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New Syntheses of 6-Deoxy-L-gulose and 6-Deoxy-L-talose[1)]

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Treatment of methyl 2,3,4,-tri-*O*-benzoyl-6-deoxy-6-iodo-α-D-mannopyranoside (**1**) or methyl 4-*O*-acetyl-2,3-di-*O*-benzoyl-6-deoxy-6-iodo-α-D-allopyranoside (**11**) with silver fluoride in pyridine gave the corresponding D-*lyxo*- (**2**) or D-*ribo*-hex-5-enoside (**12**), respectively. Catalytic hydrogenation of these 5-enosides yielded preferentially the 6-deoxy-L-*gulo* derivative (**4**) from the D-*lyxo*-5-enoside (**2**) and the 6-deoxy-L-*talo* derivative (**14**) from the D-*ribo*-5-enoside (**12**). Zemplén deacylation followed by acid hydrolysis of the acylated glycosides afforded 6-deoxy-L-gulose and 6-deoxy-L-talose. The product ratios upon hydrogenation of the 5-enoside derivatives with several kinds of catalysts were measured by high-performance liquid chromatography and results are summarized in Tables I and II. The proton and carbon-13 nuclear magnetic resonance spectral data of the products are also discussed.

Keywords——exocyclic unsaturated sugar; methyl 6-deoxy-β-L-guloside; methyl 6-deoxy-β-L-taloside; 6-deoxy-L-gulose; 6-deoxy-L-talose; catalytic hydrogenation; stereoselectivity; HPLC analysis; ^{1}H-NMR; ^{13}C-NMR

Polyols in human physiological fluids and tissues have recently received attention, and the levels of the polyols have been shown to change in various diseases.[2)] Previously we reported the occurrence of four kinds of 6-deoxyhexitols in uremic urine. As the standard samples for the identification of these deoxyhexitols by gas chromatographic-mass spectrometric analysis, we required authentic 6-deoxy-L-gulose and 6-deoxy-L-talose, which can be easily derived to the corresponding alditols by borohydride reduction.

The chemical preparation of 6-deoxy-L-gulose was accomplished first by Müller and Reichstein beginning with L-xylose[3)] and recently by Ireland and Wilcox starting from D-glucose.[4)] 6-Deoxy-L-talose is an interesting sugar from the biological viewpoint. It was first isolated from the cardiac glycoside sarmentoside A.[5)] Later it was identified as a component of the glycolipids produced by *Mycobacterium avium*[6)] and *Mycobacterium marianum*,[7)] of "K" lipopolysaccharide antigen of *Pseudomonas pseudomallei*[8)] and of the cell walls of *Actinomyces bovis*.[9)] This sugar has been prepared chemically from L-fucoic acid,[5)] from L-fucose[10,11)] or recently from L-rhamnose.[12)]

To date, 6-deoxy-L-idose derivatives or 6-deoxy-L-galactose derivatives have been stereospecifically prepared by the catalytic hydrogenation of exocyclic pyranoid vinyl ethers obtained from α-D-*xylo*-hex-5-enoside derivatives[13)] or α-D-*arabino*-hex-5-eno-pyranoside derivatives.[14)] This method, namely the generation of a C-methyl group at C-5 with a change of chirality at C-5 *via* the 5-enopyranoside, has been adopted for the preparation of L-daunosamine[15)] and related compounds.[16)] In every case, the anomeric α-alkoxyl group in the 5-enoside seems to be responsible for the exclusive formation of the L-isomer in the catalytic hydrogenation.

In this work, we examined whether α-D-*lyxo*- and α-D-*ribo*-hex-5-enopyranoside de-

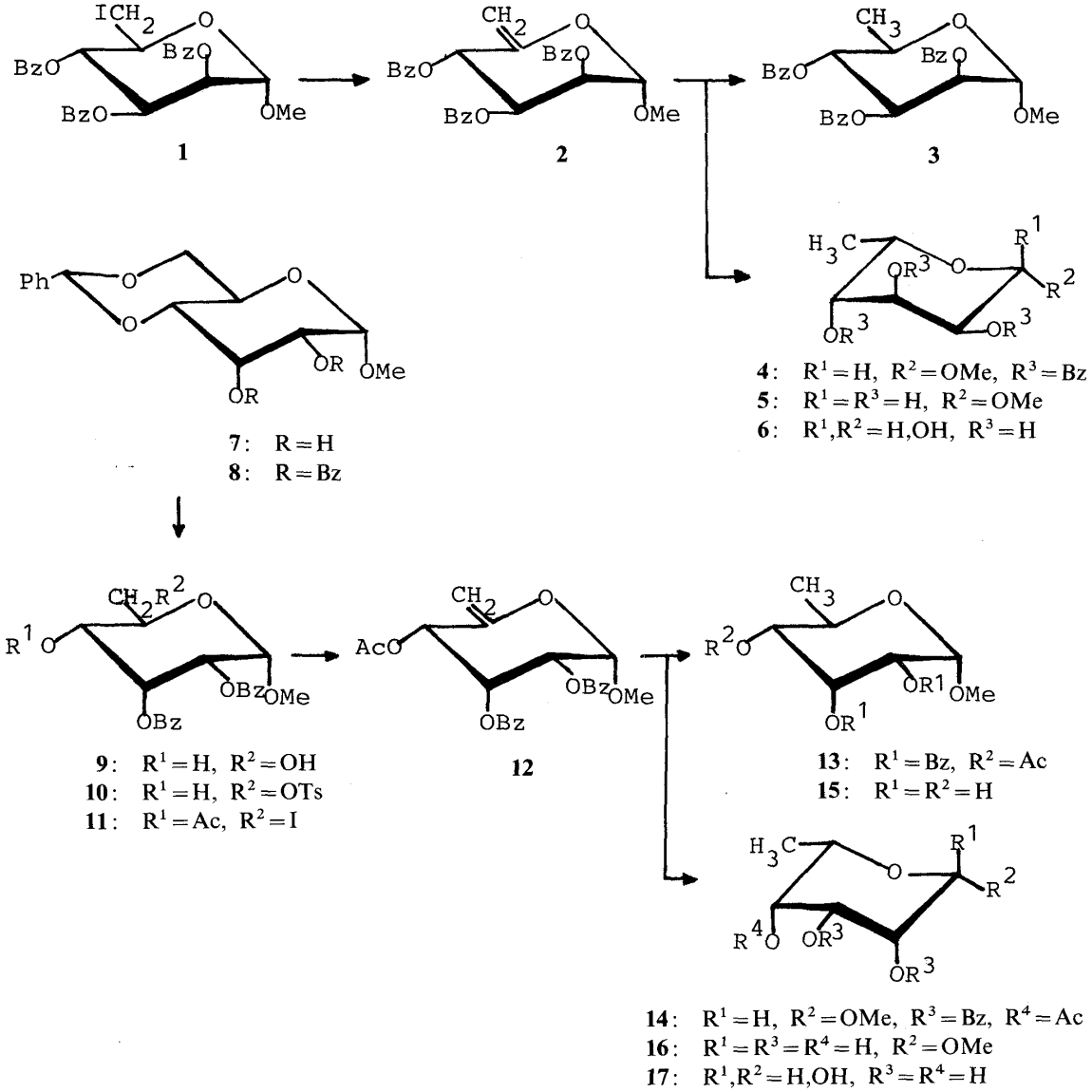

Chart 1

rivatives also show analogous behavior, yielding the corresponding 6-deoxy-L-*gulo*- and 6-deoxy-L-*talo*-pyranoside derivatives predominantly upon catalytic hydrogenation.

Preparation of Exocyclic Vinyl Hexopyranosides (2 and 12)

Treatment of methyl 2,3,4-tri-*O*-benzoyl-6-deoxy-6-iodo-α-D-mannopyranoside (**1**)[17] with anhydrous silver fluoride in pyridine for 6 h at room temperature afforded the α-D-*lyxo*-hex-5-enoside (**2**) in 84% yield. In the proton nuclear magnetic resonance (^{1}H-NMR) spectrum of **2**, the signals due to vinyl protons (H-6, H-6′) appeared as double doublets at 4.76 and 4.90 ppm with splittings of 2 Hz due to *geminal* couplings and 1.5 Hz due to long-range couplings between H-4 and the protons at C-6.

Similar treatment of methyl 4-*O*-acetyl-2,3-di-*O*-benzoyl-6-deoxy-6-iodo-α-D-allopyranoside (**11**) afforded the α-D-*ribo*-hex-5-enoside (**12**) in 61% yield. Compound **11** was prepared from methyl 4,6-*O*-benzylidene-α-D-allopyranoside (**7**) through 4 conventional reactions, benzoylation, debenzylidenation, monotosylation and finally substitution of the tosyloxy group with iodide in acetic anhydride.

TABLE I. Catalytic Hydrogenation of the Methyl α-D-*lyxo*-Hex-5-enopyranoside Derivative (**2**)

Entry	Catalyst	Solvent	Product ratio[a]		
			D-Manno[b] (**3**)	:	L-Gulo[c] (**4**)
1	PtO_2	MeOH	34	:	66
2	Pd	MeOH	22	:	78
3	Raney Ni	MeOH	18	:	82
4	Rh on Al_2O_3	MeOH	39	:	61

a) Calculated from the results of HPLC analyses. HPLC conditions: instrument, Shimadzu LC-4A; column, Shim-pack CLC-SIL [6.0 mm i.d. × 150 mm]; mobile phase, hexane–CH_2Cl_2–dioxane (80 : 10 : 10, v/v); flow rate, 1.0 ml/min; column temp., ambient; detection, SPD-2AS at 230 nm [× 1.28]. *b*) Methyl 2,3,4-tri-*O*-benzoyl-6-deoxy-α-D-mannopyranoside (**3**, retention time 7.9 min). *c*) Methyl 2,3,4-tri-*O*-benzoyl-6-deoxy-β-L-gulopyranoside (**4**, retention time 9.5 min).

TABLE II. Catalytic Hydrogenation of the Methyl α-D-*ribo*-Hex-5-enopyranoside Derivative (**12**)

Entry	Catalyst	Solvent	Product ratio[a]		
			D-Allo[b] (**13**)	:	L-Talo[c] (**14**)
1	PtO_2	MeOH	39	:	61
2	Pd	MeOH	12	:	88
3	Raney Ni	MeOH	13	:	87
4	Rh on Al_2O_3	MeOH	11	:	89

a) Calculated from the results of HPLC analyses. HPLC conditions: the same as those of Table I except the mobile phase. Mobile phase; hexane–CH_2Cl_2–dioxane (60 : 30 : 10, v/v). *b*) Methyl 4-*O*-acetyl-2,3-di-*O*-benzoyl-6-deoxy-α-D-allopyranoside (**13**, retention time 4.8 min). *c*) Methyl 4-*O*-acetyl-2,3-di-*O*-benzoyl-6-deoxy-β-L-talopyranoside (**14**, retention time 6.5 min).

Catalytic Hydrogenation of the 5-Enosides (2 and 12)

Standard samples were required for high-performance liquid chromatography (HPLC) analysis and ^{1}H-NMR data: methyl 2,3,4-tri-*O*-benzoyl-6-deoxy-α-D-mannopyranoside (**3**) was prepared from the 6-iodo derivative (**1**) according to the reported method,[17] and similar treatment of the 6-iodo-D-allo derivative (**11**) afforded methyl 4-*O*-acetyl-2,3-di-*O*-benzoyl-6-deoxy-α-D-allopyranoside (**13**).

Hydrogenation of the 5-enosides (**2** or **12**) was performed in methanol at room temperature under atmospheric pressure with various catalysts. In every case, the expected 6-deoxy-L-*gulo*- (**4**) or 6-deoxy-L-*talo* derivative (**14**) was obtained predominantly, irrespective of the catalyst used. The results are summarized in Tables I and II.

The structure of **4** was supported by the ^{1}H-NMR spectral data (see Table III); the derived first-order coupling constants ($J_{1,2}=8$, $J_{2,3}=3$, $J_{3,4}=4$, and $J_{4,5}=2$ Hz) were consistent with the L-*gulo* configuration and $^1C_4$ conformation. Compound **14** was confirmed to have the L-*talo* configuration by its ^{1}H-NMR pectral data.

Zemplén deacylation of the acylated 6-deoxy derivatives (**3**, **13** and **14**) afforded **5**, **15** and **16**, respectively. The carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectra of **5**, **15** and **16** in the Fourier transform mode with complete proton decoupling were measured in deuterium oxide at room temperature. In order to assign the signals of these compounds, the reported ^{13}C-NMR signal assignments for the carbons in the series of methyl hexopyranosides

TABLE III. ^{1}H-NMR Spectral Data for Methyl Hex-5-enopyranosides (**2** and **12**) and Methyl 6-Deoxyhexopyranoside Derivatives (**3**, **4**, **13** and **14**)

Compound	Chemical shifts[a] (δ in ppm) [coupling constants (Hz) in parentheses]									
	H-1 ($J_{1,2}$)	H-2 ($J_{2,3}$)	H-3 ($J_{3,4}$)	H-4 ($J_{4,5}$)	H-5 ($J_{5,6}$)	H-6, H-6′ ($J_{6,6'}$)	C–CH_3	OCH_3	Aryl	OAc
2	5.07 d (2)	5.78 dd (3)	5.92 dd (10)	6.36 m (1.5)[b]	—	4.76, 4.90 dd (2)		3.57 s	7.20—8.18 m	—
12	5.20 d (4)	5.48 dd (3)	5.90 dd (3)	5.60 dd (1)[b]	—	4.80, 4.94 dd (1)		3.57 s	7.20—8.18 m	2.07 s
3	4.91 d (2)	← 5.58—5.94[c] →			4.20 m (6)	—	1.39 d (9)	3.51 s	7.22—8.16 m	—
4	5.05 d (8)	3.33 dd (3)	5.90 dd (4)	5.38 dd (2)	4.47 oct (6)	—	1.37 d	3.58 s	7.24—8.30 m	—
13	5.08 d (4)	5.22 dd (3)	5.95 dd (3)	4.84 dd (8)	4.35 m (6)	—	1.23 d	3.50 s	7.20—8.24 m	1.99 s
14	4.66 d (2)	5.38[d] (2)	5.78 br s (2)	5.38[d] (2)	3.92 q (6)	—	1.38 d	3.56 s	7.20—8.26 m	2.07 s

a) Measured in $CDCl_3$ with TMS as an internal standard. *b*) Coupling constants of H-4 and the protons at C-6. *c*) Signals of H-2, H-3 and H-4 overlap each other. *d*) Signals of H-2 and H-4 overlap each other. Signal multiplicities: d, doublet; dd, double doublet; m, multiplet; oct, octet; q, quartet; s, singlet.

and their 6-deoxy analogues were compared (see Table IV). These data revealed some interesting general features. For example, there is no major difference between the chemical shifts at C-1, C-2 and C-3 of methyl hexopyranoside and those of the 6-deoxy analogues. Upon deoxygenation at C-6, an upfield shift of about 4 ppm at C-5 and a downfield shift at C-4 were observed.

Adopting the above empirical rule, the assignment of ^{13}C-NMR spectra of **5**, **15** and **16** were carried out as listed in Table IV. Dorman and Roberts pointed out that different values for the downfield shift at C-4 due to the deoxygenation of C-6 in the *manno*- and *galacto*-systems might result from the difference of configuration at C-4.[18] This explanation is supported by the fact that compounds having an equatorial hydroxyl group at C-4 (*gluco*-, *altro*- and *allo*-systems) showed a 5—6 ppm shift and those having an axial hydroxyl group at C-4 (*gulo*- and *talo*-systems) showed a 2—3 ppm shift.

Acid hydrolysis of **5** and **16** afforded free 6-deoxy-L-gulose and 6-deoxy-L-talose, respectively.

Experimental

Solutions were concentrated with a Büchi Rotavapor EL below 45 °C *in vacuo*. Melting points were determined with a Yanagimoto MP-S2 micro melting point apparatus, and are uncorrected. Optical rotations were measured with a Union Giken PM-201 automatic digital polarimeter in a 0.5 dm tube. ^{1}H- and ^{13}C-NMR spectra were recorded at 100 and 25 MHz, with JEOL JNM-MH-100 and -FX-100 spectrometers, respectively. Tetramethylsilane (TMS) was used as an internal standard. Chemical shifts are given in ppm from TMS. Infrared (IR) spectra were recorded with a JASCO IRA-102. HPLC was performed on a Shimadzu model LC-4A liquid chromatograph equipped with a Shimadzu variable-wavelength spectrophotometric detector (SPD-2AS) using a Shim-pack CLC-SIL column (6 mm i.d. × 150 mm). Thin layer chromatography (TLC) was performed on precoated plates of Silica gel 60 F_{254} 0.25 mm

TABLE IV. Comparison of ^{13}C-NMR Spectral Data of Several Methyl Hexopyranosides and the Corresponding 6-Deoxyhexopyranosides (δ ppm from External TMS in D_2O)

Compound	Carbon No.						
	C-1	C-2	C-3	C-4	C-5	C-6	OCH_3
Me α-D-Glc[a,j]	100.0	72.2	74.1	70.6	72.5	61.6	55.9
Me 6-deoxy-α-D-Glc[j]	100.3	72.6	73.9	76.2	68.7	17.6	56.2
Δ[b]	−0.3	−0.4	+0.2	−5.6	+3.8	+44.0	−0.3
Me α-D-Gal[c,j]	100.1	69.2	70.5	70.2	71.6	62.2	56.0
Me 6-deoxy-α-D-Gal[j]	100.5	69.0	70.6	72.9	67.5	16.5	56.3
Δ[b]	−0.4	+0.2	−0.1	−2.7	+4.1	+45.7	−0.3
Me α-D-Man[d,j]	101.9	71.2	71.8	68.0	73.7	62.1	55.9
Me 6-deoxy-α-D-Man[j]	101.9	71.0	71.3	73.1	69.4	17.7	55.8
Δ[b]	0.0	+0.2	+0.5	−5.1	+4.3	+44.4	+0.1
Me α-D-Alt[e,j]	101.1	70.0	70.0	64.8	70.0	61.3	55.4
Me 6-deoxy-α-D-Alt[j]	101.3	70.6	70.9	70.7	66.9	17.2	55.8
Δ[b]	−0.2	−0.6	−0.9	−5.9	+3.1	+44.1	−0.4
Me β-D-Glc[f,j]	104.0	74.1	76.8	70.6	76.8	61.8	58.1
Me 6-deoxy-β-D-Glc[j]	104.3	74.5	76.7	76.2	73.0	17.8	58.3
Δ[b]	−0.3	−0.4	+0.1	−5.6	+3.8	+44.0	−0.2
Me α-D-All[g,j]	100.1	68.3	72.1	68.0	67.3	61.7	56.3
Me 6-deoxy-α-D-All (**15**)	100.5	68.7	72.2	72.8	63.9	17.5	56.6
Δ[b]	−0.4	−0.4	−0.1	−4.8	+3.4	+44.2	−0.3
Me β-D-Gul[h,j]	102.6	69.1	72.3	70.5	74.9	62.1	58.1
Me 6-deoxy-β-L-Gul (**5**)	102.6	69.0	72.3	72.9	70.5	16.0	58.1
Δ[b]	0.0	+0.1	0.0	−2.4	+4.4	+46.1	0.0
β-D-Tal[i,j]	95.5	72.5[k]	69.6[k]	69.4	76.5	62.2	—
Me 6-deoxy-β-L-Tal (**16**)	102.6	72.6[k]	69.7[k]	71.6[k]	72.6[k]	16.6	58.0
Δ[b]	−7.1	−0.1	−0.1	−2.2	+3.9	+45.6	—

a) Methyl α-D-glucopyranoside. *b*) Δ: δ (Methyl hexopyranoside) − δ (methyl 6-deoxyhexopyranoside). *c*) Methyl α-D-galactopyranoside. *d*) Methyl α-D-mannopyranoside. *e*) Methyl α-D-altropyranoside. *f*) Methyl β-D-glucopyranoside. *g*) Methyl α-D-allopyranoside. *h*) Methyl β-D-gulopyranoside. *i*) β-D-Talopyranose. *j*) Data from literature: K. Bock and C. Pedersen, *Advan. Carbohydr. Chem. Biochem.*, **41**, 27 (1983). *k*) Assignments may be interchanged in each row.

thick (E. Merck). Detection was effected by ultraviolet (UV) irradiation at 254 nm and by the use of spray reagents (A), anisaldehyde–H_2SO_4–EtOH (1 : 1 : 18, v/v) at 125 °C[19]; (B), 1% $KMnO_4$ in 2% Na_2CO_3 solution. Column chromatography was performed on Silica Gel BW-820MH (70—230 mesh, Fuji-Davison Chem. Ltd., Kasugai, Japan).

Methyl 2,3,4-Tri-*O*-benzoyl-α-D-*lyxo*-hex-5-enopyranoside (2)——Dry silver fluoride (130 mg, 1.02 mmol, completely dried over H_2SO_4, beforehand) was added to a solution of methyl 2,3,4-tri-*O*-benzoyl-6-deoxy-6-iodo-α-D-mannopyranoside (**1**) (300 mg, 0.49 mmol, prepared from commercially available methyl α-D-mannopyranoside according to the reported procedure)[17] in dry pyridine (4 ml) containing a catalytic amount of 4-(dimethylamino)pyridine, and the suspension was stirred, in the dark at room temperature for 6 h. The mixture was diluted with ether (30 ml) and filtered, and the insoluble residue was washed with ether. Evaporation of the filtrate gave a syrup, which was codistilled several times with added toluene. The residue was chromatographed on a column of silica gel with benzene to give a pure product (**2**) as an amorphous powder (195 mg, 84%), $[\alpha]_D^{19}$ −160.9° (c=0.85, $CHCl_3$). IR (Nujol) cm^{-1}: 1730 (C=O, ester), 1660 (C=C), 1595 (C=C, aromatic). *Anal.* Calcd for $C_{28}H_{24}O_8$: C, 68.85; H, 4.95. Found: C, 68.48; H, 4.91.

Methyl 2,3,4-Tri-*O*-benzoyl-6-deoxy-α-D-mannopyranoside (3)——**1** (0.50 g, 0.81 mmol) was dissolved in MeOH (20 ml) containing pyridine (0.5 ml), and the mixture was shaken with H_2 in the presence of freshly prepared Raney Ni T-1 catalyst at room temperature under atmospheric pressure: the catalyst was prepared[20] from 2 g of alloy. After removal of the catalyst by filtration, the filtrate was concentrated to dryness. The residue was dissolved in $CHCl_3$ (30 ml), then the solution was washed with water, and dried ($MgSO_4$). The solvent was evaporated off to give a syrup, which was crystallized from MeOH. Recrystallization from MeOH gave pure **3** (0.25 g, 62.8%). mp 134—136 °C, $[\alpha]_D^{23}$ −166.2° (c=1.01, $CHCl_3$). [lit.[17] mp 132—133 °C, $[\alpha]_D^{20}$ −175.8° ($CHCl_3$)].

Catalytic Hydrogenation of Methyl *lyxo*- and *ribo*-Hex-5-enopyranoside Derivatives (2 and 12)——A catalyst was added to a solution of substrate (10 mg of **2** or **12**) in MeOH (5 ml): commercial Adam's catalyst having 1—3 mol of

H_2O (10 mg), freshly prepared[21] Pd black obtained by reduction of $PdCl_2$ (15 mg) in MeOH, Raney Ni catalyst activated[20] from alloy (500 mg), or commercial Rh on alumina (10 mg, Aldrich Chemical Company Inc.) was used. The mixture was hydrogenated at room temperature under the atmospheric pressure. The catalyst was removed by filtration and the solvent was evaporated off. The residue was dissolved in $CHCl_3$ and analyzed by HPLC. The results are summarized in Tables I and II.

Methyl 2,3,4-Tri-*O*-benzoyl-6-deoxy-β-L-gulopyranoside (4)——A solution of **2** (100 mg, 0.20 mmol) in MeOH (20 ml) was hydrogenated at room temperature under atmospheric pressure in the presence of Pd black, freshly prepared from $PdCl_2$ (100 mg). The catalyst was removed by filtration and the solvent was evaporated off. The residue was chromatographed on a column of silica gel with hexane–benzene (1 : 1, v/v). The earlier fractions yielded the D-*manno* derivative (**3**, 13 mg), and the later fractions gave the L-*gulo* derivative (**4**, 70 mg, 70%), which was crystallized from EtOH to give colorless prisms, mp 125—126 °C, $[\alpha]_D^{22}$ −33.0° (c=1.0, $CHCl_3$). ^{1}H-NMR: see Table III. *Anal.* Calcd for $C_{28}H_{26}O_8$: C, 68.56; H, 5.34. Found: C, 68.74; H, 5.33.

Methyl 6-Deoxy-β-L-gulopyranoside (5)——A solution of **4** (200 mg, 0.41 mmol) in MeOH (15 ml) was treated with 0.5 N methanolic sodium methoxide (0.5 ml). The mixture was stirred for 5 h at room temperature, and the progress of deacylation was monitored by TLC. After neutralization of the reaction mixture with dry Amberlite IR-120 (H^+) resin, the solvent was removed by evaporation to give a syrupy residue, which was chromatographed on a column of silica gel with $CHCl_3$–MeOH (10 : 1, v/v) to give a pure product **5** (65 mg, 89.5%) syrup, $[\alpha]_D^{19}$ +78.2° (c= 1.31, MeOH). ^{1}H-NMR (ppm in D_2O): 1.18 (3H, d, $J_{5,6}$=7 Hz, C_5-CH_3), 3.49 (3H, s, OCH_3), 4.54 (1H, d, $J_{1,2}$= 8 Hz, H-1) (*in* pyridine-d_5), 1.18 (3H, d, $J_{5,6}$=7 Hz, C_5-CH_3), 3.62 (3H, s, OCH_3), 5.13 (1H, d, $J_{1,2}$=8 Hz, H-1). ^{13}C-NMR: see Table IV.

6-Deoxy-L-gulose (6)——A solution of **5** (60 mg, 0.37 mmol) in 5% H_2SO_4 (6 ml) was heated at 95 °C for 3 h. The acid was neutralized with excess barium carbonate, and the mixture was filtered and concentrated *in vacuo* to give a thick syrup, which was chromatographed on a column of silica gel with $CHCl_3$–MeOH (10 : 1, v/v) to give pure **6** (46 mg, 83.2%) as a syrup, $[\alpha]_D^{20}$ +33.5° (c=0.87, H_2O), [lit.[3] $[\alpha]_D^{21}$ +40.8° (c=1.6, H_2O), lit.[4] $[\alpha]_D^{22}$ +40.3° (c=1.60, H_2O), *cf.* 6-deoxy-D-gulose[22] $[\alpha]_D^{20}$ −35.7° (H_2O)]. A portion of this product (30 mg) was converted to the 4-bromophenylhydrazone as described by Müller and Reichstein.[3] The hydrazone was recrystallized from EtOH: fine needles mp 136—137 °C. $[\alpha]_D^{20}$ +17.6° (c=0.96, EtOH), [lit.[3] mp 136 °C, lit.[23] mp 135—137 °C, $[\alpha]_D^{25}$ +13.2° (c=1.0, EtOH), lit.[4] mp 135—136 °C, $[\alpha]_D^{23}$ +14.5° (c=1.1, EtOH)].

Methyl 4,6-*O*-Benzylidene-α-D-allopyranoside (7)——Acetic anhydride (50 ml) was added to a solution of methyl 4,6-*O*-benzylidene-2-*O*-tosyl-α-D-glucopyranoside[24] (7 g, 27.7 mmol) in dimethyl sulfoxide (100 ml) and the mixture was stirred at room temperature for 15 h, then poured into ice-water (500 ml). The whole was stirred for 2 h. The crystals which separated were collected by filtration and washed thoroughly with water. The product was recrystallized from EtOH to give white crystals (5.95 g, 85.2%), mp 160—163 °C, $[\alpha]_D^{21}$ +46° (c=1.20, $CHCl_3$), [lit.[25] mp 165—167 °C, $[\alpha]_D^{25}$ +44.9° (DMF), lit.[26] mp 162—164 °C, $[\alpha]_D^{28}$ +45° (c=1.0, $CHCl_3$)]. According to the reported method,[26] this uloside (5.80 g) was converted to methyl 4,6-*O*-benzylidene-2-*O*-tosyl-α-D-allopyranoside (4.67 g, 76.8%). A suspension of this alloside (2.5 g, 5.73 mmol) in MeOH (125 ml) was treated with 2% sodium amalgam (30 g). The mixture was stirred at room temperature for 15 h, then filtered, and the residue was washed with hot MeOH (30 ml). The combined filtrate and washings were neutralized with AcOH in MeOH, then evaporated to dryness. The residue was purified by silica gel column chromatography with $CHCl_3$–MeOH (100 : 1 v/v, 300 ml) to obtain **7** (1.10 g, 67.9%), which was crystallized from AcOEt to give colorless needles, mp 62—63 °C, $[\alpha]_D^{25}$ +116° (c= 0.76, MeOH). [lit.[24] mp 175—177 °C, $[\alpha]_D$ +117° (DMF), lit.[27] mp 60 °C (dihydrate), $[\alpha]_D^{30}$ +110.0° (DMF), mp 148—149 °C (anhydrous), $[\alpha]_D^{28}$ +126.0° (DMF), lit.[28] mp 58—60 °C (dihydrate), mp 167—168 °C (anhydrous), $[\alpha]_D$ +128° (c=1, $CHCl_3$), lit.[29] mp 173—175 °C]. *Anal.* Calcd for $C_{14}H_{18}O_6 \cdot 1/2H_2O$: C, 57.73; H, 6.57. Found: C, 57.79; H, 6.49.

Methyl 2,3-Di-*O*-benzoyl-4,6-*O*-benzylidene-α-D-allopyranoside (8)——Benzoyl chloride (6 ml, 51.2 mmol) was added in portions to an ice cold solution of **7** (2.50 g, 8.84 mmol) in pyridine (25 ml). After being stirred for 30 min at 0—5 °C, the reaction mixture was stirred at room temperature overnight, then poured into ice-water (200 ml). The whole was further stirred. The aqueous phase was removed and the oily residue was washed with ice-water (100 ml × 2) and then crystallized from EtOH to obtain white crystals (3.55 g, 81.9%), mp 163—164 °C. Recrystallization from MeOH gave an analytical sample, mp 164—165 °C, $[\alpha]_D^{22}$ +53.6° (c=1.22, $CHCl_3$). *Anal.* Calcd for $C_{28}H_{26}O_8$: C, 68.56; H, 5.34. Found: C, 68.63; H, 5.29.

Methyl 2,3-Di-*O*-benzoyl-α-D-allopyranoside (9)——A suspension of **8** (3.0 g, 6.12 mmol) in MeOH (60 ml) was hydrogenated with Pd catalyst at room temperature under atmospheric pressure until absorption of H_2 ceased; the catalyst was freshly prepared[20] from $PdCl_2$ (1.50 g). After removal of the catalyst and the solvent, **9** was obtained as an amorphous power (2.51 g, 99%). To obtain an analytical sample, a part of the product was chromatographed on a column of silica gel with $CHCl_3$–MeOH (10 : 1, v/v). $[\alpha]_D^{22}$ +28.1° (c=0.61, $CHCl_3$). IR ($CHCl_3$) cm^{-1}: 3450 (br, OH), 1720 (C=O, ester), 1600 (C=C, aromatic). *Anal.* Calcd for $C_{21}H_{22}O_8$: C, 62.68; H, 5.51. Found: C, 62.83; H, 5.40.

Methyl 2,3-Di-*O*-benzoyl-6-*O*-tosyl-α-D-allopyranoside (10)——A solution of TsCl (0.90 g, 4.72 mmol) in $CHCl_3$ (5 ml) was added dropwise with stirring to an ice-cold solution of **9** (1.20 g, 2.90 mmol) in pyridine (12 ml). After being

stirred for 2 h, the mixture was poured into ice-water (50 ml), and the whole was stirred for 30 min, then partitioned between $CHCl_3$ and water. The aqueous layer was extracted with $CHCl_3$ (20 ml × 2) and the combined extracts were washed with water (20 ml), 10% HCl (30 ml × 2), satd. $NaHCO_3$ soln. (30 ml), and water (20 ml), then dried ($MgSO_4$) and evaporated to dryness. The residue was chromatographed on a column of silica gel with $CHCl_3$–ether–MeOH (400 : 10 : 1, v/v). From the earlier fractions, methyl 2,3-di-*O*-benzoyl-4,6-di-*O*-tosyl-α-D-allopyranoside, (80 mg, 3.9%), was isolated as an amorphous powder, $[\alpha]_D^{23}$ +79.1° (*c*=1.57, $CHCl_3$). *Anal.* Calcd for $C_{35}H_{34}O_{12}S_2$: C, 59.14; H, 4.82. Found: C, 59.16; H, 4.53. IR (KBr) cm^{-1}: 1725 (C=O, ester), 1600 (C=C, aromatic), 1190, 1175 (SO_2). ^{1}H-NMR ($CDCl_3$): 2.21, 2.23 (each 3H, s, $C_6H_4CH_3$ × 2), 3.40 (3H, s, OCH_3), 7.24—8.24 (18H, m, aromatic protons). The major product, compound **10**, was isolated from the slower-moving fractions (0.80 g, 49.7%), as an amorphous powder, $[\alpha]_D^{22}$ +28.1° (*c*=1.09, $CHCl_3$). *Anal.* Calcd for $C_{28}H_{28}O_{10}S$: C, 60.42; H, 5.07. Found: C, 59.97; H, 4.91. IR (KBr) cm^{-1}: 3500 (br, OH), 1725 (C=O, ester), 1600 (C=C, aromatic), 1190, 1175 (SO_2). ^{1}H-NMR ($CDCl_3$) δ: 2.36 (3H, s, $C_6H_4CH_3$), 3.44 (3H, s, OCH_3), 7.20—8.16 (14H, m, aromatic protons). From the subsequent fractions, the starting material (**9**, 0.47 g, 39.2%) was recovered.

Methyl 4-*O*-Acetyl-2,3-di-*O*-benzoyl-6-deoxy-6-iodo-α-D-allopyranoside (11)——A mixture of **10** (190 mg, 0.34 mmol), NaI (200 mg, 1.33 mmol) and Ac_2O (4 ml) was warmed on a water-bath (at 90—95 °C) for 3 h, then poured into ice-water (30 ml). The whole was stirred, neutralized with $NaHCO_3$, and extracted with $CHCl_3$ (20 ml × 2). The combined extracts were washed with 5% $Na_2S_2O_3$ and water, dried ($MgSO_4$) and evaporated to dryness. The residue was chromatographed on a column of silica gel with $CHCl_3$ to give the pure product (164 mg, 87%), as an amorphous powder, $[\alpha]_D^{22}$ +46.3° (*c*=1.31, $CHCl_3$). *Anal.* Calcd for $C_{23}H_{23}IO_8$: C, 49.84; H, 4.18. Found: C, 50.34; H, 4.35. IR (KBr) cm^{-1}: 1755, 1725 (C=O, ester), 1600 (C=C, aromatic). ^{1}H-NMR ($CDCl_3$) δ: 2.00 (3H, s, OAc), 3.60 (3H, s, OCH_3), 7.20—8.24 (10H, m, aromatic protons).

Methyl 4-*O*-Acetyl-2,3-di-*O*-benzoyl-α-D-*ribo*-hex-5-enopyranoside (12)——**11** (150 mg, 0.27 mmol) was treated as described for the conversion of **1** to **2** to give **12** (70 mg, 60.7%) as an amorphous powder, $[\alpha]_D^{21}$ +125.6° (*c*=0.61, $CHCl_3$), IR (KBr) cm^{-1}: 1750, 1720 (C=O, ester), 1665 (C=C), 1600 (C=C, aromatic), ^{1}H-NMR ($CDCl_3$) δ: 2.07 (3H, s, OAc), 3.57 (3H, s, OCH_3), 4.80, 4.94 (2H, d, $J_{6,6'}$=1 Hz, H-6, H-6'), 5.20 (1H, d, $J_{1,2}$=4 Hz, H-1), 5.48 (1H, dd, $J_{2,3}$=3 Hz, H-2), 5.60 (1H, dd, $J_{4,6}$=1 Hz, H-4), 5.90 (1H, dd, $J_{3,4}$=3 Hz, H-3), 7.20—8.18 (10H, m, aromatic protons). *Anal.* Calcd for $C_{23}H_{22}O_8$: C, 64.78; H, 5.20. Found: C, 64.47; H, 5.19.

Methyl 4-*O*-Acetyl-2,3-di-*O*-benzoyl-6-deoxy-α-D-allopyranoside (13)——**11** (110 mg, 0.20 mmol) was treated as described for the conversion of **1** to **3** to give **13** (72 mg, 85%) as a syrup, $[\alpha]_D^{17}$ +97.6° (*c*=0.59, $CHCl_3$). IR ($CHCl_3$) cm^{-1}: 1725 (C=O, ester), 1605 (C=C, aromatic), ^{1}H-NMR: see Table III. *Anal.* Calcd for $C_{23}H_{24}O_8 \cdot 1/2H_2O$: C, 63.15; H, 5.76. Found: C, 62.83; H, 5.44.

Methyl 4-*O*-Acetyl-2,3-di-*O*-benzoyl-6-deoxy-β-L-talopyranoside (14)——A solution of **12** (120 mg, 0.28 mmol) in MeOH (25 ml) was treated as described for the hydrogenation of **2** using Pd black as the catalyst. The products were separated by silica gel column chromatography with benzene–ether (20 : 1, v/v). The D-*allo* derivative (**13**, 10 mg). The L-*talo* derivative (**14**, 95 mg, 79.1%), as a syrup, $[\alpha]_D^{23}$ +125.6° (*c*=1.60, $CHCl_3$), IR ($CHCl_3$) cm^{-1}: 1725 (C=O, ester), 1600 (C=C, aromatic), ^{1}H-NMR: see Table III. *Anal.* Calcd for $C_{23}H_{24}O_8$: C, 64.47; H, 5.65. Found: C, 64.23; H, 5.61.

Methyl 6-Deoxy-α-D-allopyranoside (15)——Deacylation of **13** (63 mg, 0.147 mmol) as described for **4** afforded **15** (23 mg, 87.8%). ^{1}H-NMR (D_2O) δ: 1.23 (3H, d, $J_{5,6}$=7 Hz, C_5-CH_3), 3.36 (3H, s, OCH_3), 4.69 (1H, d, $J_{1,2}$=4 Hz, H-1). ^{13}C-NMR: see Table IV.

Methyl 6-Deoxy-β-L-talopyranoside (16)——Deacylation of **14** (100 mg, 0.256 mmol) as described for **4** afforded **16** (41 mg, 89.9%). Crystallization of the product from ether–hexane gave colorless prisms mp 105—106 °C, $[\alpha]_D^{18}$ +68.2° (*c*=0.47, MeOH), ^{1}H-NMR (D_2O) δ: 1.27 (3H, d, $J_{5,6}$=6 Hz, C_5-CH_3), 3.52 (3H, s, OCH_3), 4.44 (1H, s, H-1). ^{13}C-NMR: see Table IV. *Anal.* Calcd for $C_7H_{14}O_5$: C, 47.18; H, 7.92. Found: C, 47.33; H, 7.70.

6-Deoxy-L-talose (17)——Hydrolysis of **16** (40 mg, 0.22 mmol) as described for **5** afforded **17** (31 mg, 84.2%). Crystallization from EtOH gave colorless prisms, mp 126—128 °C. [lit.[5] mp 116—118 °C, lit.[11] mp 126—127 °C].

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References and Notes

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