Organic Letters

Supporting Information for the Communication Entitled
" Reductive Ring Opening of *o*-Nitrobenzylidene Acetals of Monosaccharides: Synthesis and Photolysis of Some Photolabile Sugars"

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Reductive Ring Opening of *o*-Nitrobenzylidene Acetals of Monosaccharides: Synthesis and Photolysis of Some Photolabile Sugars.

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Methyl 2,3-di-*O*-acetyl-6-*O*-(2-nitrobenzyl)-α-ᴅ-glucopyranoside (2a) To a solution of **1a** (311 mg, 0.76 mmol) in CH_2Cl_2 (7.5 mL) was added triethylsilane (1.45 ml, 9.08 mmol) and boron trifluoride etherate at 0 ˚C under argon atmosphere. The reaction mixture was warmed to room temperature and stirred for 3 h. The reaction mixture was diluted with CH_2Cl_2 (30 mL), washed with $NaHCO_3$ aq. (40 mL), dried over anhydrous $MgSO_4$ and filtered. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography (SiO_2/$CHCl_3$) to afford **2a** (276 mg, 0.67 mmol, 88%). **2a**: pale yellow oil. ^1H NMR (270 MHz, $CDCl_3$): δ 2.09 (s, 3H), 2.11 (s, 3H), 2.81 (br s, 1H), 3.42 (s, 3H), 3.76-3.87 (m, 4H), 4.88 (dd, *J*=3.6, 9.6 Hz, 1H), 4.93 (d, *J*=3.6 Hz, 1H), 4.97 (s, 2H), 5.30 (t, *J*=9.6 Hz, 1H), 7.45 (t, *J*=7.6 Hz, 1H), 7.65 (t, *J*=7.6 Hz, 1H), 7.77 (d, *J*=7.6 Hz, 1H), 8.05 (d, *J*=7.6 Hz, 1H); ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 20.7 (q), 20.8 (q), 55.2 (q), 69.6 (d), 69.9 (t), 70.2 (t), 70.5 (d), 70.7 (d), 73.3 (d), 96.8 (d), 124.6 (d), 128.1 (d), 128.7 (d), 133.6 (d), 134.6 (s), 147.3 (s), 170.3 (s), 171.7 (s).

Methyl 2,3-di-*O*-acetyl-6-*O*-(2-nitrobenzyl)-α-D-mannopyranoside (2b) The same procedure was followed as that for **2a** except that **1b** (320 mg, 0.78 mmol) was used. After workup and chromatography 234 mg of **2b** (0.57 mmol, 73%) was obtained. **2b**: pale yellow oil. ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.08 (s, 3H), 2.12 (s, 3H), 2.56 (br s, 1H), 3.41 (s, 3H), 3.83-3.95 (m, 3H), 4.01-4.04 (m, 1H), 4.71 (s, 1H), 4.99 (s, 2H), 5.17-5.22 (m, 2H), 7.45 (dd, *J*=7.3, 7.8 Hz, 1H), 7.64 (dd, *J*=7.3, 7.6 Hz, 1H), 7.78 (d, *J*=7.6 Hz, 1H), 8.04 (d, *J*=7.8 Hz, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 20.9 (q), 21.0 (q), 55.2 (q), 66.2 (d), 69.7 (d), 70.25 (t), 70.31 (t), 71.5 (d), 72.0 (d), 98.6 (d), 124.5 (d), 128.0 (d), 128.7 (d), 133.4 (d), 134.5 (s), 147.3 (s), 169.9 (s), 170.8 (s).

Methyl 6-*O*-(2-nitrobenzyl)-α-D-glucopyranoside (3a) To a solution of **2a** (103 mg, 0.25 mmol) in methanol (5 mL) was added a solution of sodium methoxide (32 mg, 0.59 mmol) in methanol (2 mL) at room temperature and stirred for 30 min. The reaction mixture was neutralized by adding Dowex 50Wx8 (H^+ form). After the resin was filtered off, the solvent was evaporated under reduced pressure. The residue was purified by preparative gel permeation chromatography to afford **3a** (58 mg, 0.18 mmol, 71%). **3a**: pale yellow oil. ^{1}H NMR (CD_3OD) δ 3.25-3.33 (m, 2H), 3.45 (s, 3H), 3.58-3.85 (m, 4H), 4.69 (d, *J* = 4.0 Hz, 1H), 4.98 (s, 2H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.93 (d, *J* = 7.6 Hz, 1H) ; ^{13}C NMR (CD_3OD) δ 55.6 (q), 70.9 (t), 71.4 (t), 71.6 (d), 72.5 (d), 73.4 (d), 75.1 (d), 101.1 (d), 125.5 (d), 129.2 (d), 129.9 (d), 134.6 (d), 135.9 (s), 148.8 (s). UV/vis (MeOH) 261 nm (ε 4890).

Methyl 6-*O*-(2-nitrobenzyl)-α-D-mannopyranoside (3b) The same procedure was followed as that for **3a** except that **2b** (122 mg, 0.30 mmol) was used. After workup and chromatography 49 mg of **3b** (0.15 mmol, 50%) was obtained. **3b**: pale yellow oil. ^{1}H NMR (CDCl$_3$) δ 3.29 (s, 3H), 3.35-3.84 (m, 5H), 4.66 (s, 2H), 4.88 (s, 2H), 7.36 (dd, *J* = 7.3, 7.8 Hz, 1H), 7.56 (dd, *J* = 7.3, 7.6 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.94 (d, *J* = 7.8 Hz, 1H) ; ^{13}C NMR (CDCl$_3$) δ 55.1 (q), 68.3 (d), 70.4 (t), 70.6 (t), 70.7 (d), 71.8 (d), 77.0 (d), 100.8 (d), 124.6 (d), 128.1 (d), 128.9 (d), 133.5 (d), 134.3 (s), 147.4 (s). UV/vis (MeOH) 257 nm (ε 4450).

Methyl 2, 6-di-*O*-(2-nitrobenzyl)-α-D-mannopyranoside (6) and Methyl 3, 6-di-*O*-(2-nitrobenzyl)-α-D-mannopyranoside (7)

(i) The same procedure was followed as that for **2a** except that **4** (344 mg, 0.75 mmol) was used. After workup and chromatography 125 mg of **6** (0.27 mmol, 36%) and 104 mg of **7** (0.22 mmol, 30%) were obtained.

(ii) The same procedure was followed as that for **2a** except that **5** (containing 17 of **4**, 350 mg, 0.76 mmol) was used. After workup and chromatography 21 mg of **6** (0.045 mmol, 6%) and 163 mg of **7** (0.35 mmol, 46%) were obtained.

6: pale yellow oil. ^{1}H NMR (CDCl$_3$) δ 2.84 (br s, 2H), 3.40 (s, 3H), 3.75 (br s, 1H), 3.82 (s, 1H), 3.88 (br s, 4H), 4.86 (s, 1H), 4.98 (s, 2H), 5.03 (s, 2H), 7.42 (t, *J*=7.7 Hz, 2H), 7.56 (t, *J*=7.7 Hz, 1H), 7.60 (t, *J*=7.7 Hz, 1H), 7.80 (d, *J*=7.7 Hz, 2H), 8.03 (d, *J*=7.7 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ 55.1 (q), 69.0 (d), 69.7 (t), 70.2 (t), 70.6 (t), 71.1 (d), 71.7 (d), 78.9 (d), 98.0 (d), 124.5 (d), 124.6 (d), 127.9 (d), 128.2 (d), 128.7 (d), 128.9 (d), 133.5 (d), 133.6 (d), 134.1 (s), 134.8 (s), 147.0 (s), 147.2 (s). UV/vis (MeOH) 261 nm (ε 10900). **7**: pale yellow oil. ^{1}H NMR (CDCl$_3$) δ 2.61 (br s, 2H), 3.41 (s, 3H), 3.72-3.82 (m, 2H), 3.87 (br s, 2H), 4.01 (t, *J*=9.4 Hz, 1H), 4.13 (s, 1H), 4.82 (s, 1H), 4.95 (d, *J*=13.5 Hz, 1H), 4.98 (s, 2H), 5.12 (d, *J*=13.5 Hz, 1H), 7.43 (dd, *J*=6.8, 7.3 Hz, 1H), 7.47 (dd, *J*=6.8, 7.3 Hz, 1H), 7.64 (dd, *J*=7.6, 7.3 Hz, 1H), 7.65 (dd, *J*=7.6, 7.3 Hz, 1H), 7.79 (d, *J*=7.6 Hz, 2H), 8.04 (d, *J*=6.8 Hz, 1H), 8.05 (d, *J*=6.8

Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 55.2 (q), 67.2 (d), 67.6 (d), 68.6 (t), 70.2 (t), 70.7 (t), 70.8 (d), 80.4 (d), 100.6 (d), 124.5 (d), 124.7 (d), 128.0 (d), 128.6 (d), 128.7 (d), 129.5 (d), 133.5 (d, 2C), 134.6 (s, 2C), 147.2 (s), 147.6 (s). UV/vis (MeOH) 260 nm (ε 10800).

Methyl 3,4-di-*O*-acetyl-2,6-di-*O*-(2-nitrobenzyl)-α-D-mannopyranoside (8) and Methyl 2,4-di-*O*-acetyl-3,6-di-*O*-(2-nitrobenzyl)-α-D-mannopyranoside (9) Diols **6** and **7** were treated with Ac_2O–pyridine to afford diacetyl derivatives **8** and **9**, respectively. **8**: pale yellow oil. ^{1}H NMR ($CDCl_3$) δ 2.03 (s, 3H), 2.07 (s, 3H), 3.45 (s, 3H), 3.74 (s, 2H), 3.96-4.01 (br s, 2H), 4.89 (s, 1H), 4.97 (d, *J*=10.1 Hz, 2H), 5.06 (d, *J*=10.1 Hz, 2H), 5.36 (dd, *J*=9.9, 3.1 Hz, 1H), 5.51 (t, *J*=9.9 Hz, 1H), 7.41 (t, *J*=7.3 Hz, 1H), 7.44 (t, *J*=7.3 Hz, 1H), 7.59 (t, *J*=7.3 Hz, 2H), 7.87 (d, *J*=7.3 Hz, 1H), 7.92 (d, *J*=7.3 Hz, 1H), 8.06 (d, *J*=7.3 Hz, 1H), 8.08 (d, *J*=7.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 20.86 (q), 20.94 (q), 55.2 (q), 67.0 (d), 69.92 (d), 69.98 (t, 3C), 71.4 (d), 77.5 (d), 98.5 (d), 124.4 (d), 124.5 (d), 127.7 (d), 127.9 (d), 128.4 (d), 128.6 (d), 133.6 (d), 133.7 (d), 134.6 (s), 134.9 (s), 146.6 (s), 146.8 (s), 169.6 (s), 170.0 (s). **9**: pale yellow oil. ^{1}H NMR ($CDCl_3$) δ 2.04 (s, 3H), 2.11 (s, 3H), 3.43 (s, 3H), 3.72 (s, 2H), 3.74-4.04 (m, 2H), 4.78 (s, 1H), 4.88-5.04 (m, 4H), 5.36 (t, *J*=9.9 Hz, 1H), 5.36 (s, 1H), 7.43 (t, *J*=7.7 Hz, 2H), 7.59-7.68 (m, 3H), 7.88 (d, *J*=7.7 Hz, 1H), 8.07 (d, *J*=7.7 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.0 (q, 2C), 55.3 (q), 68.0 (d), 68.2 (d), 68.6 (t), 69.9 (d), 70.0 (t), 70.1 (t), 76.2 (d), 98.6 (d), 124.5 (d), 124.6 (d), 127.8 (d), 128.0 (d), 128.5 (d), 128.8 (d), 133.56 (d), 133.60 (d), 134.2 (s), 134.9 (s), 146.9 (s, 2C), 169.8 (s), 170.0 (s).

Photolysis of photolabile sugars in MeOH.

A solution of **2a** (74 mg, 0.22 mmol) in methanol (1.5 mL) was photolized by Rayonet Photochemimal Reactor (RPR 3500 Å × 12) for 15 h. After the solvent was evaporated under reduced pressure, the residue was separated by preparative gel permeation chromatography to afford methyl glucopyranoside (26 mg, 0.13 mmol, 60%).

The same procedure was followed as that for **2a** except that **2b**, **6**, and **7** were used. After workup and chromatography 71%, 76% and 87% of methyl mannopyranoside was obtained, respectively.

Structural Elucidation of Methyl 2, 6-di-*O*-(2-nitrobenzyl)-α-D-mannopyranoside (6).

^{1}H NMR spectra of **6** and **8** as well as differential NOE spectra of **8** were shown in Chart S1. (a) ^{1}H NMR spectra of **6** in $CDCl_3$. (b) ^{1}H NMR spectra of **8** in $CDCl_3$. (c) Differential NOE spectra of **8** in $CDCl_3$ (irradiated at anomeric ring proton). After the acetylation of **6**, two signals (indicated by open circles) shifted downfield, suggesting that two secondary hydroxyl groups were acetylated in this reaction. In the differential NOE experiment, NOE signals were observed in the methyl proton of methoxy group and the 2-H ring proton when the anomeric ring proton was irradiated (indicated by solid circles). No NOE were observed in the downshifted signals in **8**, which means an *o*-nitrobenzyl group is attached to the 2- position (2-OH group was not acetylated). These observation means that **6** has two *o*-nitrobenzyl groups at 2- and 6- positions.

Structural Elucidation of Methyl 3, 6-di-*O*-(2-nitrobenzyl)-α-D-mannopyranoside (7).

^{1}H NMR spectra of **7** and **9** as well as differential NOE spectra of **9** were shown in Chart S2. (a) ^{1}H NMR spectra of **7** in $CDCl_3$. (b) ^{1}H NMR spectra of **9** in $CDCl_3$. (c) Differential NOE spectra of **9** in $CDCl_3$ (irradiated at anomeric ring proton). After the acetylation of **7**, two signals (indicated by open circles) shifted downfield, suggesting that two secondary hydroxyl groups were acetylated in this reaction. In the differential NOE experiment, NOE signals were observed in the methyl proton of methoxy group and the 2-H ring proton when the anomeric ring proton was irradiated (indicated by solid circles). NOE were observed in the downshifted signals in **9**, which means an *o*-nitrobenzyl group is attached to the 3- position (2-OH group was acetylated). These observation means that **7** has two *o*-nitrobenzyl groups at 3- and 6-positions.

Chart S1

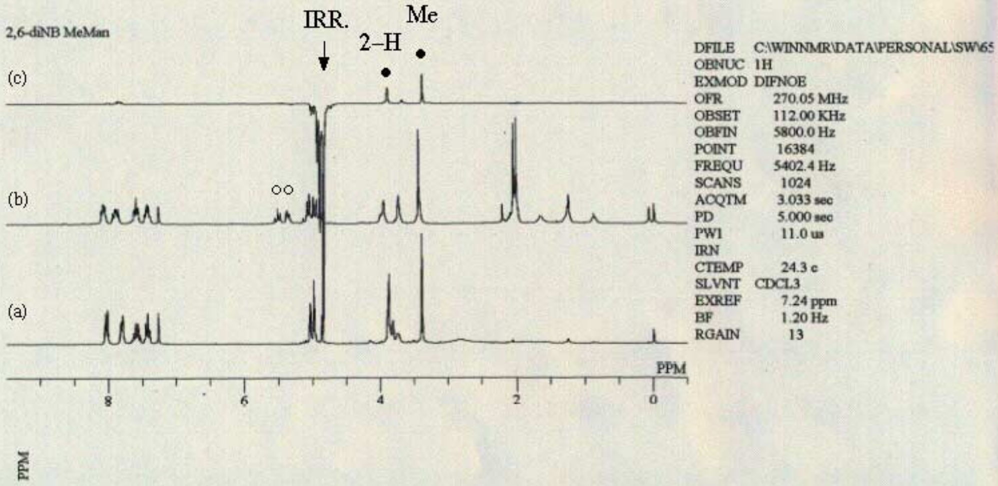

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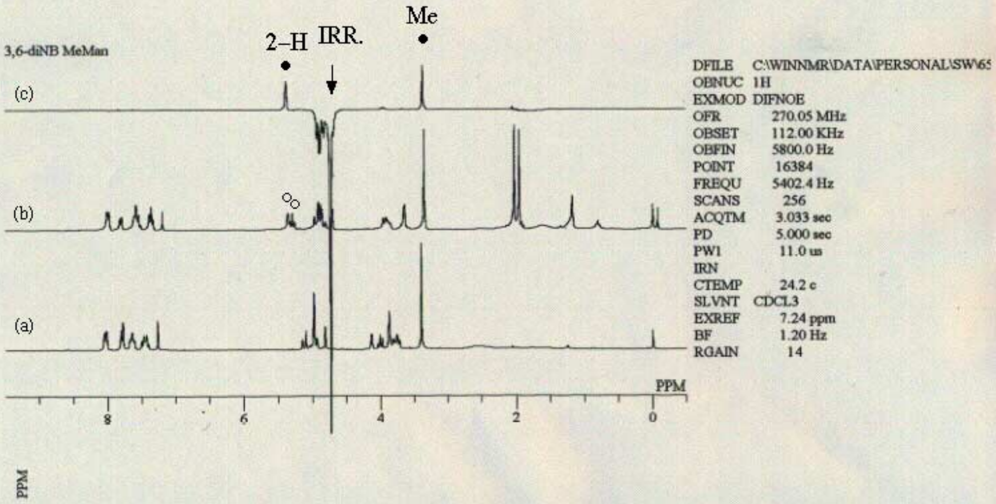
Chart S2



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