.63 g) in methanol (6.3 mL) was added 2.01M methanolic hydrogen chloride (2.2 mL) under ice-cooling, the mixture stirred for 1.5 h at room temperature, the acid neutralized with solid $NaHCO_3$, and the solution evaporated. The residue was mixed with acetone, the suspension filtered through Celite, the filtrate evaporated, and the crystalline residue (0.6 g) washed with hexane, to afford **4** (0.41 g, 94%) as pale-

yellow needles, m.p. 128–132°, used without purification in the next step. Recrystallization from hot acetone–hexane gave a pure sample of **4**: colorless needles, m.p. 131–132°, $[\alpha]_D^{32}$ +147° (*c* 0.89, MeOH).

Anal. Calc. for $C_8H_{16}O_5$: C, 49.99; H, 8.39. Found: C, 49.70; H, 8.23.

*3-Deoxy-1,2-*O*-isopropylidene-3-*C*-methyl-*α*-*D*-glucofuranose* (**5**). — To a solution of **4** (0.46 g, 2.39 mmol) in acetic anhydride (9.2 mL) was slowly added a mixture of conc. H_2SO_4 (0.13 mL, 2.44 mmol) and acetic anhydride (1.15 mL) under ice-cooling. After being kept for 3 h at room temperature, the mixture was poured into cold water, the acid neutralized with solid $NaHCO_3$, and the mixture extracted with ethyl acetate. The extract was washed with saturated, aqueous NaCl solution, dried, and evaporated, to give a yellow syrup (0.83 g) which was dissolved in methanol (8.4 mL), the solution ice-cooled, and M methanolic NaOH solution (9.6 mL) added. After being kept for 1 h at room temperature, the base was neutralized with CO_2 gas, and the solution evaporated. The residual solid was extracted with acetone, and the extracts were evaporated to a brown syrup, which was chromatographed on silica gel (17 g) with 3:1 chloroform–methanol, to afford a colorless syrup of 3-deoxy-3-*C*-methyl-D-glucose (0.37 g, 86% from **4**).

Anal. Calc. for $C_7H_{14}O_5$: C, 47.19; H, 7.92. Found: C, 46.51; H, 7.65.

To a solution of the free sugar (16.7 g, 93.7 mmol) in dry acetone (670 mL) was added a solution of anhydrous iron(III) chloride (8.85 g, 54.6 mmol) in dry acetone (89 mL) under ice-cooling, and the mixture was stirred for 2.5 h at room temperature, and processed as in preparation (*a*) of **9**, to give a brown syrup of crude 3-deoxy-1,2:5,6-di-*O*-isopropylidene-3-*C*-methyl-α-D-glucofuranose (24.1 g): ^{1}H-n.m.r.: δ 0.97 (d, 3 H, *J* 8.0 Hz, Me-3), 1.32, 1.37, 1.43, and 1.54 (each s, 12 H, 2 CMe_2), 2.1–2.7 (m, 1 H, H-3), 3.8–4.25 (m, 4 H, H-4,5,6,6'), 4.42 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-2), and 5.88 (d, 1 H, H-1). A mixture of the crude syrup (24.1 g) and 90% aqueous acetic acid (520 mL) was heated for 1.5 h at 60°, and then evaporated to a red-brown syrup (30.9 g) which was chromatographed on silica gel (200 g) with 1:2 benzene–ethyl acetate, to afford **5** (19.5 g, 95% from the free sugar) as a colorless syrup: $[\alpha]_D^{15}$ −23° (*c* 1.14); ^{1}H-n.m.r.: δ 0.96 (d, 3 H, *J* 7.4 Hz, Me-3), 1.20 and 1.51 (each s, each 3 H, CMe_2), 4.37 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-2), and 5.82 (d, 1 H, H-1).

Anal. Calc. for $C_{10}H_{18}O_5$: C, 55.03; H, 8.31. Found: C, 55.18; H, 8.29.

*5-*O*-Benzyl-3,6-dideoxy-1,2-*O*-isopropylidene-3-*C*-methyl-α-D-glucofuranose* (**10**) *and its free sugar* (**23**). — To a solution of **9** (5.12 g, 25.3 mmol) in dry THF (125 mL) was added 55% NaH (2.21 g, 50.6 mmol) under ice-cooling. After the mixture had been stirred for 1.5 h at room temperature, benzyl bromide (6.0 mL, 50.6 mmol) was added, stirring was continued for 2 days at room temperature, and the mixture was poured into cold water, and extracted with chloroform (3 × 300 mL). The extracts were combined, dried, and evaporated to a syrup (14.7 g), which was chromatographed on silica gel (740 g) with 50:1 benzene–ethyl acetate, to afford **10** (a pale-yellow syrup, 6.30 g, 85%) and **9** (0.52 g, 10%): **10**, $[\alpha]_D^{26}$ −15° (*c* 0.86); ^{1}H-n.m.r.: δ 0.85 (d, 3 H, *J* 7.5 Hz, Me-3), 1.30 and 1.52 (each s, each 3 H, CMe_2), 1.38 (d, 3 H, *J* 5.7 Hz, 3 H-6), 2.49 (dq, 1 H, $J_{3,4}$ 4.0 Hz, H-3), 3.57 (dq, 1 H, $J_{4,5}$ 9.0 Hz, H-5),

4.08 (dd, 1 H, H-4), 4.33 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-2), 4.41 and 4.67 (each d, each 1 H, J_{gem} 11.5 Hz, CH_2Ph), 5.79 (d, 1 H, H-1), and 7.35 (s, 5 H, Ph).

Anal. Calc. for $C_{17}H_{24}O_4$: C, 69.83; H, 8.27. Found: C, 70.05; H, 8.22.

A mixture of **10** (6.3 g) and 50% aqueous acetic acid (126 mL) was boiled under reflux for 1 h, cooled, and evaporated to a yellow syrup, which was chromatographed on silica gel (250 g) with 2:1 benzene–ethyl acetate, to afford **23** (4.92 g, 91%) as a colorless syrup.

Anal. Calc. for $C_{14}H_{20}O_4$: C, 66.64; H, 7.99. Found: C, 66.72; H, 7.95.

*3,6-Dideoxy-1,2-*O*-isopropylidene-3-*C*-methyl-*α*-*D*-xylo-hexofuranos-5-ulose* (**12**). — To a stirred, ice-cooled solution of **9** (345 mg, 1.71 mmol) in acetone (6.9 mL) was added a 1.28-mL portion of the Jones reagent prepared with CrO_3 (1.34 g), conc. H_2SO_4 (1.15 mL), and water (3.85 mL). After being kept for 1.5 h at room temperature, the green reaction-mixture was made neutral (pH 7) with cold, saturated, aqueous $NaHCO_3$, and extracted with ether. The extract was washed with saturated, aqueous, NaCl solution, dried, and evaporated, to afford a yellow oil (313 mg), which was chromatographed on silica gel (8.5 g) with 6:1 benzene–ethyl acetate, to give **12** (285 mg, 84%) as a colorless oil: $[\alpha]_D^{16}$ −87° (*c* 1.68); $\nu_{max}^{CHCl_3}$ 1728 and 1712 cm^{-1}; ^{1}H-n.m.r.: δ 0.84 (d, 3 H, *J* 8.0 Hz, Me-3), 1.32 and 1.51 (each s, each 3 H, CMe_2), 2.21 (s, 3 H, H-6), 2.64 (dq, 1 H, $J_{3,4}$ 4.5 Hz, H-3), 4.34 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-2), 4.63 (d, 1 H, H-4), and 5.87 (d, 1 H, H-1).

Anal. Calc. for $C_{10}H_{16}O_4$: C, 59.98; H, 8.05. Found: C, 59.89; H, 7.86.

*3,5,6-Trideoxy-1,2-*O*-isopropylidene-3-*C*-methyl-5-*C*-methylene-α-*D*-xylo-hexofuranose* (**13**). — A mixture of 55% NaH (0.69 g, 15.8 mmol) and dry Me_2SO (48 mL) was stirred for 45 min at 75–80° under an argon atmosphere, and then cooled to room temperature. To this solution of methylsulfinylmethanide anion in Me_2SO was added methyltriphenylphosphonium bromide (6.18 g, 17.3 mmol), and the mixture was stirred for 0.5 h at room temperature under argon. A solution of **12** (1.05 g, 5.24 mmol) in dry Me_2SO (10.5 mL) was added dropwise to the resulting, orange-yellow suspension of the ylide, ice-cooled, during 12 min, the mixture stirred for 1.5 h at room temperature, poured into ice–water (200 mL), and extracted with ether (5 × 70 mL). The extracts were combined, washed three times with saturated, aqueous NaCl solution, dried, and evaporated. The residue was chromatographed on silica gel (100 g) with 15:1 benzene–ethyl acetate, to afford colorless, oily **13** (0.98 g, 94%): $[\alpha]_D^{28}$ −107° (*c* 2.02); ^{1}H-n.m.r.: δ 0.70 (d, 3 H, *J* 7.5 Hz, Me-3), 1.31 and 1.51 (each s, each 3 H, CMe_2), 1.66 (s, 3 H, H-6), 2.33 (dq, 1 H, $J_{3,4}$ 4.5 Hz, H-3), 4.35 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-2), 4.58 (d, 1 H, $J_{3,4}$ 4.5 Hz, H-4), 4.87 and 5.06 (each broad s, 2 H, $=CH_2$), and 5.82 (d, 1 H, H-1).

Anal. Calc. for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.37; H, 8.88.

*3,5-Dideoxy-1,2-*O*-isopropylidene-3,5-di-*C*-methyl-β-*L*-idofuranose* (**14**) *and its* α-*D*-gluco *epimer* (**15**). — To a stirred, ice-cooled solution of **13** (4.60 g, 23.2 mmol) in dichloromethane (23 mL) was added 10.0M BMe_2S (3.0 mL, 30 mmol) during 20 min under argon. Stirring was continued for 1.5 h at room temperature, the mixture was ice-cooled, ethanol (11.6 mL), 3M NaOH (44.1 mL), and 30% H_2O_2

(22.3 mL) were successively added, the mixture was stirred for 1 h at room temperature, and extracted with chloroform, and the extract was washed with saturated, aqueous NaCl solution, dried, and evaporated to a colorless syrup (7.1 g), which was chromatographed on silica gel (750 g) with 8:1 chloroform–acetone, to afford **14** as a colorless syrup (R_F 0.29; 3.40 g, 68%) and **15** as colorless crystals (R_F 0.36; 0.87 g, 17%).

A pure sample of **14** was obtained by chromatography on silica gel with 2:1 benzene–ethyl acetate: $[\alpha]_D^{19}$ −24° (*c* 1.60); ^{1}H-n.m.r.: δ 0.87 (d, 3 H, *J* 7.5 Hz, Me-3), 1.11 (d, 3 H, *J* 7.0 Hz, Me-5), 1.30 and 1.51 (each s, each 3 H, CMe_2), 1.5–1.8 (b, 1 H, OH), 1.7–2.1 (m, 1 H, H-5), 2.26 (dq, 1 H, *J* 7.5, $J_{3,4}$ 4.0 Hz, H-3), 3.41 (dd, 1 H, $J_{6,6'}$ 10.5, $J_{5,6}$ 6.0 Hz, H-6), 3.57 (dd, 1 H, $J_{5,6'}$ 5.0 Hz, H-6'), 3.88 (dd, 1 H, $J_{4,5}$ 10.0 Hz, H-4), 4.30 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-2), and 5.74 (d, 1 H, H-1).

Anal. Calc. for $C_{11}H_{20}O_4$: C, 61.09; H, 9.32. Found: C, 61.03; H, 9.16.

A pure sample of **15** was obtained by recrystallization from hexane: colorless needles, m.p. 64–65°; $[\alpha]_D^{19}$ −35° (*c* 1.07); ^{1}H-n.m.r.: δ 0.82 (d, 3 H, *J* 7.0 Hz, Me-5), 0.85 (d, 3 H, *J* 7.5 Hz, Me-3), 1.29 and 1.50 (each s, each 3 H, CMe_2), 1.7–2.1 (m, 1 H, H-5), 2.27 (dq, 1 H, *J* 7.5, $J_{3,4}$ 4.0 Hz, H-3), 2.4–3.0 (b, 1 H, OH), 3.3–3.6 (m, 2 H, H-6,6'), 3.98 (dd, 1 H, $J_{4,5}$ 10.5 Hz, H-4), 4.32 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-2), and 5.80 (d, 1 H, H-1).

Anal. Calc. for $C_{11}H_{20}O_4$: C, 61.09; H, 9.32. Found: C, 60.84; H, 9.06.

6-O-Benzyl-3,5-dideoxy-1,2-O-isopropylidene-3,5-di-C-methyl-β-L-idofuranose (**16**). — A sample of **14** (178 mg) was benzylated with benzyl bromide (195 μL, 2 equiv.) by the procedure described in the case of **9**. The crude product (0.48 g) was chromatographed on silica gel (25 g) with 25:1 benzene–ethyl acetate, to afford colorless, syrupy **16** (224 mg, 89%). Purification by chromatography on a column of silica gel with 25:9 benzene–ethyl acetate gave a pure sample: $[\alpha]_D^{20}$ −6° (*c* 0.96); ^{1}H-n.m.r.: δ 0.83 (d, 3 H, *J* 7.5 Hz, Me-3), 1.11 (d, 3 H, *J* 6.5 Hz, Me-5), 1.28 and 1.49 (each s, each 3 H, CMe_2), 1.8–2.2 (m, 1 H, H-5), 2.22 (dq, 1 H, $J_{3,4}$ 4.0 Hz, H-3), 3.27 (d, 2 H, *J* 5.5 Hz, H-6,6'), 3.83 (dd, 1 H, $J_{4,5}$ 10.5 Hz, H-4), 4.27 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-2), 4.41 (s, 2 H, CH_2Ph), 5.67 (d, 1 H, H-1), and 7.27 (s, 5 H, Ph).

Anal. Calc. for $C_{18}H_{26}O_4$: C, 70.56; H, 8.55. Found: C, 70.76; H, 8.34.

Conversion of **16** *into* **37**. — A mixture of **16** (218 mg) and 50% aqueous acetic acid (4.4 mL) was kept for 2.5 h at 80°, and then cooled and evaporated. The residue was chromatographed on silica gel (18 g) with 2:1 benzene–ethyl acetate, to afford the free sugar (R_F 0.24; 148 mg, 82%) as a colorless syrup, unchanged **16** (R_F 0.85; 11 mg, 5%), and an unidentified by-product (R_F 0.56; 19 mg). A Grignard reaction of the free sugar (148 mg) with methylmagnesium iodide, prepared from Mg (135 mg) and methyl iodide (0.38 mL) in ether, was conducted as described for **23**, to give the addition product (86 mg, 55%) and unchanged, free sugar (44 mg, 30%) after chromatographic separation on silica gel (16 g) with 1:2 benzene–ethyl acetate. The addition product proved to be identical with the sample of **37** derived from **23**: R_F 0.30 in 1:2 benzene–ethyl acetate; ^{1}H-n.m.r.: δ 0.90 (d, 3 H, *J* 7.0 Hz, Me-2 or -4), 1.04 (d, 3 H, *J* 7.5 Hz, Me-2 or -4), 1.12 (d, 3 H, $J_{6,7}$ 6.5 Hz, H-7), 1.5–2.1 (m, 2 H,

H-2,4), 2.4–3.2 (b, 3 H, 3-OH), 3.39 (d, 2 H, $J_{1,2}$ 5.0 Hz, H-1,1'), 3.2–3.9 (m, 3 H, H-3,5,6), 4.40 (s, 2 H, CH_2Ph), and 7.21 (s, 5 H, Ph).

1,6-Anhydro-3,5-dideoxy-3,5-di-C-*methyl*-α-L-*idofuranose* (**17**) *and* β-D-gluco *epimer* (**18**). — A mixture of **14** (42.6 mg) and 70% aqueous TFA (0.4 mL) was kept for 2 h at room temperature, and then poured into ice-cooled, saturated $NaHCO_3$ solution containing solid $NaHCO_3$. The mixture was extracted with ethyl acetate, and the extract was dried and evaporated. The residual syrup (37 mg) was chromatographed on Kieselgel 60 (3 g) with 1:1 benzene–ethyl acetate, to afford **17** (8.9 mg, 29%): R_F 0.26 (6:1 chloroform–acetone) and 0.50 (2:1 benzene–acetone); $[\alpha]_D^{19}$ +7° (*c* 1.02); ^{1}H-n.m.r.: δ 0.85 and 1.29 (each d, each 3 H, each *J* 8.0 Hz, Me-3 and -5), 1.8–2.7 (m, 3 H, H-3,5, OH), 3.49 (dd, 1 H, $J_{5,6} = J_{6,6'} = 12.0$ Hz, H-6), 3.87 (dd, 1 H, $J_{5,6'}$ 6.0 Hz, H-6'), 4.11 (d, 1 H, $J_{2,3}$ 5.0 Hz, H-2), 4.25 (dd, 1 H, $J_{3,4}$ 7.0, $J_{4,5}$ 3.0 Hz, H-4), and 5.12 (s, 1 H, H-1).

By the procedure described for **14**, a sample of **15** (36.7 mg) afforded the corresponding 1,6-anhydride **18** (8.8 mg, 33%): R_F 0.27 (6:1 chloroform–acetone) and 0.52 (2:1 benzene–acetone); $[\alpha]_D^{19}$ +25° (*c* 0.76); ^{1}H-n.m.r.: δ 1.21 and 1.32 (each d, each 3 H, each *J* 8.0 Hz, Me-3 and -5), 1.4–1.8 (m, 1 H, H-5), 2.0–2.5 (m, 1 H, H-3), 2.06 (s, 1 H, OH), 3.57 (d, 1 H, $J_{6,6'}$ 12.0, $J_{5,6'}$ 0 Hz, H-6'), 3.90 (dd, 1 H, $J_{5,6}$ 4.0 Hz, H-6), 4.09 (d, 1 H, $J_{3,4}$ 8.0, $J_{4,5}$ 0 Hz, H-4), 4.16 (d, 1 H, $J_{2,3}$ 4.2 Hz, H-2), and 5.06 (s, 1 H, H-1).

6-O-*Acetyl-3-deoxy-1,2*-O-*isopropylidene-3*-C-*methyl*-α-D-*glucofuranose* (**7**). — A mixture of **5** (428 mg, 1.96 mmol), dry pyridine (4.3 mL), acetic anhydride (194 μL, 2.06 mmol), and DMAP (24 mg, 196 μmol) was kept for 25 min at 0° and then poured into ice–water. The mixture was extracted with ethyl acetate (2 × 15 mL), and the extracts were successively washed with saturated, aqueous $KHSO_4$, $NaHCO_3$, and NaCl solutions, dried, and evaporated. The residual syrup was chromatographed on silica gel (26 g) with 3:2 benzene–ethyl acetate, to afford colorless, syrupy **7** (432 mg, 85%) and syrupy 5,6-diacetate of **5** (35 mg, 11%): **7**, $[\alpha]_D^{16}$ −17° (*c* 1.36); ^{1}H-n.m.r.: δ 0.95 (d, 3 H, *J* 7.0 Hz, Me-3), 1.29 and 1.49 (each s, each 3 H, CMe_2), 2.09 (s, 3 H, Ac), 2.40 (d, 1 H, *J* 4.0 Hz, OH), 2.47 (dq, 1 H, $J_{3,4}$ 4.0 Hz, H-3), 3.7–4.0 (m, 1 H, H-5), 4.08 (dd, 1 H, $J_{4,5}$ 4.0 Hz, H-4), 4.16 (dd, 1 H, $J_{5,6}$ 6.5, $J_{6,6'}$ 11.8 Hz, H-6), 4.36 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-2), 4.46 (dd, 1 H, $J_{5,6'}$ 2.7 Hz, H-6'), and 5.78 (d, 1 H, H-1).

Anal. Calc. for $C_{12}H_{20}O_6$: C, 55.37; H, 7.74. Found: C, 55.11; H, 7.54.

6-O-*Acetyl-3-deoxy-1,2*-O-*isopropylidene-3*-C-*methyl*-α-D-xylo-*hexofuranos-5-ulose* (**19**). — A sample of **7** (418 mg) was oxidized by the procedure described in the preparation of **12**, to give **19** (357 mg, 86%) as colorless crystals. Recrystallization from ethyl acetate–hexane afforded a pure sample: colorless needles, m.p. 121–122°, $[\alpha]_D^{18}$ −94° (*c* 1.01); ν_{max}^{KBr} 1757 and 1732 cm^{-1}; ^{1}H-n.m.r.: δ 0.88 (d, 3 H, *J* 7.0 Hz, Me-3), 1.30 and 1.48 (each s, each 3 H, CMe_2), 2.14 (s, 3 H, Ac), 2.68 (dq, 1 H, $J_{3,4}$ 5.0 Hz, H-3), 4.38 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-2), 4.72 (d, 1 H, H-4), 4.89 (s, 2 H, H-6,6'), and 5.95 (d, 1 H, H-1).

Anal. Calc. for $C_{12}H_{28}O_6$: C, 55.81; H, 7.02. Found: C, 55.59; H, 6.85.

6-O-Acetyl-3,5-dideoxy-1,2-O-isopropylidene-3-C-methyl-5-C-methylene-α-D-xylo-hexofuranose (**20**). — 4M Methylsulfinylmethanide anion in Me_2SO[9] (1.0 mL) was added to a suspension of methyltriphenylphosphonium bromide (1.48 g, 4.14 mmol) in dry ether (17.9 mL). After being stirred for 50 min at room temperature under argon, the mixture was cooled to −50°. A solution of **19** (357 mg, 1.38 mmol) in dry ether (1.8 mL) was then added dropwise to the cooled ylide solution. The stirred mixture was allowed to warm to 0° during 15 min, and stirring was continued for 15 min at room temperature. The mixture was processed as usual, and the crude product was chromatographed on silica gel (35 g) with 4:1 hexane–acetone, to afford **20** (183 mg, 52%) as a colorless syrup: $[\alpha]_D^{18}$ −76° (*c* 1.09); ^{1}H-n.m.r.: δ 0.73 (d, 3 H, *J* 7.5 Hz, Me-3), 1.30 and 1.51 (each s, each 3 H, CMe_2), 2.05 (s, 3 H, Ac), 2.36 (dq, 1 H, $J_{3,4}$ 5.0 Hz, H-3), 4.41 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-2), 4.53 (s, 2 H, H-6,6′), 4.74 (broad d, 1 H, H-4), 5.2–5.4 (m, 2 H, $=CH_2$), and 5.84 (d, 1 H, H-1).

Anal. Calc. for $C_{13}H_{20}O_5$: C, 60.92; H, 7.87. Found: C, 60.68; H, 7.66.

3,5-Dideoxy-1,2-O-isopropylidene-3-C-methyl-5-C-methylene-α-D-xylo-hexofuranose (**21**). — A mixture of **20** (132 mg), methanol (2.6 mL), and aqueous M NaOH (0.77 mL) was stirred under ice-cooling for 15 min, made neutral with CO_2, and evaporated. The residue was extracted with acetone, and the extract was evaporated to a solid, which was chromatographed on silica gel (5 g) with 2:1 benzene–ethyl acetate, to afford **21** (105 mg, 95%) as colorless crystals. Recrystallization from ether–pentane gave a pure sample: colorless plates, m.p. 46–47°, $[\alpha]_D^{20}$ −102° (*c* 0.72); ^{1}H-n.m.r.: δ 0.70 (d, 3 H, *J* 7.5 Hz, Me-3), 1.28 and 1.48 (each s, each 3 H, CMe_2), 2.1–2.7 (m, 2 H, H-3, OH-6), 3.99 (s, 2 H, H-6,6′), 4.33 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-2), 4.74 (broad d, 1 H, $J_{3,4}$ 3.0 Hz, H-4), 5.14 (s, 2 H, $=CH_2$), and 5.78 (d, 1 H, H-1).

Anal. Calc. for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found: C, 61.44; H, 8.29.

Homogeneous hydrogenation of **21**. — A mixture of **21** (9.2 mg, 43 μmol), chlorotris(triphenylphosphine)rhodium(I)[13] (16 mg, 17.2 μmol), and benzene (0.46 mL) was stirred with hydrogen under atmospheric pressure for 3 h at room temperature, evaporated, and the residue passed through Florisil (1 g) with ether, and the solution evaporated. The residue was chromatographed on silica gel (1 g) with 7:1 chloroform–acetone, to afford **15** (7.7 mg, 83%) and **14** (1.2 mg, 13%).

1,6-Anhydro-3,5-dideoxy-3-C-methyl-5-C-methylene-β-D-xylo-hexofuranose (**22**). — By the procedure described for **14**, a sample of **21** (74 mg) was converted into **22** (32 mg, 60%): colorless plates, m.p. 67.5–68.5° (chloroform–hexane), $[\alpha]_D^{19}$ −35° (*c* 0.93); ^{1}H-n.m.r.: δ 1.04 (d, 3 H, *J* 7.0 Hz, Me-3), 2.0–2.5 (m, 2 H, H-3, OH-2), 4.07 (broad d, 1 H, $J_{3,4}$ 3.0 Hz, H-4), 4.22 (s-like, 2 H, H-6,6′), 4.60 (d, 1 H, $J_{2,3}$ 6.5 Hz, H-2), 4.81 and 4.87 (each broad s, each 1 H, $=CH_2$), and 5.16 (s, 1 H, H-1).

Anal. Calc. for $C_8H_{12}O_3$: C, 61.52; H, 7.74. Found: C, 61.55; H, 7.63.

Preparation of **17** *by homogeneous hydrogenation of* **22**. — By the procedure described for hydrogenation of **21**, a sample of **22** (13.5 mg) was hydrogenated with $(Ph_3P)_3RhCl$ (32 mg), to afford **17** (11 mg, 80%) after chromatography on a column of silica gel with 1:1 benzene–ethyl acetate, by which, no isomeric product (**18**) was

detected in the reduction product. The product (**17**) was fully characterized by ^{1}H-n.m.r. spectroscopy, elemental analysis, and optical rotation: $[\alpha]_D^{19}$ +6° (*c* 0.55).

Anal. Calc. for $C_8H_{14}O_3$: C, 60.74; H, 8.92. Found: C, 61.00; H, 9.12.

2-O-Benzyl-1,4,7-trideoxy-4-C-methyl-D-glycero-L-gulo-*heptitol* (**24**). — A solution of **23** (3.88 g, 15.4 mmol) in dry ether (39 mL) was added dropwise to a stirred, ice-cold ether solution of methylmagnesium iodide prepared from Mg (3.74 g, 154 mmol) and methyl iodide (9.58 mL, 154 mmol) in dry ether (155 mL). After being stirred for 20 h at room temperature, water was carefully added to decompose the excess of Grignard reagent, the resulting precipitate was dissolved in M HCl, and the aqueous layer was separated from the ether layer, and extracted with chloroform (5 × 100 mL). The organic layers were combined, washed with saturated, aqueous NaCl solution, dried, and evaporated. The residual syrup was chromatographed on silica gel (200 g) with 1 : 1 benzene–ethyl acetate, to afford **24** (3.38 g, 82%) and the starting, free sugar **23** (0.23 g, 6%): **24**, a colorless syrup, $[\alpha]_D^{14}$ −40° (*c* 1.06); ^{1}H-n.m.r.: δ 0.82 (d, 3 H, *J* 7.2 Hz, Me-4), 1.16 (d, 3 H, *J* 6.3 Hz, 3 H-1 or 3 H-7), 1.29 (d, 3 H, *J* 6.0 Hz, 3 H-1 or 3 H-7), 4.42 and 4.63 (each d, each 1 H, J_{gem} 12.0 Hz, CH_2Ph), and 7.33 (s, 5 H, Ph).

Anal. Calc. for $C_{15}H_{24}O_4$: C, 67.13; H, 9.02. Found: C, 67.09; H, 8.86.

2-O-Benzyl-1,4,7-trideoxy-5,6-O-isopropylidene-4-C-methyl-D-glycero-L-gulo-*heptitol* (**25**). — A mixture of **24** (3.38 g, 12.6 mmol) and DMP (2.32 mL, 18.9 mmol), dry DMF (34 mL), and anhydrous *p*-toluenesulfonic acid (0.43 g) was kept for 20 min at room temperature, the acid neutralized with triethylamine, and the solution poured into cold water. The mixture was extracted with chloroform (3 × 100 mL) and the extracts were washed with saturated, aqueous NaCl, dried, and evaporated. The residual syrup was chromatographed on silica gel (200 g) with 10 : 1 benzene–ethyl acetate, to give **25** (3.69 g, 95%) as a colorless syrup: $[\alpha]_D^{26}$ −11° (*c* 1.58); ^{1}H-n.m.r.: δ 0.87 (d, 3 H, *J* 7.0 Hz, Me-4), 1.21 and 1.29 (each d, each 3 H, *J* 6.0 Hz, 3 H-1 or 3 H-7), 1.38 (s, 6 H, CMe_2), 4.45 and 4.65 (each d, each 1 H, J_{gem} 12.0 Hz, CH_2Ph), and 7.36 (s, 5 H, Ph).

Anal. Calc. for $C_{18}H_{28}O_4$: C, 70.10; H, 9.15. Found: C, 69.79; H, 8.91.

(2R,3R,4R)-3-Hydroxy-2-methyl-4-pentanolide (**28**). — A solution of **25** (320 mg) in methanol (6.4 mL) was stirred with palladium black under bubbling with hydrogen gas for 10 min, and the suspension filtered. The filtrate was evaporated to a colorless syrup (233 mg, 99%), which was dissolved in acetone (2.2 mL), and the solution cooled in an ice bath. A solution of $NaIO_4$ (328 mg) in water (3.3 mL) was added, and the mixture was stirred for 10 min, diluted with water (5 mL), and extracted with chloroform. The extract was washed with saturated, aqueous NaCl solution, dried, and evaporated. The residual aldehyde (161 mg, 91%) was hydrolyzed with 90% TFA (1.6 mL) for 5 min, the acid neutralized with $NaHCO_3$, and the mixture saturated with NaCl, and extracted with ethyl acetate (10 × 4 mL). The extracts were combined, dried, and evaporated, to afford a syrup (250 mg) of the free sugar which was then oxidized with bromine (0.14 mL) in 1 : 1 water–1,4-dioxane (2.7 mL) for 24 h at 25°. The mixture was extracted with ethyl acetate (4 × 7 mL),

and the extracts were combined, successively washed with saturated, aqueous $Na_2S_2O_3$ and NaCl solutions, dried, and evaporated. The brown, oily residue (452 mg) was chromatographed on silica gel (7 g) with 1 : 1 benzene–ethyl acetate, to give **28** (64.2 mg, 48% from **25**) as a colorless oil: ^{1}H-n.m.r.: δ 1.26 (d, 3 H, J 7.7 Hz, Me-2), 1.37 (d, 3 H, J 7.0 Hz, Me-4), 2.61 (dq, 1 H, $J_{2,3}$ 4.6 Hz, H-2), 3.30 (broad s, 1 H, OH), 4.11 (dd, 1 H, $J_{3,4}$ 5.0 Hz, H-3), and 4.65 (dq, 1 H, H-4); lit.[1g] for enantiomer of **28**; δ 4.12 (dd, 1 H, $J_{2,3} = J_{3,4} = 5.0$ Hz, H-3), and 4.66 (dq, 1 H, J 6.6 Hz, H-4); lit.[11] for (±)-**28**: δ 4.00 (dd, 1 H, $J_{2,3} = J_{3,4} = 5$ Hz, H-3), and 4.50 (dq, J 6 Hz, H-4).

*3-O-Acetyl-2-O-benzyl-1,4,7-trideoxy-5,6-O-isopropylidene-4-C-methyl-*D-glycero-L-gulo-*heptitol* (**26**). — To a solution of **25** (3.69 g, 12.0 mmol) in ethyl acetate (74 mL) were added acetic anhydride (1.35 mL, 14.4 mmol) and DMAP (1.5 g, 12.3 mmol). After being kept at room temperature for 0.5 h, the mixture was washed with water (2 × 30 mL), dried, and evaporated. The residue was chromatographed on silica gel (400 g) with 30 : 1 benzene–ethyl acetate, to afford **26** (4.07 g, 96%) as a colorless syrup: $[\alpha]_D^{26}$ +14° (*c* 0.80); ^{1}H-n.m.r.: δ 0.90 (d, 3 H, J 7.1 Hz, Me-4), 1.15 (d, 3 H, J 6.2 Hz, 3 H-1), 1.19 (d, 3 H, J 5.8 Hz, 3 H-7), 1.34 (s, 6 H, CMe_2), 2.05 (s, 3 H, Ac), 1.8–2.35 (m, 1 H, H-4), 3.47 (dd, 1 H, $J_{4,5}$ 3.0, $J_{5,6}$ 7.8 Hz, H-5), 3.64 (dq, 1 H, $J_{2,3}$ 6.2 Hz, H-2), 3.83 (dq, 1 H, H-6), 4.53 (s, 2 H, CH_2Ph), 5.07 (dd, 1 H, $J_{3,4}$ 4.2 Hz, H-3), and 7.35 (s, 5 H, Ph).

Anal. Calc. for $C_{20}H_{30}O_5$: C, 68.54; H, 8.63. Found: C, 68.27; H, 8.43.

*2,3-Anhydro-1,4,7-trideoxy-5,6-*O*-isopropylidene-4-*C*-methyl-*D-glycero-L-ido-*heptitol* (**29**). — A portion of **26** (835 mg, 2.38 mmol) was hydrogenolyzed in methanol (25 mL) over palladium black under bubbling with hydrogen gas for 15 min at room temperature, and the suspension filtered. The filtrate was evaporated to a colorless syrup (622 mg), which was immediately dissolved in dry pyridine (6.2 mL) and mesyl chloride (0.28 mL, 3.62 mmol) was added under ice-cooling. After being kept at room temperature for 20 min, the mixture was poured into cold water, and extracted with chloroform (3 × 50 mL). The extracts were combined, washed successively with saturated $KHSO_4$, $NaHCO_3$, and NaCl solution, dried, and evaporated, to afford a sample of crude **27** (805 mg, 100%) as a pale-yellow syrup. A solution of **27** (758 mg) in dry chloroform (7.6 mL) was cooled in an ice bath, and 4.17M sodium methoxide in methanol (0.65 mL, 2.71 mmol) was added. After being stirred under ice-cooling for 10 min, the mixture was diluted with chloroform, washed with saturated, aqueous NaCl solution, dried, and evaporated. The residue was chromatographed on silica gel (40 g) with 10 : 1 benzene–ethyl acetate, and then distilled, to give **29** (368 mg, 82% from **26**) as a colorless oil: b.p. 72–77° (bath temp)/3 mmHg; ^{1}H-n.m.r.: δ 1.07 (d, 3 H, J 6.8 Hz, Me-4), 1.26 (d, 3 H, J 6.0 Hz, 3 H-7), 1.31 (d, 3 H, J 5.2 Hz, 3 H-1), 1.36 and 1.38 (each s, each 3 H, CMe_2), 1.3–1.85 (m, 1 H, H-4), 2.59 (dd, 1 H, $J_{3,4}$ 7.0, $J_{2,3}$ 2.2 Hz, H-3), 2.87 (dq, 1 H, H-2), 3.50 (dd, 1 H, $J_{4,5}$ 4.8, $J_{5,6}$ 8.5 Hz, H-5), and 3.92 (dq, 1 H, H-6).

*2,4,7-Trideoxy-5,6-*O*-isopropylidene-2,4-di-*C*-methyl-*D-glycero-L-ido-*heptose trimethylene dithioacetal* (**30**) *and its positional isomer* (**35**). — A solution of 1,3-

dithiane (879 mg, 7.09 mmol) in dry THF (8.8 mL) was cooled to −35° under argon, and 1.64M butyllithium in hexane (4.32 mL, 7.08 mmol) was added dropwise. After being stirred for 2 h at −20°, the mixture was recooled to −35°. A solution of **29** (142 mg, 709 μmol) in THF (0.3 mL) was added dropwise to this stirred solution, and stirring was continued for 2 h at −20° and for 3 days at 5°. The mixture was now poured into cold water, and extracted with chloroform (3 × 20 mL). The extracts were combined, washed with saturated, aqueous NaCl solution, dried, and evaporated. The residue was chromatographed on silica gel (20 g) with 6:1 benzene–ethyl acetate, to afford **30** (50 mg, 22%) and **35** (154 mg, 68%).

Compound **30**. $[\alpha]_D^{14}$ +14° (*c* 1.0); ^{1}H-n.m.r.: δ 1.00 and 1.22 (each d, each 3 H, each *J* 7.0 Hz, Me-2 and -4), 1.28 (d, 3 H, *J* 5.8 Hz, 3 H-7), 1.43 (s, 6 H, CMe_2), 1.5–2.4 (m, 4 H, H-2,4, $SCH_2CH_2CH_2S$), 2.57 (d, 1 H, *J* 3.0 Hz, OH), 2.67–3.10 (m, 4 H, $SCH_2CH_2CH_2S$), 3.62 (dd, 1 H, $J_{4,5}$ 2.2, $J_{5,6}$ 8.5 Hz, H-5), 3.97 (dq, 1 H, H-6), 3.6–4.0 (m, 1 H, H-3), and 4.17 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1).

Anal. Calc. for $C_{15}H_{28}O_3S_2$: C, 56.21; H, 8.81; S, 20.00. Found: C, 55.93; H, 8.62; S, 19.68.

Acetyl derivative (**31**) *of* **30**. — By the procedure described in the preparation of **26**, a sample of **30** (50 mg) was acetylated, to afford a chromatographically pure sample of **31** (50 mg, 88%) as a colorless syrup: ^{1}H-n.m.r.: δ 2.09 (s, 3 H, OAc) and 5.22 (dd, 1 H, *J* 6.2 Hz, H-3).

Compound **35**. ^{1}H-n.m.r.: δ 1.18 (d, 3 H, *J* 6.3 Hz, Me-3), 1.33 (d, 6 H, Me-1′, 3 H-6), 1.41 (s, 6 H, CMe_2), 1.62–2.60 (m, 4 H, H-2,3, $SCH_2CH_2CH_2S$), 2.60–3.15 (m, 4 H, $SCH_2CH_2CH_2S$), 3.58 (dd, 1 H, $J_{3,4}$ 1.8, $J_{4,5}$ 9.0 Hz, H-4), 3.95 (dq, 1 H, $J_{1',2}$ 6.0 Hz, H-1′), 3.85–3.95 (broad, 1 H, OH), 4.07 (dq, 1 H, H-5), and 4.36 (d, 1 H, $J_{1,2}$ 3.0 Hz, H-1).

Acetyl derivative (**36**) *of* **35**. ^{1}H-n.m.r.: δ 2.07 (s, 3 H, OAc) and 5.25 (dq, 1 H, $J_{1',2} = J_{1',Me} = 6.5$ Hz, H-1′).

1-O-*Benzyl-2,4,7-trideoxy-2,4-di*-C-*methyl*-D-glycero-L-ido-*heptitol* (**37**). — To a mixture of **31** (50 mg, 138 μmol) and mercury(II) oxide (120 mg, 554 μmol) in 80% aqueous acetone (3.5 mL) was added mercury(II) chloride (150 mg, 552 μmol), and the mixture was stirred for 20 min at 70°, cooled, and filtered through Celite. The filter cake was washed with acetone, the filtrate and washings were combined, the acetone was evaporated, the aqueous solution extracted with chloroform (3 × 5 mL), and the extracts were combined, and successively washed with aqueous, 10% KI solution and saturated aqueous NaCl solution, dried, and evaporated. The residue was chromatographed on silica gel (4 g) with 10:1 benzene–ethyl acetate, to afford **32** (35 mg, 93%) as a colorless syrup: ^{1}H-n.m.r.: δ 1.37 (s, 6 H, CMe_2), 2.05 (s, 3 H, OAc), 5.40 (dd, 1 H, $J_{3,4}$ 5.0 Hz, H-3), and 9.70 (s, 1 H, C*H*O). To a cooled solution of **31** (35 mg, 129 μmol) in dry THF (0.35 mL) was added $LiAlH_4$ (5 mg, 132 μmol). The mixture was stirred for 10 min at room temperature, and then $Na_2SO_4 \cdot 10\ H_2O$ was added, the mixture filtered, and the filtrate evaporated. The residue was chromatographed on silica gel (3 g) with 1:2 benzene–ethyl acetate, to

give **33** (28.5 mg, 96%) as a colorless syrup: ^{1}H-n.m.r.: δ 1.25 (d, 3 H, $J_{6,7}$ 5.9 Hz, 3 H-7), 1.38 (s, 6 H, CMe_2), and 3.92 (dq, 1 H, $J_{5,6}$ 8.5 Hz, H-6).

A mixture of **33** (28.5 mg, 123 μmol), NaH (6.2 mg, 258 μmol), and dry THF (0.25 mL) was stirred for 0.5 h at room temperature, benzyl bromide (16 μL, 135 μmol) was added, the mixture was stirred at room temperature, and processed, and the crude product was chromatographed on silica gel (4 g) with 10:1 benzene–ethyl acetate, to afford **34** (31.4 mg, 79%) as a colorless syrup which was dissolved in 50% difluoroacetic acid (0.32 mL), the solution kept for 0.5 h at 0°, and evaporated, and the residue chromatographed on silica gel (3 g) with 1:2 benzene–ethyl acetate, to give **37** (25.3 mg, 92%) as a colorless syrup: R_F 0.30 in 1:2 benzene–ethyl acetate; $[\alpha]_D^{19}$ −6° (*c* 1.41); ^{1}H-n.m.r.: δ 0.93 (d, 3 H, *J* 6.8 Hz, Me-2 or -4), 1.05 (d, 3 H, *J* 7.5 Hz, Me-2 or -4), 1.13 (d, 3 H, *J* 6.5 Hz, 3 H-7), 1.65–2.15 (m, 2 H, H-2,4), 3.13 (broad, 3 H, 3 OH), 3.35–3.90 (m, 3 H, H-3,5,6), 3.42 (d, 2 H, $J_{1,2}$ 5.0 Hz, H-1,1′), 4.46 (s, 2 H, CH_2Ph), and 7.32 (s, 5 H, Ph).

Anal. Calc. for $C_{16}H_{26}O_4$: C, 68.05; H, 9.28. Found: C, 68.26; H, 9.20.

*3,5-Dideoxy-3,5-di-*C*-methyl-*L*-idose diethyl dithioacetal* (**38**). — (*a*) To a solution of **14** (3.3 g, 15.2 mmol) in ethanethiol (100 mL) was added $BF_3 \cdot Et_2O$ (1.0 mL) under ice-cooling. The mixture was kept for 1 h at room temperature, the acid neutralized with 50% aqueous K_2CO_3 solution, and the solution concentrated. The concentrate was diluted with ethyl acetate, the suspension filtered through Celite, and the filtrate dried, and evaporated to a yellow syrup (8.4 g), which was purified by chromatography on silica gel (215 g) with 1:2 toluene–ethyl acetate, to give **38** (4.1 g, 95%) as a colorless syrup: $[\alpha]_D^{14}$ +118° (*c* 2.65); ^{1}H-n.m.r.: δ 0.99 and 1.04 (each d, each 3 H, each *J* 7.0 Hz, Me-3 and -5), 1.29 (t, 6 H, *J* 7.0 Hz, SCH_2Me), and 2.5–2.8 (m, 4 H, SCH_2Me).

Anal. Calc. for $C_{12}H_{26}O_3S_2$: C, 51.03; H, 9.28; S, 22.70. Found: C, 50.82; H, 8.99; S, 22.54.

(*b*) By the procedure just described, the 1,6-anhydro compound (**17**) could also be converted into **38** (in 95% yield).

*2,4,6-Tri-*O*-benzyl-3,5-dideoxy-3,5-di-*C*-methyl-*L*-idose diethyl dithioacetal* (**39**). — To a solution of **38** (140 mg, 495 μmol) in dry DMF (0.7 mL) was added NaH (71 mg, 2.97 mmol) under ice-cooling, the mixture stirred for 1 h at room temperature, benzyl bromide (0.35 mL, 2.94 mmol) added, and the mixture stirred for 18 h at room temperature, poured into ice water, and extracted with chloroform. The extract was washed with saturated, aqueous NaCl solution, and evaporated. To the residue were added dichloromethane (10 mL), water (0.09 mL), and triethylamine (0.34 mL), and the mixture was stirred for 24 h at room temperature, concentrated, and the concentrate extracted with ethyl acetate. The extract was washed with saturated, aqueous NaCl solution, dried, and evaporated. The residue was chromatographed on silica gel (28 g) with 20:1 hexane–ethyl acetate, to afford **39** (202 mg, 74%). An analytical sample was obtained by chromatography on a column of silica gel with 1:3 hexane–benzene: $[\alpha]_D^{20}$ +39° (*c* 1.15).

Anal. Calc. for $C_{33}H_{44}O_3S_2$: C, 71.70; H, 8.02; S, 11.60. Found: C, 71.91; H, 7.86; S, 11.39.

*2,4,6-Tri-*O*-benzyl-3,5-dideoxy-3,5-di-*C*-methyl-*L*-idose* (**40**). — Red mercury(II) oxide (1.57 g, 7.25 mmol) and mercury(II) chloride (3.93 g, 14.5 mmol) were successively added to a solution of **39** (1.0 g, 1.81 mmol) in 80% aqueous acetone (80 mL) under vigorous stirring, and stirring was continued for 45 min at room temperature. The resulting suspension was processed as described for **31**, to afford a crude syrup (1.6 g), containing **40**, which was chromatographed on Kieselgel 60 (20 g) with 7:1 hexane–ethyl acetate, to give **40** (0.71 g, 88%) as a colorless syrup: ^{1}H-n.m.r.: δ 0.97 (d, 3 H, *J* 7.0 Hz, Me-3 or -5), 1.07 (d, 3 H, *J* 7.5 Hz, Me-3 or -5), 1.8–2.6 (m, 2 H, H-3,5), 3.1–3.5 (m, 2 H, H-6,6′), 3.5–3.8 (m, 2 H, H-2,4), 4.3–4.62 (m, 6 H, CH_2Ph), 7.24 (s, 15 H, 3 Ph), and 9.54 (d, 1 H, *J* 2.0 Hz, C*H*O).

Mixture (**41**) *of 3,5,7-tri-*O*-benzyl-1,4,6-trideoxy-4,6-di-*C*-methyl-*L*-glycero-*D*-ido-heptitol* and D-gulo *epimer*. — To a solution of methylmagnesium iodide in ether (6.2 mL) [prepared from Mg (92 mg) and methyl iodide (0.28 mL)] was added dropwise a solution of **40** (155 mg, 0.35 mmol) in ether (1.6 mL) under ice-cooling. After being stirred at room temperature for 1 h, the mixture was processed in the usual way, and the crude product was purified by chromatography on a column of silica gel (4 g) with 3:1 hexane–ethyl acetate, to afford syrupy **41** (144 mg, 90%) as a 7:1 mixture of the C-2-epimers. This sample was used without further purification in the next step. The epimeric ratio was estimated from the fact that, when a sample (59 mg) of **41** was further chromatographed on silica gel (10 g) with the same solvent system, it gave the major isomer (R_F 0.34, 50 mg) and the minor one (R_F 0.29, 7 mg), whose structures were confirmed by ^{1}H-n.m.r. spectroscopy.

*3,5,7-Tri-*O*-benzyl-1,4,6-trideoxy-4,6-di-*C*-methyl-*keto-L-ido-*2-heptulose* (**I**). — To a suspension of pyridinium chlorochromate (PCC) (860 mg, 3.09 mmol) and powdered molecular sieves 3A (1.03 g) in dichloromethane (3.3 mL) was added a solution of **41** (615 mg, 1.33 mmol) in dichloromethane (6 mL). After being stirred at room temperature for 4 h, an additional amount of PCC (290 mg, 1.35 mmol) was added, and stirring was continued for 1.5 h. The mixture was filtered through a short column filled with silica gel (12 g) and the column was washed with ether. The filtrate and washings were combined, and evaporated to a colorless syrup (638 mg), which was chromatographed on silica gel (60 g) with 5:1 hexane–ethyl acetate, to afford pure **I** (524 mg, 86%) as a colorless syrup: $[\alpha]_D^{17}$ +23° (*c* 0.76); $\nu_{max}^{CHCl_3}$ 1720 and 1708 cm^{-1}; ^{1}H-n.m.r.: δ 0.94 and 1.02 (each d, each 3 H, each *J* 7.0 Hz, Me-4 and -6), 2.09 (s, 3 H, H-1), 1.8–2.4 (m, 2 H, H-4,6), 3.2–3.4 (m, 2 H, H-7,7′), 3.55 (dd, 1 H, *J* 3.0, *J* 6.5 Hz, H-5), 3.67 (d, 1 H, $J_{3,4}$ 4.0 Hz, H-3), 4.1–4.6 (m, 6 H, 3 CH_2Ph), and 7.22 (s, 15 H, 3 Ph).

Anal. Calc. for $C_{30}H_{36}O_4$: C, 78.23; H, 7.88. Found: C, 78.21; H, 7.95.

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