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Syntheses of 3-Deoxy-3-*C*-methyl-3-nitro-D- and L-glucosides and Their Denitrohydrogenation with Tributyltin Hydride

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Cyclization, with nitroethane in the presence of sodium methoxide, of the dialdehyde produced by periodate oxidation of methyl β-D-glucopyranoside and acetylation led to methyl 2,4,6-tri-*O*-acetyl-3-*C*-methyl-3-nitro-β-D- and -α-L-glucopyranoside (**1**, 12% and **2**, 8.8%). In the case of methyl α-D-glucopyranoside, products **3** (8.6%) and **4** (8.0%) were antipodes of **1** and **2**, respectively. Denitrohydrogenation of **1** or **3** with tributyltin hydride in toluene led to 3-deoxy-3-*C*-methyl-β-D-pyranosides (gluco, **5**, 61% and allo, **6**, 22%) or L-pyranosides (gluco, **9**, 65% and allo, **10**, 19%), respectively. This sequence of the reaction was a novel method for the syntheses of 3-deoxy-3-*C*-methyl-L-glucose and -L-allose. Denitrohydrogenation of **2** or **4** led to a mixture of 3-deoxy-3-*C*-methyl-α-L-pyranosides (allo, **7**, 39% and gluco, **8**, 41%) or mixture of 3-deoxy-3-*C*-methyl-α-D-pyranosides (allo, **11**, 38% and gluco, **12**, 41%), respectively. Methyl 2-*O*-acetyl-4,6-*O*-benzylidene-3-deoxy-3-nitro-β-D-glucopyranoside was denitrohydrogenated to the corresponding 3-deoxy sugar (**14**) in 68% yield.

Deoxy sugars are important constituents of some natural products, especially of antibiotics. The deoxy sugars may be prepared by the reduction of oxiranes with lithium aluminium hydride.[1] The most direct methods for preparing monodeoxy sugars are by homolytic replacement of a good leaving group modified from a hydroxyl group. Thiocarbonates,[2] *O*-alkyl thiobenzoates,[3] *O*-alkyl *S*-methyl dithiocarbonates,[3] [alkoxy(thiocarbonyl)]imidazolides,[3,4] dimethyl thiocarbamates,[5] trifluoromethanesulfonates[6] and thionocarbonates[7] were deoxygenated.

3-Deoxy-3-*C*-methylhexopyranosides were synthesized from 2,3-anhydro sugars and methyllithium[8] or methylmagnesium chloride,[9,10] from 3-oxo sugars by Wittig reaction and the following reduction,[11] from 3-deoxy-3-nitro-3-*C*-methyl sugar by electrochemical reduction,[12] and from 3-*O*-acetyl-3-*C*-methyl sugar by photoreduction.[13]

An efficient method became available for replacing the nitro group of secondary or tertiary nitro compounds by hydrogen using tributyltin hydride in refluxing benzene or toluene in the presence of azobisisobutyronitrile.[14–16] The reaction proceeds via free radical chain mechanism. The reduction was selective without affecting other functional groups such as chloro, cyano, alkoxycarbonyl, carbonyl, sulfinyl, sulfonyl, and carbon–carbon double bond.

Cyclization, with nitroethane or nitromethane in the presence of sodium methoxide, of the dialdehyde produced by periodate cleavage of methyl α- or β-D-glucopyranoside, led to 3-deoxy-3-nitro sugars.[17–20] In this paper the authors wish to report the synthesis of 3-deoxy-3-*C*-methyl-3-nitro-D- and -L-glucopyranosides and their denitrohydrogenation with tributyltin hydride.

Results and Discussion

Preparation of Nitro Sugars. Baer obtained crystalline mixture of methyl 3-deoxy-3-*C*-methyl-3-nitrohexopyranosides in 18—20% yield[17] from the dialdehyde, prepared by periodate oxidation of methyl α-D-glucopyranoside, and nitroethane in methanol in the presence of sodium methoxide. Catalytic hydrogenation of the product afforded two stereoisomeric amino glycosides, which were separated, acetylated, and hydrolysed to a pair of enantiomers of reducing amino sugars. The acetylated products were reported to be β-L-gluco (or allo) and α-D-gluco (or allo) derivatives. When a sequence of the above reaction was performed from methyl β-D-glucopyranoside, a set of nitrogeneous glycosides were obtained as the antipodes of the products from methyl α-D-glucopyranoside, having α-L-gluco (or allo) and β-D-gluco (or allo) configurations.[17]

The author acetylated crystalline cyclized products from the dialdehyde, prepared by periodate cleavage of methyl β-D-glucopyranoside, and nitroethane. The acetylated products were separated with a column of silica gel (benzene–ethyl acatate 4:1) to crystals **1** (12%) and a sirup **2** (8.8%) which were both levorotatory.

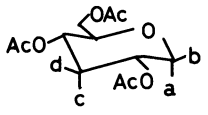
In ^{1}H NMR spectrum of **1** in $CDCl_3$, H-1, H-2, and H-4 appeared as doublets with $J_{1,2}$=7.9 Hz and $J_{4,5}$=10.1 Hz, indicating that these hydrogens were axial. Irradiation of the C–CH_3 induced nuclear Overhauser effect (NOE) to H-1 and H-5. Therefore, the C–CH_3 was axial. ^{13}C NMR spectrum showed C-1 at δ 100.5 and O–CH_3 at δ 57.0, indicating the presence of equatorial OCH_3.[21] Taking into account that **1** was levorotatory, **1** was methyl 2,4,6-tri-*O*-acetyl-3-deoxy-3-*C*-methyl-3-nitro-β-D-glucopyranoside.

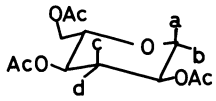
^{1}H NMR spectrum of **2** in $CDCl_3$ showed C–CH_3 at δ 1.89. Irradiation of the C–CH_3 induced NOE to H-5 but not to H-1. Thus the C–CH_3 and O–CH_3 were axial and H-1 was equatorial. The doublet signal due to H-1 and H-2 with small splitting ($J_{1,2}$=4.3 Hz) in ^{1}H NMR and C-1 at δ 96.5 and OCH_3 at 56.0 ppm in ^{13}C NMR indicated the presence of axial OCH_3. $J_{4,5}$

(10.2 Hz) proved the diaxial H-4 and H-5 arrangement. Considering that **2** was levorotatory and that Baer obtained a pair of enantiomers of reducing amino sugars by catalytic hydrogenation,[17] **2** was methyl 2,4,6-tri-*O*-acetyl-3-deoxy-3-*C*-methyl-3-nitro-α-L-glucopyranoside.

When the above reaction sequence was performed with the dialdehyde from methyl α-D-glucopyranoside, acetylated products, crystals **3**, (8.6%) and a sirup **4**, (8.0%), were both dextrorotatory. NMR spectra of these products coincided with those of the products from methyl β-D-glucopyranoside. Therefore, **3** and **4** were methyl 2,4,6-tri-*O*-acetyl-3-deoxy-3-*C*-methyl-3-nitro-β-L-glucopyranoside and -α-D-glucopyranoside, antipodes of **1** and **2**, respectively.

All the products, **1**—**4**, had the nitro and the vicinal hydroxyl groups in equatorial orientation. In **2** and **3**, the epimerization was observed at C-1 and C-5, evidently owing to base-catalyzed epimerization of the starting dialdehydes.[20]





	a	b	c	d
1	H	OMe	Me	NO_2
4	OMe	H	Me	NO_2
5	H	OMe	H	Me
6	H	OMe	Me	H
11	OMe	H	Me	H
12	OMe	H	H	Me

	a	b	c	d
2	OMe	H	Me	NO_2
3	H	OMe	Me	NO_2
7	OMe	H	Me	H
8	OMe	H	H	Me
9	H	OMe	H	Me
10	H	OMe	Me	H

Denitrohydrogenation. The nitro group of tertiary or secondary nitro compounds is replaced by hydrogen with tributyltin hydride. Refluxing a mixture of a nitro compound, tributyltin hydride and azobisisobutyronitrile (AIBN) in benzene or toluene for 1—2 h in a stream of nitrogen gave the denitrohydrogenated product in good yield.[14]

$$RNO_2 + n\text{-}Bu_3SnH \longrightarrow RH + n\text{-}Bu_3SnONO$$

A mixture of **1**, tributyltin hydride and AIBN in toluene was boiled under reflux for 1.5 h in a stream of nitrogen. The solution was evaporated and chromatographed on a column of silica gel (benzene–ethyl acetate 4:1) to give levorotatory products, **5** (61%) and **6** (22%).

^{1}H NMR spectrum of **5** showed the presence of C-CH_3 (δ 0.92, doublet) and diaxial H-1 and H-2 ($J_{1,2}$=7.8 Hz). Signals of C-1 (δ 103.0) and OCH_3 (δ 56.6) in ^{13}C NMR supported the presence of equatorial OCH_3 and axial H-1. Signal of H-3 (sextet, $J_{2,3}$=$J_{3,4}$=10.6 Hz, $J_{3,Me}$=6.4 Hz) showed that H-3 and H-4 were axial. Consequently, **5** was methyl 2,4,6-tri-*O*-acetyl-3-deoxy-3-*C*-methyl-β-D-glucopyranoside.

^{13}C NMR spectrum of **6** showed axial C-CH_3 at δ 9.2, differing from equatorial C-CH_3 at δ 13.2 in **5**. Signal of H-3 (sextet, $J_{2,3}$=$J_{3,4}$=4.7 Hz, $J_{3,Me}$=7.2 Hz) showed that H-3 and C-CH_3 were equatorial and axial, respectively. $J_{1,2}$ (5.8 Hz) and $J_{4,5}$ (6.8 Hz) were rather small for diaxial protons. But C-1 at δ 99.2 and OMe at δ 56.5 in ^{13}C NMR supported the presence of axial H-1. Therefore, **6** was proved to be methyl 2,4,6-tri-*O*-acetyl-3-deoxy-3-*C*-methyl-β-D-allopyranoside. These results showed that the predominant product had an equatorial methyl in denitrohydrogenation.

Denitrohydrogenation of **3**, antipode of **1**, gave methyl 2,4,6-tri-*O*-acetyl-3-deoxy-3-*C*-methyl-β-L-glucopyranoside (**9**, 65%) and -allopyranoside (**10**, 19%). This reaction was proved to be a novel method for the syntheses of 3-deoxy-3-*C*-methyl-L-glucose and -L-allose.

Products of denitrohydrogenation of **2** were a levorotatory mixture of C-3 epimers with 51:49 ratio on the basis of the methyl peak of methoxyl group in ^{1}H NMR. Coupling constants of H-3, $J_{2,3}$ and $J_{3,4}$, were both 5.5 Hz for a minor product (**7**, 39%) and both 10.4 Hz for a major product **8** (41%). These showed that **7** and **8** had axial and equatorial C-CH_3, respectively. Consequently, **7** and **8** were methyl 2,4,6-tri-*O*-acetyl-3-deoxy-3-*C*-methyl-α-L-allopyranoside and -glucopyranoside, respectively. We could not find an appropriate developer for the separation of the mixture on TLC and on a column of silica gel. Similarly, denitrohydrogenation of **4**, antipode of **2**, gave a mixture of methyl 2,4,6-tri-*O*-acetyl-3-deoxy-3-*C*-methyl-α-D-allopyranoside (**11**, 38%) and -glucopyranoside (**12**, 41%) with the ratio of 48:52.

The stereochemistry of denitrohydrogenation was explained as follows. For the β-glycosides, intermediate C-3 radical was preferentialy attacked from axial direction by tributyltin hydride to form a product with equatorial methyl, for equatorial attack was sterically hindered with axial H-2 and H-4. For the α-glycosides, axial attack was considerably hindered with axial methoxyl group at C-1. Therefore, axial and equatorial attack occurred with the same difficulty.

The secondary nitro sugar, methyl 2-*O*-acetyl-4,6-*O*-benzylidene-3-deoxy-3-nitro-β-D-glucopyranoside (**13**), synthesized by cyclization of the dialdehyde from methyl β-D-glucopyranoside with nitromethane,[19] was denitrohydrogenated with tributyltin hydride to give methyl 2-*O*-acetyl-4,6-*O*-benzylidene-3-deoxy-β-D-glucopyranoside (**14**) in 68% yield. Secondary nitro compounds were generally denitrohydrogenated in lower yield than tertiary nitro compounds.[14]

Experimental

Melting points were measured in capillary tubes with a Yamato melting-point apparatus MP-21 and are uncorrected. Column chromatography was performed on

Wakogel C-200 (100—200 mesh). ^{1}H NMR spectra were recorded with a JEOL JNM-GX-400 spectrometer (400 MHz) and ^{13}C NMR spectra with a JEOL FX-90Q spectrometer (22.5 MHz) using tetramethylsilane as an internal standard in deuteriochloroform unless otherwise stated. Chemical shifts and coupling constants were recorded in δ and Hz units. TLC was performed on precoated HPTLC plates, silica gel 60 (E. Merck). Optical rotations were determined with a Jasco DIP-140 digital polarimeter.

Methyl 2,4,6-Tri-*O*-acetyl-3-deoxy-3-*C*-methyl-3-nitro-β-D-glucopyranoside (1) and -α-L-glucopyranoside (2). Methyl β-D-glucopyranoside (38.8 g) was oxidized with sodium periodate (85.6 g) to the sirupy colorless dialdehyde, which was treated with nitroethane in the presence of sodium methoxide in methanol to the crystalline product (12.3 g) according to Baer.[17] The crystalline product (10 g) in pyridine (180 ml) was acetylated with acetic anhydride (50 ml) overnight at room temperature. The reaction mixture was poured into water and extracted with chloroform. The extract was evaporated and treated with ethanol to crystals (**1**, 6.7 g). The mother liquor was evaporated and passed through a column of silica gel (60×5 cm, hexane–ethyl acetate 1:1). The additional crystalline **1**, (2.1 g) and a sirup **2**, (6.4 g) were obtained.

1: 8.8 g (12% yield from methyl β-D-glucopyranoside): Mp 124—125 °C; $[\alpha]_D^{22}$ −25.5° (*c* 1, chloroform); ^{1}H NMR δ=5.71 (H-4, 1H, d, $J_{4,5}$=10.1), 5.67 (H-2, 1H, d, $J_{1,2}$=7.9), 4.44 (H-1, 1H, d), 4.27 (H-6R, 1H, q, $J_{5,6R}$=4.6, $J_{6,6}$=12.4), 4.15 (H-6S, 1H, q, $J_{5,6S}$=2.8), 3.75 (H-5, 1H, octet), 3.51 (OMe, 3H, s) and 1.78 (CMe, 3H, s). NOE of H-1 (+12%) and H-5 (+12%) were measured by irradiation at δ 1.78. ^{13}C NMR δ=170.6, 168.2, 168.1 (C=O Me), 100.5 (C-1), 91.1 (C-3), 71.5, 71.4, 69.6 (C-2,4,5), 62.2 (C-6), 57.0 (OMe), 20.7, 20.5, 20.3 (CO<u>Me</u>), and 12.0 (C<u>Me</u>).

Found: C, 46.17; H, 5.82; N, 3.89%. Calcd for $C_{14}H_{21}NO_{10}$: C, 46.28; H, 5.83; N, 3.86%.

2: 6.4 g (8.8% yield from methyl β-D-glucopyranoside), $[\alpha]_D^{22}$ −96.7° (*c* 1, chloroform); ^{1}H NMR δ=5.63 (H-2, 1H, d, $J_{1,2}$=4.3), 5.58 (H-4, 1H, d, $J_{4,5}$=10.2), 5.11 (H-1, d), 4.31 (H-6S, 1H, q, $J_{5,6S}$=4.5, $J_{6,6}$=12.3), 4.11 (H-6R, 1H, q, $J_{5,6R}$=2.4), 3.94 (H-5, 1H, octet), 3.41 (OMe, 3H, s), and 1.89 (CMe, 3H, s). NOE of H-5 (+12%) was measured by irradiation at δ 1.89. ^{13}C NMR δ=170.5, 169.1, 168.3 (C=O Me), 96.5 (C-1), 91.2 (C-3), 71.2, 69.4, 66.2 (C-2,4,5), 61.8 (C-6), 56.0 (OMe), 20.6, 20.4, 20.2 (CO<u>Me</u>), and 13.1 (C<u>Me</u>).

Found: C, 46.28; H, 5.83; N, 3.61%. Calcd for $C_{14}H_{21}NO_{10}$: C, 46.28; H, 5.83; N, 3.86%.

Methyl 2,4,6-Tri-*O*-acetyl-3-deoxy-3-*C*-methyl-3-nitro-β-L-glucopyranoside (3) and -α-D-glucopyranoside (4). Methyl α-D-glucopyranoside (38.8 g) was oxidized with sodium periodate (85.6 g), and treated with nitroethane to crystals (7.9 g, 17% yield).[17] The crystalline product (5.9 g) was acetylated in a similar manner as the preceded procedure. Crystals (**3**, 4.7 g, 8.6% from methyl α-D-glucoside) and a sirup (**4**, 4.2 g, 8.0% from methyl α-D-glucoside) were obtained.

3: Mp 124—125 °C; $[\alpha]_D^{18}$ +29.0° (*c* 1, chloroform); ^{13}C NMR δ= 170.4, 168.1, 167.8 (C=O Me, each s), 100.8 (C-1, d), 91.3 (C-3, s), 71.9, 71.8, 70.1 (C-2,4,5, each d), 62.6 (C-6, t), 56.6 (OMe, q), 20.6, 20.3, 20.2 (CO<u>Me</u>, q), and 12.2 (C<u>Me</u>, q).

Found: C, 46.21; H, 5.81; N, 3.74%. Calcd for $C_{14}H_{21}NO_{10}$: C, 46.28; H, 5.83; N, 3.86%.

4: $[\alpha]_D^{22}$ +102° (*c* 1, chloroform); ^{13}C NMR δ=170.2, 168.9, 168.1 (C=O Me, each s), 96.8 (C-1, d), 91.5 (C-3, s), 71.6, 70.0, 66.6 (C-2,4,5, each d), 62.2 (C-6, t), 55.9 (OMe, q), 20.4, 20.2, 20.0 (CO<u>Me</u>, each q), and 13.2 (C<u>Me</u>, q).

Found: C, 45.98; H, 5.79; N, 3.86%. Calcd for $C_{14}H_{21}NO_{10}$: C, 46.28; H, 5.83; N, 3.86%.

Denitrohydrogenation of 1. A mixture of **1** (1.0 g, 2.7 mmol), tributyltin hydride (3 ml, 11 mmol), and AIBN solution (120 mg in 10 ml of toluene) in toluene (100 ml) was boiled under reflux.[14] A half an hour later, AIBN solution (60 mg in 5 ml of toluene) was added. Boiling under reflux for an hour, the solution was evaporated and chromatographed on a column of silica gel (60×3 cm, benzene–ethyl acetate 4:1). Methyl 2,4,6-tri-*O*-acetyl-3-deoxy-3-*C*-methyl-β-D-glucopyranoside (**5**, 0.52 g, 61%) and -allopyranoside (**6**, 0.19 g, 22%) were crystallized from ethanol and from hexane, respectively.

5: Mp 85 °C; $[\alpha]_D^{22}$ −39.7° (*c* 1, chloroform); ^{1}H NMR δ=4.79 (H-4, 1H, t, $J_{3,4}$=$J_{4,5}$=10.2), 4.70 (H-2, 1H, q, $J_{1,2}$=7.8, $J_{2,3}$=10.8), 4.34 (H-1, 1H, d), 4.23 (H-6R, 1H, q, $J_{5,6R}$=4.9, $J_{6,6}$=12.2), 4.10 (H-6S, 1H, q, $J_{5,6S}$=2.4), 3.63 (H-5, 1H, octet), 3.48 (OMe, 3H, s), 2.10, 2.09, 2.08 (3×COMe, 3×3H, each s), 1.91 (H-3, 1H, octet, $J_{3,Me}$=6.4), and 0.92 (CMe, 3H, d). ^{13}C NMR δ=170.7, 169.8 (overlapped) (C=O Me, each s), 103.0 (C-1, d), 74.6, 72.9, 70.4 (C-2,4,5, each d), 62.6 (C-6, t), 56.6 (OMe, q), 39.8 (C-3, d), 20.8, 20.7 (overlapped) (CO<u>Me</u>, q), and 13.6 (C<u>Me</u>, q).

Found: C, 52.60; H, 7.10%. Calcd for $C_{14}H_{22}O_8$: C, 52.82; H, 6.97%.

6: Mp 55 °C; $[\alpha]_D^{19}$ −35.5° (*c* 0.5, chloroform); ^{1}H NMR δ=4.94 (H-4, 1H, q, $J_{3,4}$=4.7, $J_{4,5}$=6.8), 4.82 (H-2, 1H, q, $J_{1,2}$=5.8, $J_{2,3}$=4.7), 4.60 (H-1, 1H, d), 4.25 (H-6, 2H, d, $J_{5,6}$=4.9), 3.98 (H-5, 1H, sextet), 3.45 (OMe, 3H, s), 2.66 (H-3, 1H, sextet, $J_{3,Me}$=7.2), 2.11, 2.090, 2.086 (3×COMe, 3×3H, each s), and 0.99 (CMe, 3H, d); ^{13}C NMR δ=170.7, 169.8, 169.7 (C=O Me, each s), 99.2 (C-1, d), 63.4 (C-5, t), 56.5 (OMe, q), 30.7 (C-3, d), 20.83, 20.75 (overlapped) (CO<u>Me</u>), and 9.2 (C<u>Me</u>, q).

Found: C, 52.71; H, 7.08%. Calcd for $C_{14}H_{22}O_8$: C, 52.82; H, 6.97%.

Denitrohydrogenation of 2. Compound **2** (1.0 g) was denitrohydrogenated in a similar manner as **1**. NMR spectra of the sirupy product (0.70 g, 80% yield) showed that it was a mixture of two components, methyl-2,4,6-tri-*O*-acetyl-3-deoxy-3-*C*-methyl-α-L-allopyranoside (**7**) and -glucopyranoside (**8**). According to the methyl peak of methoxyl group, components ratio **7**/**8** was 49/51. Separation of the components was unsuccessful on TLC and on a column of silica gel. $[\alpha]_D^{20}$ −114° (*c* 0.5, chloroform).

Found: C, 53.03; H, 7.20%. Calcd for $C_{14}H_{22}O_8$: C, 52.82; H, 6.97%.

7: ^{1}H NMR δ=4.94 (H-2, 1H, q, $J_{1,2}$=3.7, $J_{2,3}$=5.5), 4.94 (H-4, 1H, q, $J_{3,4}$=5.5, $J_{4,5}$=11.2), 4.65 (H-1, 1H, d), 4.29 (H-6R, 1H, q, $J_{5,6R}$=5.0, $J_{6,6}$=12.1), 4.17 (H-6S, 1H, q, $J_{5,6S}$=2.4), 4.07 (H-5, 1H, octet), 3.40 (OMe, 3H, s), 2.69 (H-3, 1H, q, $J_{3,Me}$=7.3), 2.12, 2.09, 2.08 (3×COMe, 3×3H, each s), and 1.12 (CMe, 3H, d). ^{13}C NMR δ=97.9 (C-1, d), 69.6, 68.4, 63.7 (C-2,4,5, each d), 62.6 (C-6, t), 55.5 (OMe, q), 33.3 (C-3, d), 20.9, 20.7 (overlapped) (CO<u>Me</u>, each q), and 8.51 (C<u>Me</u>, q). Signals of carbonyl carbons were appeared at 170.7, 170.3,

169.8, and 169.3, of which assignment to **7** or **8** was not determined.

8: ^{1}H NMR δ=4.83 (H-2, 1H, q, $J_{1,2}$=3.7, $J_{2,3}$=10.5), 4.78 (H-4, 1H, t, $J_{3,4}$=$J_{4,5}$=10.4), 4.62 (H-1, 1H, d), 4.22 (H-6R, 1H, q, $J_{5,6R}$=4.9, $J_{6,6}$=12.2), 4.05 (H-6S, 1H, q, $J_{5,6S}$=2.4), 3.88 (H-5, 1H, octet), 3.42 (OMe, 3H, s), 2.27 (H-3, 1H, sextet, $J_{3,Me}$=6.4), 2.12, 2.09, 2.07 (3×COMe, 3×3H, each s), and 0.92 (CMe, 3H, d); ^{13}C NMR δ=96.1 (C-1, d), 73.1, 70.5, 68.1 (C-2,4,5, each d), 62.9 (C-6, t), 55.2 (OMe, q), 34.9 (C-3, d), 20.9, 20.7 (overlapped) (COMe, each q), and 13.4 (CMe, q). Concerning signals of carbonyl carbons, see the data of **7**.

Denitrohydrogenation of 3. Compound **3** (1.0 g) was denitrohydrogenated in a similar manner as **1**. Methyl 2,4,6-tri-*O*-acetyl-3-deoxy-3-*C*-methyl-β-L-glucopyranoside (**9**, 0.57 g, 65%) and -allopyranoside (**10**, 0.17 g, 19%) were obtained.

9: Mp 85 °C; $[\alpha]_D^{20}$ +40.5° (*c* 1, chloroform); ^{13}C NMR δ=170.5, 169.7, 169.6 (COMe, each s), 103.2 (C-1, d), 75.0, 73.4, 71.1 (C-2,4,5, each d), 63.0 (C-6, t), 56.2 (OMe, q), 40.1 (C-3, d), 20.6 (overlapped) (COMe, q), and 13.7 (CMe, q).

Found: C, 52.83; H, 7.06%. Calcd for $C_{14}H_{22}O_8$: C, 52.82; H, 6.97%.

10: Mp 56 °C; $[\alpha]_D^{20}$ +36.5° (*c* 1, chloroform); ^{1}H NMR: 4.94 (H-4, 1H, q, $J_{3,4}$=4.7, $J_{4,5}$=6.7), 4.82 (H-2, 1H, q, $J_{1,2}$=5.8, $J_{2,3}$=4.7), 4.60 (H-1, 1H, d), 4.25 (H-6, 2H, d, $J_{5,6}$=5.2), 3.98 (H-5, 1H, sextet), 3.48 (OMe, 3H, s), 2.66 (H-3, 1H, sextet, $J_{3,Me}$=7.1), 2.11 2.089, 2.085 (3×COMe, 3×3H, each s), and 0.99 (CMe, 3H, d).

Found: C, 52.54; H, 7.02%. Calcd for $C_{14}H_{22}O_8$: C, 52.82; H, 6.97%.

Denitrohydrogenation of 4. Compound **4** (1.0 g) was denitrohydrogenated in a similar manner as **1**. A mixture of methyl 2,4,6-tri-*O*-acetyl-3-deoxy-3-*C*-methyl-α-D-allopyranoside (**11**) and -glucopyranoside (**12**) (0.71 g, 79% yield) was obtained. $[\alpha]_D^{20}$ +116° (*c* 0.5, chloroform).

Found: C, 53.06; H, 7.02%. Calcd for $C_{14}H_{22}O_8$: C, 52.82; H, 6.97%.

According to the methyl peak of methoxyl group, products ratio **11**/**12** was 48/52.

11: ^{1}H NMR δ=4.93 (H-2, 1H, q, $J_{1,2}$=3.8, $J_{2,3}$=5.5), 4.93 (H-4, 1H, q, $J_{3,4}$=5.6, $J_{4,5}$=11.0), 4.65 (H-1, 1H, d), 4.29 (H-6R, 1H, q, $J_{5,6R}$=5.2, $J_{6,6}$=12.2), 4.17 (H-6S, 1H, q, $J_{5,6S}$=2.4), 4.06 (H-5, 1H, octet), 3.40 (OMe, 3H, s), 2.68 (H-3, 1H, q), 2.13, 2.11, 2.08 (3×COMe, 3×3H, each s), and 1.12 (CMe, 3H, d).

12: ^{1}H NMR δ=4.82 (H-2, 1H, q, $J_{1,2}$=3.7, $J_{2,3}$=10.4), 4.77 (H-4, 1H, t, $J_{3,4}$=$J_{4,5}$=10.4), 4.62 (H-1, 1H, d), 4.21 (H-6R, 1H, q, $J_{5,6R}$=5.0, $J_{6,6}$=12.2), 4.05 (H-6S, 1H, q, $J_{5,6S}$=2.4), 3.88 (H-5, 1H, octet), 3.42 (OMe, 3H, s), 2.27 (H-3, 1H, sextet), 2.12, 2.09, 2.07 (3×COMe, 3×3H, each s), and 0.92 (CMe, 3H, d).

Denitrohydrogenation of Methyl 2-*O*-Acetyl-4,6-*O*-benzylidene-3-deoxy-3-nitro-β-D-glucopyranoside (13). Compound **13**[19] (1.0 g, 2.8 mmol) was denitrohydrogenated in a similar manner as **1**. Methy 2-*O*-acetyl-4,6-*O*-benzylidene-3-deoxy-β-D-glucopyranoside (**14**, 0.60 g, 68% yield) were obtained as crystals after the evaporation of the developer. Mp 147—148 °C; $[\alpha]_D^{22}$ −89.2° (*c* 1, chloroform). ^{1}H NMR δ=5.51 (C_6H_5CH, 1H, s), 4.81 (H-2, 1H, octet, $J_{1,2}$=7.6, $J_{2,3e}$=4.9, $J_{2,3a}$=11.6), 4.43 (H-1, 1H, d), 4.33 (H-6e, 1H, q, $J_{5,6e}$=4.9, $J_{6,6}$=10.4), 3.76 (H-6a, 1H, t, $J_{5,6a}$=10.4), 3.62 (H-5, 1H, octet, $J_{4,5}$=9.3), 3.45 (H-4, 1H, multiplet), 2.51 (H-3e, 1H, sextet, $J_{3,3}$=11.6, $J_{3e,4}$=4.9) and 1.73 (H-3a, 1H, q, $J_{3a,4}$=11.6).

Found: C, 62.06; H, 6.60%. Calcd for $C_{16}H_{26}O_6$: C, 62.32; H, 6.54%.

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