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Branched-chain Sugars. XXIV. Synthesis of Methyl 6-Deoxy-3-*C*-methyl-β-D-gulopyranoside (Methyl β-Virenoside)[1]

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Methyl 6-deoxy-3-*C*-methyl-β-D-gulopyranoside (methyl β-virenoside) was prepared from D-galactose. An attempted synthesis of the virenoside by the inversion at *C*-4 of methyl 6-deoxy-3-*C*-methyl-α-D-allopyranoside was unsuccessful.

Virenose is a new naturally occuring branched-chain sugar found as a component of the antitumor antibiotic virenomycin produced by *Actiomyces virens* sp. nov.[2] Kulyaeva and her coworkers have reported the isolation of virenose as a methyl glycoside and established its absolute configuration as methyl 6-deoxy-3-*C*-methyl-β-D-gulopyranoside (**1**) from NMR, MS, and IR spectral data, and $[M]^{cupra\ A,B}$ rotational values.[3]

It is one of the most common branched-chain sugars, 6-deoxy-3-*C*-methylhexoses.[4] For the introduction of *C*-methyl branching, it is known that the reaction of methylmagnesium iodide and methyl 4,6-*O*-benzylidene-2-deoxy-α-D-*threo*-[5] and -α-D-*erythro*-hexopyranosid-3-uloses,[6] and methyl 4,6-*O*-benzylidene-α-D-*ribo*-hexopyranosid-3-ulose[7] gave the corresponding branched-chain sugars having the desired configuration at *C*-3 position. This paper describes the synthesis of **1** from methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-*xylo*-hexopyranosid-3-ulose obtained from D-galactose,[8] though another synthesis *via* the configurational inversion at *C*-4 of methyl 2,3-di-*O*-benzyl-6-deoxy-3-*C*-methyl-4-*O*-(methylsulfonyl)-α-D-allopyranoside (**6**) derived from D-glucose was unsuccessful.

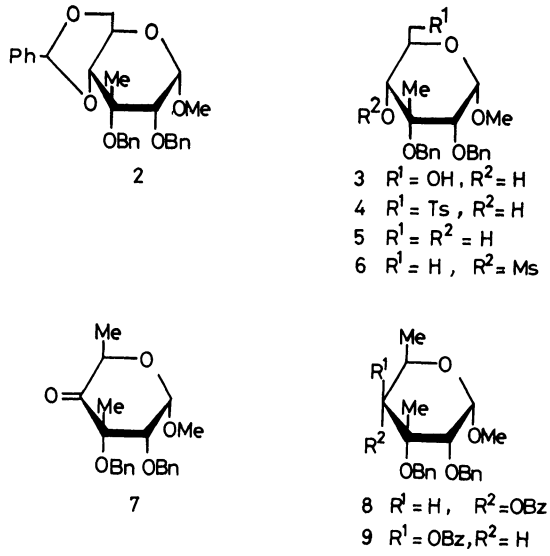

Fig. 1.

Results and Discussion

Methyl 4,6-*O*-benzylidene-3-*C*-methyl-α-D-allopyranoside[7] obtained from D-glucose through five steps conversions was converted into the corresponding 2,3-di-*O*-benzyl derivative (**2**) in 78% yield by treating with sodium hydride and benzyl bromide in dimethyl sulfoxide. The benzylidene group of **2** was removed by refluxing in 70% acetic acid to produce **3** in 78% yield. Monotosylation of **3** in pyridine gave the corresponding 6-*O*-tosylate (**4**) in 80% yield. Reduction of **4** in tetrahydrofuran with lithium aluminium hydride gave methyl 2,3-di-*O*-benzyl-6-deoxy-3-*C*-methyl-α-D-allopyranoside (**5**) in 65% yield.

For the inversion of the configuration at *C*-4 of **5**, oxidation-reduction method was tried at first. Oxidation of **5** with dimethyl sulfoxide and trifluoroacetic anhydride gave the corresponding 4-ulose (**7**) in 78% yield. However, reduction of **7** with sodium borohydride gave only **5**. Because the conformation of **7** is deduced to be *C*1, the above result is attributed to the steric hindrance of the axial benzyloxy group at *C*-3. As the second procedure, the S_N2 inversion at *C*-4 was tried. Usual mesylation of **5** gave the corresponding 4-*O*-mesylate (**6**) in 83% yield. Unfortunately, all attempts for the conversion of **6** into the 4-*O*-benzoyl derivative (**9**) of D-*gulo* configuration by treatment with sodium benzoate were failed. Treatment of **6** in hexamethylphosphoric triamide at 180 °C for 24 h gave an ester exchange product, methyl 4-*O*-benzoyl-2,3-di-*O*-benzyl-3-*C*-methyl-α-D-allopyranoside (**8**) in 30% yield, which is identical with that obtained by benzoylation of **5**.

On the other hand, oxidation of methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-galactopyranoside[9] with dimethyl sulfoxide and trifluoroacetic anhydride in dichloromethane gave the corresponding 3-ulose (**10**) in 80% yield. Reaction of **10** in benzene with methylmagnesium iodide gave predominantly one compound (**11**), which was separated by column chromatography from a trace of the corresponding 3-epimer in 85% yield. This result indicates that the Grignard reagent attacks the carbonyl function from the equatorial side as was in the case of the corresponding 2-deoxy-3-ulose.[5] Treatment of **11** with acetone in the presence of anhydrous copper-(II) sulfate and catalytic amount of sulfuric acid gave the 2,3-*O*-isopropylidene derivative (**12**) in high yield, indicating the presence of *cis*-hydroxyl groups in **11**.

Reaction of **11** with *N*-bromosuccinimide in carbon tetrachloride in the presence of excess barium carbonate afforded methyl 4-*O*-benzoyl-6-bromo-6-deoxy-3-*C*-methyl-α-D-gulopyranoside (**13**) in 75% yield. The reduction of **13** in benzene with tributylstannane in the presence of α,α'-azobisisobutyronitrile gave the corresponding 6-deoxy derivative (**14**) in 70% yield. Base-catalyzed removal of the 4-*O*-benzoyl group of **14** gave

Table 1. Physical constants of **1** and **16**

	Mp/°C	$[\alpha]_D$/° (in $CHCl_3$)	^1H NMR parameters					
			H-1 ($J_{1,2}$)	H-2	H-4 ($J_{4,5}$)	H-5 ($J_{5,6}$)	H-6	Other protons
1	134—135	−30	4.41d (8.0)	3.39d	3.26d (1.2)	4.22q (6.5)	1.28d	1.40(CMe), 3.54(OMe), 2.52(OH)
Reported **1**[a)]	131	−39	4.31d (7.5)	3.31d	3.16d (1.2)	4.12q (6.0)	1.24d	1.39(CMe)
16	140—141	−24	4.58d (8.0)	4.81d	4.80d (1.2)	4.23q (6.5)	1.14d	1.12(CMe), 3.54(OMe), 2.14(2×OAc)
Reported **16**	140	−27						

a) The NMR spectrum was recorded with a Hitachi R-20A (60 MHz) spectrometer.

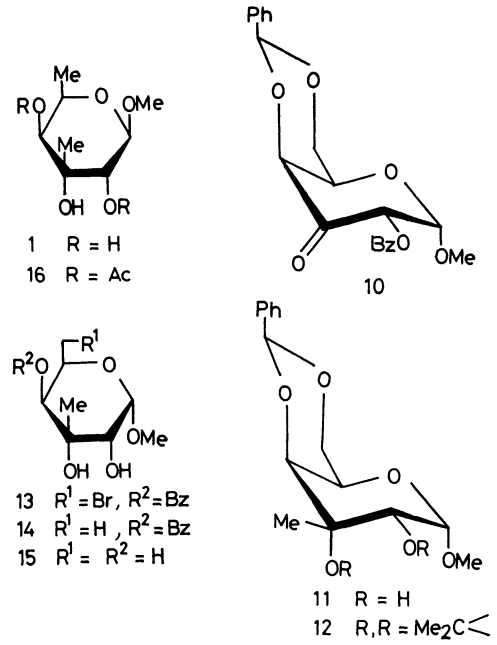

Fig. 2.

the de-*O*-benzoylated product (**15**) in 65% yield. Anomerization of **15** in methanol with cationic ion-exchanger IR-120 by refluxing for 20 h gave crystalline methyl β-D-virenoside (**1**) in 80% yield. The physical constants of **1** are in good agreement with those reported[2)] (Table 1). The usual acetylation of **1** gave the corresponding 2,4-diacetate (**16**).

Experimental

All the melting points are uncorrected. The solutions were evaporated under reduced pressure at a bath temperature not exceeding 45 °C. Specific rotations were measured in a 0.5-dm tube with a Carl Zeiss LEP-Al polarimeter by the use of chloroform as the solvent. The IR spectra were recorded with a Hitachi Model EPI-G2 spectrometer. The NMR spectra were taken with a JEOL PS-100 spectrometer using tetramethylsilane as an internal standard in deuteriochloroform unless otherwise stated. Chemical shifts and coupling constants were recorded in δ and Hz units and IR frequencies in cm^{-1}.

Methyl 2,3-Di-O-benzyl-4,6-O-benzylidene-3-C-methyl-α-D-allopyranoside (2). To a suspension of sodium hydride (0.5 g, 20.8 mmol) and methyl 4,6-*O*-benzylidene-3-*C*-methyl-α-D-allopyranoside (2 g, 6.75 mmol) in dry dimethyl sulfoxide (15 ml) was added gradually benzyl chloride (1.7 g, 13.4 mmol). The mixture was then heated for 1 h at 70 °C on a water-bath, poured into ice water, and then extracted with chloroform. The extract was washed with water, dried with anhydrous magnesium sulfate, and evaporated to give a syrup that was purified on a preparative TLC (benzene–ethyl acetate 10 : 1) to give a colorless syrup (2.5 g, 78%). $[\alpha]_D^{13}$ +58° (*c* 0.4), NMR: 7.1—7.3 (3×Ph; m), 5.40 (PhCH; s), 4.96 and 4.69 (2×$PhCH_2$; each s), 4.72 and 3.32 (H-1 and H-2; each d, $J_{1,2}$=4.0), 4.60—4.18 (H-6 and H-6′; m), 3.60 (H-5; m), 3.30 (H-4; d, $J_{4,5}$=8.0), 3.42 (OMe), 1.46 (CMe). Found: C, 72.96; H, 6.68%. Calcd for $C_{29}H_{32}O_6$: C, 73.10; H, 6.72%.

Methyl 2,3-Di-O-benzyl-3-C-methyl-α-D-allopyranoside (3). A solution of **2** (1.2 g, 2.5 mmol) in 70% acetic acid (4 ml) was kept for 10 h at room temperature, evaporated, and the residue was purified on a preparative TLC (toluene–chloroform–methanol 4 : 4 : 1) to give a syrup in 80% (0.78 g) yield. $[\alpha]_D^{13}$ +41.4° (*c* 0.6); NMR: 7.32 (Ph; s), 5.20—4.48 (2×$PhCH_2$; m, J=10.5), 4.77 and 3.35 (H-1 and H-2; each d, $J_{1,2}$=4.0), 3.30 (H-4; d, $J_{4,5}$=10.0), 3.7—3.9 (H-5, H-6, and H-6′; m), 3.41 (OMe), 2.2 and 2.45 (2×OH; each broad s), 1.48 (CMe). Found: C, 68.23; H, 7.31%. Calcd for $C_{22}H_{28}O_6$: C, 68.04; H, 7.21%.

Methyl 2,3-Di-O-benzyl-3-C-methyl-6-O-(p-tolysulfonyl)-α-D-allopyranoside (4). Reaction of **3** (5 g, 12.8 mmol) in dry pyridine (20 ml) with *p*-toluenesulfonyl chloride (2.7 g, 14.2 mmol) at room temperature overnight and usual work-up of the reaction mixture gave **4** (5.2 g, 75%) as a syrup. $[\alpha]_D^{13}$ +41° (*c* 1.5); NMR: 7.32 (Ph; m), 5.16—4.44 (2×$PhCH_2$; m. J=10.5), 4.73 and 3.32 (H-1 and H-2; each d, $J_{1,2}$=4.0), 3.33 (H-4; d, $J_{4,5}$=10.0), 4.0—4.4 (H-5, H-6, and H-6′; m), 3.38 (OMe), 2.41 (PhMe), 1.46 (CMe). Found: C, 64.32; H, 6.34%. Calcd for $C_{29}H_{34}O_8S$: C, 64.20; H, 6.27%.

Methyl 2,3-Di-O-benzyl-6-deoxy-3-C-methyl-α-D-allopyranoside (5). Lithium aluminium hydride (1.0 g, 32.5 mmol) was gradually added to a solution of **4** (4 g, 7.4 mmol) in dry tetrahydrofuran (100 ml), and the mixture was boiled for 6 h. A small amount of ethyl acetate and water were successively added to the reaction mixture, and the precipitate formed was filtered and washed with ether. The filtrate and washings were evaporated to a syrup, which was purified on a preparative TLC (benzene–ethyl acetate 10 : 1) to give syrupy **5** (1.78 g, 65%). $[\alpha]_D^{12}$ +43.6° (*c* 1.0); NMR: 7.32 (Ph; m), 5.10—4.80 ($PhCH_2$×2; m, J=10.5), 4.71 and 3.34 (H-1 and H-2; each d, $J_{1,2}$=4.0), 2.93 (H-4; dd, $J_{4,5}$=10.0, $J_{4,OH}$=12.0), 3.40 (OMe), 1.44 (CMe), 2.35 (OH; d), 1.20 (H-6; d). Found: C, 70.55; H, 7.32%. Calcd for $C_{22}H_{28}O_5$: C, 70.96; H, 7.52%.

Methyl 2,3-Di-O-benzyl-6-deoxy-3-C-methyl-4-O-(methylsulfo-

nyl)-α-D-allopyranoside (6). Methanesulfonyl chloride (0.6 g, 5.2 mmol) was added to a solution of **5** (1 g, 2.7 mmol) in dry pyridine (5 ml) cooled in an ice–water bath. The resulting solution was kept for 12 h at room temperature, poured into water, and then extracted with chloroform. The extracts were washed with saturated aqueous sodium hydrogencarbonate and water. Evaporation of the dried extract gave a syrupy **6** (1 g, 83%), $[\alpha]_D^{13}$ +79.5° (*c* 0.9); NMR: 7.36 (Ph; s), 5.10—4.56 ($PhCH_2\times2$; m, J=10.5), 4.68 and 3.31 (H-1 and H-2; each d, $J_{1,2}$=4.0), 4.19 (H-4; d, $J_{4,5}$=10.0), 4.45 (H-5; oct, $J_{5,6}$=6.0), 3.40 (OMe), 2.99 (Ms), 1.48 (CMe), 1.25 (H-6; d). Found: C, 61.62; H, 6.61%. Calcd for $C_{23}H_{30}O_7S$: C, 61.33; H, 6.66%.

Methyl 4-O-Benzoyl-2,3-di-O-benzyl-6-deoxy-3-C-methyl-α-D-allopyranoside (8). *i)* : A solution of **5** (0.6 g, 1.32 mmol) and sodium benzoate (0.38 g, 2.6 mmol) in hexamethylphosphoric triamide (6 ml) was heated at 180 °C for 24 h, filtered, and then poured into water. The resulting solution was extracted with chloroform. The extract was washed with water and evaporated. The residue was extracted with ether again, and the usual work-up of the extract gave a syrup (0.42 g) which was purified on a preparative TLC (toluene–ethyl acetate 16 : 1) to give **8** (0.18 g, 30%) as a syrup. $[\alpha]_D^{14}$ +26.9° (*c* 0.5); NMR: 8.10—7.8 and 7.50—7.30 ($2\times$Ph; m), 5.52 (H-5; m, $J_{5,6}$=6.0), 4.4—4.8 ($2\times PhCH_2$; m), 4.90 and 3.68 (H-1 and H-2; each d, $J_{1,2}$=4.0), 3.87 (H-4; d, $J_{4,5}$=6.0), 3.48 (OMe), 1.52 (CMe), 1.47 (H-6; d). Found: C, 73.25; H, 6.78%. Calcd for $C_{29}H_{32}O_6$: C, 73.11; H, 6.72%.

ii) : To a solution of **5** (0.1 g, 0.27 mmol) in dry pyridine (5 ml) was added benzoyl chloride (0.1 g, 0.7 mmol), and the usual work-up after 10 h gave **8** (0.9 g, 71%) identical with that obtained above.

Methyl 2,3-Di-O-benzyl-6-deoxy-3-C-methyl-α-D-ribo-hexopyranosid-4-ulose (7). To a solution of dry dimethyl sulfoxide (0.5 g, 6.4 mmol) and dry dichloromethane (2 ml) was added successively trifluoroacetic anhydride (0.54 g, 4.0 mmol) in dichloromethane (2 ml) with stirring during 10 min at −78 °C, and then a solution of **6** (0.5 g, 1.34 mmol) in dichloromethane (2 ml). The reaction mixture was stirred at −78 °C for 20 min, neutralized with triethylamine (4 ml), and extracted with chlorofolm. The extract was washed with water, and then evaporate to give a syrup which was chromatographed on a silica-gel column (toluene–ethyl acetate 16 : 1) to afford **7** (0.38 g, 78%). $[\alpha]_D^{14}$ +101° (*c* 0.4). IR: 1740 (C=O); NMR: 7.4—7.2 ($2\times$Ph; m), 4.9—4.5 ($PhCH_2$; m), 4.80 and 3.59 (H-1 and H-2; each d, $J_{1,2}$=4.0), 4.50 (H-5; q, $J_{5,6}$=6.0), 1.20 (H-6; d), 3.51 (OMe), 1.51 (CMe). Found: C, 71.77; H, 7.21%. Calcd for $C_{22}H_{26}O_5$: C, 71.35; H, 7.02%.

Methyl 4,6-O-Benzylidene-2-O-benzoyl-α-D-xylo-hexopyranosid-3-ulose (10). A similar oxidation of **7** to that of **5** gave the corresponding 3-ulose (**10**) in 80% yield. $[\alpha]_D^{27}$ +142° (*c* 1.8); IR: 1730 (C=O); NMR 7.8—8.2 and 7.2—7.6 ($2\times$Ph; m), 5.59 (PhCH), 6.1 and 5.36 (H-1 and H-2; each d, $J_{1,2}$=3.8), 4.54 (H-4; d, $J_{4,5}$=1.5), 3.97 (H-5; m), 4.15 (H-6′; dd, $J_{5,6}$=2.0), 4.42 (H-6; dd, $J_{6,6'}$=13, $J_{5,6}$=1.5), 3.48 (OMe). Found: C, 65.65; H, 5.42%. Calcd for $C_{21}H_{20}O_7$: C, 65.62; H, 5.21%.

Methyl 4,6-O-Benzylidene-3-C-methyl-α-D-gulopyranoside (11). To a suspension of magnesium turning (4.5 g, 185 mmol) in dry ether (150 ml) was added methyl iodide (25 g, 176 mmol) dropwise with stirring at room temperature. After 20 min, **10** (15 g, 39 mmol) was added to the Grignard solution with the aid of a small amount of benzene. After stirring for 6 h, the reaction mixture was worked up in the usual way to give a syrupy **11** in 85% (10.1 g) yields. $[\alpha]_D^{28}$ +102° (*c* 1.0); NMR: 7.2—7.52 (Ph; m), 5.50 (PhCH), 4.86 (H-1; d, $J_{1,2}$=3.8), 3.78 (H-2; dd, $J_{2,OH}$=12.0), 3.77 (H-4; s), 3.90 (H-5; broad s), 4.30 (H-6; dd, $J_{6,6'}$=13, $J_{5,6}$=2.0), 4.04 (H-6′; dd, $J_{5,6'}$=2.0), 3.3 (3-OH), 3.46 (OMe), 2.64 (2-OH; d), 1.35 (CMe). Found: C, 60.75; H, 6.64%. Calcd for $C_{15}H_{20}O_6$: C, 60.81; H, 6.76%.

Methyl 4,6-O-Benzylidene-3-C-methyl-2,3-O-isopropylidene-α-D-gulopyranoside (12). A suspension of **11** (0.38 g, 1.28 mmol) and copper(II) sulfate (0.4 g, 2.5 mmol) in dry acetone (2 ml) containing catalytic amount of sulfuric acid was stirred for 12 h, filtered, and then evaporated to dryness. The residue was extracted with chloroform, and the usual work-up of the extract gave a syrup which was purified on a TLC (benzene–acetone 5 : 1) to give pure **12** as a syrup (0.35 g, 81%). $[\alpha]_D^{26}$ +8.6° (*c* 0.6); NMR: 7.5—7.2 (Ph; m), 5.50 (PhCH), 5.18 and 3.71 (H-1 and H-2; each d, $J_{1,2}$=1.2), 4.18 (H-4; s), 4.0 (H-5; m), 4.34 (H-6; dd, $J_{6,6'}$=12.2, $J_{5,6}$=2.0), 3.92 (H-6′; dd, $J_{5,6'}$=2.0), 3.62 (OMe), 1.46, 1.50 and 1.52 ($3\times$CMe; each s). Found: C, 64.31; H, 7.33%. Calcd for $C_{18}H_{24}O_6$: C, 64.28; H, 7.14%.

Methyl 4-O-Benzoyl-6-bromo-6-deoxy-3-C-methyl-α-D-gulopyranoside (13). A suspension of **11** (8 g, 0.028 mol), *N*-bromosuccinimide (8.96 g, 0.05 mol), and barium carbonate (8.8 g, 0.04 mol) in dry carbon tetrachloride (150 ml) was boiled for 7 h, filtered, and the filtrate was worked up in the usual way to give **13** as a syrup in 75% (8.5 g) yield. $[\alpha]_D^{27}$ +120.7° (*c* 1.8); NMR: 7.9—8.1 and 7.3—7.5 (PhCO; m), 4.92 and 3.79 (H-1 and H-2; each d, $J_{1,2}$=3.8), 5.26 (H-4; s), 4.46 (H-5; dd, $J_{5,6'}$=8.0, $J_{5,6}$=4.0), 3.44 (H-6′; dd, $J_{6,6'}$=11.0), 3.26 (H-6; dd), 3.54 (OMe), 1.26 (CMe). Found: C, 48.31; H, 5.20%. Calcd for $C_{15}H_{19}O_6Br$: C, 48.00; H, 5.06%.

Methyl 4-O-Benzoyl-6-deoxy-3-C-methyl-α-D-gulopyranoside (14). To a solution of **13** (5 g, 0.013 mol) in anhydrous benzene (100 ml) was added tributylstannane (7.5 g, 0.025 mol) and catalytic amount of α,α′-azobisisobutyronitrile. The mixture was refluxed for 15 h, concentrated and the tin compound in the residue was removed on a silica gel column using hexane as the eluent. Thereafter, the elution with benzene–acetone (10 : 1) gave syrupy **14** in 70% (2.7 g) yield, which was crystallized from ethyl acetate. Mp 133—134 °C, $[\alpha]_D^{28}$ +142° (*c* 1.0); NMR: 8.0—8.16 and 7.30—7.60 (PhCO; m), 4.87 (H-1: d, $J_{1,2}$=4.0), 3.78 (H-2; dd, $J_{2,OH}$=12.0), 5.12 (H-4; s), 4.41 (H-5; q, $J_{5,6}$=6.0), 3.84 (OH-3; s), 3.52 (OMe), 2.40 (OH-2; d), 1.25 (CMe), 1.17 (H-6; d). Found: C, 60.64; H, 6.89%. Calcd for $C_{15}H_{20}O_6$: C, 60.81; H, 6.76%.

Methyl 6-Deoxy-3-C-methyl-α-D-gluopyranoside (15). A solution of **14** (1.5 g, 5 mmol) and sodium (0.4 g, 17 mmol) in dry methanol (60 ml) was refluxed for 4 h, and concentrated to dryness. The residue was extracted several times with dichloromethane, and the usual work-up of the extract gave **15** as a syrup in 65% yield. $[\alpha]_D^{27}$ +123° (*c* 0.3); NMR (CD_3OD): 4.79 and 3.58 (H-1 and H-2; each d, $J_{1,2}$=4.0), 4.25 (H-5; q, $J_{5,6}$=6.0), 3.13 (H-4; s), 3.48 (OMe), 1.26 (CMe), 1.17 (H-6; d). Found: C, 49.85; H, 7.29%. Calcd for $C_8H_{16}O_5$: C, 49.99; H, 8.39%.

Methyl 6-Deoxy-3-C-methyl-β-D-gulopyranoside (Methyl β-D-Virenoside) (1). A suspension of **15** (0.3 g, 1.6 mmol) and cationic resin (IR-120, 1.5 g) in dry methanol (40 ml) was refluxed for 24 h. The anomerization could be monitored by TLC. The reaction mixture was filtered, and the filtrate was evaporated. The residual syrup was purified on a preparative TLC (chloroform–methanol 4 : 1) to give **1** in 80% (0.24 g) yield, which was crystallized from hexane–chloroform. Found: C, 49.74; H, 8.24%. Calcd for $C_8H_{16}O_5$: C, 49.99; H, 8.39%.

Methyl 2,4-Di-O-acetyl-6-deoxy-3-C-methyl-β-D-gulopyranoside

(16). Acetylation of **1** (30 mg, 0.16 mmol) with acetic anhydride in pyridine for 24 h at room temperature, and the usual work-up of the mixture and purification of the product by a preparative TLC (benzene–aceton 5 : 1) gave **16** in 82% (25 mg) yield, which was recrystallized from methanol. Found: C, 52.27; H, 7.34%. Calcd for $C_{12}H_{20}O_7$: C, 52.16; H, 7.30%.

References

1) Part XXIII: M. Matsuzawa, K. Sato, T. Yasumori, and J. Yoshimura, submitted to this Bulletin.

2) M. G. Brazhnikova, M. K. Kudinova, V. V. Kulyaeva, N. P. Potapova, and V. I. Ponomalenko, *Antibiotiki*, **11**, 967 (1977).

3) V. V. Kulyaeva, M. K. Kudinova, N. P. Potapova, L. M. Rubasheva, M. G. Brazhnikova, B. V. Rosynoi, and A. R. Bekker, *Bioorg. Khim.*, **4**, 1087 (1978).

4) H. Grisebach and R. Schmid, *Angew. Chem.*, **84**, 192 (1972).

5) G. B. Howarth, W. A. Szarek, and J. K. N. Jones, *Carbohydr. Res.*, **7**, 284 (1968).

6) B. Flaherty, S. Nahar, W. G. Overrend and N. R. Williams, *J. Chem. Soc., Perkin Trans. 1*, **1973**, 632.

7) F. A. Carey and K. O. Hodgson, *Carbohydr. Res.*, **12**, 463 (1970).

8) J. Yoshimura, N. Hong, and K. Sato, *Chem. Lett.*, **1980**, 1131.

9) W. Szeja, *Synthesis*, **1979**, 821.