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Catalytic Regioselective Oxidation of Glycosides

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Supporting Information

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Catalytic Regioselective Oxidation of Glycosides**

Manuel Jäger, Marcel Hartmann, Johannes G. de Vries, and Adriaan J. Minnaard**

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EXPERIMENTAL SECTION

General Information

Solvents and Reagents

All solvents used for extraction, filtration and chromatography were of commercial grade, and used without further purification. Reagents were purchased from Sigma-Aldrich, Acros, ABCR, and Carbosynth and were used without further purification. For purification via column chromatography silica gel from either Silicycle (Silica Flash 40-63 μm , 230-400 mesh, abbreviated as SG1) or from Sigma Aldrich (Silica Amorphus, precipitated, Davisil grade 62, pore size 150 Å, 60-200 mesh, abbreviated as SG2) was used. [(Neocuproine)PdOAc]₂OTf₂, methyl- β -maltoside and methyl- β -cellobioside were prepared according to the literature procedures.^{[25] [26] [27]}

Analysis

TLC was performed on Merck silica gel 60, 0.25 mm plates and visualization was done by UV and staining with Seebach's reagent (a mixture of phosphomolybdic acid (25 g), cerium (IV) sulfate (7.5 g), H₂O (500 mL) and H₂SO₄ (25 mL)) and potassium permanganate stain (a mixture of KMnO₄ (3g), K₂CO₃ (10g), water (300mL)).

¹H-, ¹³C-, APT-, COSY-, HSQC-, NOESY were recorded on a Varian AMX400 (400, 100.59 MHz, respectively) using DMSO-*d*₆, MeOD-*d*₄ or D₂O as solvent. Chemical shift values are reported in ppm with the solvent resonance as the internal standard (DMSO-*d*₆: 2.50 for ¹H, δ 39.51 for ¹³C; MeOD-*d*₄: δ 3.31 for ¹H, δ 49.15 for ¹³C; D₂O: δ 4.80 for ¹H; acetonitrile-*d*₃: δ 1.94 for ¹H, δ 118 for ¹³C). Data are reported as follows: chemical shifts (δ), multiplicity (s = singlet, d = doublet, t = triplet, q =quartet, br = broad, m = multiplet), coupling constants J (Hz), and integration. High Resolution Mass measurements were performed using a ThermoScientific LTQ OrbitrapXL spectrometer.

Synthesis of Oxo-glucopyranosides

General Procedure (acetonitrile/water as solvent)

Methyl glycoside (4 mmol, 1.0 eq) and 2,6-dichlorobenzoquinone (12 mmol, 3.0 eq) were suspended in acetonitrile/de-ionized water (10:1, 0.3 M). The catalyst [(2,9-dimethyl-1,10-phenanthroline)-Pd(μ -OAc)]₂(OTf)₂ (0.1 mmol, 2.5 mol%) was added and the mixture was stirred at rt until the reaction was finished, as indicated by TLC (DCM/MeOH 5:1). Toluene (50 mL) was added and the mixture was extracted twice with water (7 mL). The combined water layers were washed once with ethyl ether (35 mL), filtered and concentrated *in vacuo* to give the pure keto-sugar.

Methyl- α -D-ribo-hexapyranoside-3-ulose (3)

Methyl- α -glucopyranoside (777 mg, 4.0 mmol, 1.0 eq) was oxidized according to general procedure using 2,6-dichloro-1,4-benzoquinone (2.12 g, 12.0 mmol, 3.0 eq.) and [(2,9-dimethyl-1,10-phenanthroline)-Pd(μ -OAc)]₂(OTf)₂ (105 mg, 2.5 mol%) in acetonitrile/water (13.4 mL, 10 : 1, 0.3 M in substrate) within 3 h. Methyl- α -D-ribo-hexapyranosid-3-ulose (751 mg, 3.9 mmol) was isolated in 96% yield as a dark brown solid. ¹H NMR^[28] (400 MHz, 298 K, DMSO-*d*₆) : δ = 4.95 (d, *J* = 4.2 Hz, 1H), 4.29 (dd, *J* = 4.2, 1.5 Hz, 1H), 4.07 (dd, *J* = 9.8, 1.4 Hz, 1H), 3.69 (dd, *J* = 11.9, 1.9 Hz, 1H), 3.59 (dd, *J* = 11.9, 4.9 Hz, 1H), 3.46 (ddd, *J* = 9.7, 4.9, 1.8 Hz, 1H), 3.26 (s, 3H). ¹³C NMR (50 MHz, DMSO-*d*₆) : δ = 206.1, 102.2, 75.4, 74.6, 71.9, 60.7, 54.4. HRMS (ESI) calculated for C₇H₁₂O₆Na ([M+Na]⁺): 215.053, found: 215.052 IR ν_{max} /cm⁻¹: 3436 (OH), 2947 (C-H), 1736 (C=O), 1031 (C-O)

Methyl- β -D-ribo-hexapyranoside-3-ulose (5)

Methyl- β -glucopyranoside (777 mg, 4.0 mmol, 1.0 eq) was oxidized according to general procedure using 2,6-dichloro-1,4-benzoquinone (2.12 g, 12.0 mmol, 3.0 eq) and [(2,9-dimethyl-1,10-phenanthroline)-Pd(μ -OAc)]₂(OTf)₂ (105 mg, 2.5 mol%) in acetonitrile/water (13.4 mL, 10 : 1, 0.3 M in substrate) within 5 h. Methyl- β -D-ribo-hexapyranosid-3-ulose (686 mg, 3.6 mmol) was isolated in 89% yield as a dark brown solid. ¹H NMR^[10,29] (400 MHz, 298 K, DMSO-*d*₆) : δ = 4.20 (d, *J* = 8.0 Hz, 1H), 4.05

(dd, $J = 10.2, 1.6$ Hz, 1H), 3.97 (dd, $J = 8.0, 1.6$ Hz, 1H), 3.73 (dd, $J = 11.9, 1.7$ Hz, 1H), 3.58 (dd, $J = 12.0, 5.1$ Hz, 1H), 3.45 (s, 3H), 3.21 (ddd, $J = 10.2, 5.1, 1.7$ Hz, 1H). ^{13}C NMR (50 MHz, 298 K, DMSO- d_6): $\delta = 206.3, 104.8, 76.6, 76.6, 72.2, 60.8, 56.2$. HRMS (ESI) calculated for $\text{C}_7\text{H}_{12}\text{O}_6\text{Na}$ ($[\text{M}+\text{Na}]^+$): 215.053, found: 215.052 IR $\nu_{\text{max}}/\text{cm}^{-1}$: 3382 (OH), 2953 (C-H), 1738 (C=O), 1036 (C-O)

Methyl-2-(acetylamino)-2-deoxy- α -D-ribo-hexapyranoside-3-ulose (7)

Methyl-N-acetyl-glucosamine-pyranoside (941 mg, 4 mmol, 1.0 eq) was oxidized according to general procedure using 2,6-dichloro-1,4-benzoquinone (2.12 g, 12.0 mmol, 3.0 eq) and [(2,9-dimethyl-1,10-phenanthroline)-Pd(μ -OAc)] $_2$ (OTf) $_2$ (105 mg, 2.5 mol%) in acetonitrile/water (13.4 mL, 10 : 1, 0.3 M in substrate) within 4 h. Methyl-2-(acetylamino)-2-deoxy- α -D-ribo-hexapyranosid-3-ulose (792 mg, 3.4 mmol) was isolated in 85% as a dark brown solid. ^1H NMR $^{[30]}$ (400 MHz, 298 K, DMSO- d_6) : $\delta = 8.02$ (d, $J = 8.2$ Hz, 1H), 5.49 (d, $J = 6.0$ Hz, 1H), 4.98 (d, $J = 4.0$ Hz, 1H), 4.84 (s, 1H), 4.77 (dd, $J = 7.9, 3.7$ Hz, 1H), 4.17 (dd, $J = 9.5, 5.5$ Hz, 1H), 3.71 (d, $J = 11.7$ Hz, 1H), 3.66 – 3.57 (m, 1H), 3.57 – 3.49 (m, 1H), 3.26 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (50 MHz, DMSO- d_6): $\delta = 203.0, 169.7, 100.6, 75.6, 72.2, 60.7, 58.6, 54.5, 22.2$. HRMS (ESI) calculated for $\text{C}_9\text{H}_{15}\text{NO}_6\text{H}$ ($[\text{M}+\text{H}]^+$): 234.0972, found: 234.0972, $\text{C}_9\text{H}_{15}\text{O}_6\text{Na}$ ($[\text{M}+\text{Na}]^+$): 256.079, found: 256.079 IR $\nu_{\text{max}}/\text{cm}^{-1}$: 3296 (OH), 2878 (C-H), 1734 (C=O), 1035 (C-O)

Methyl-2-deoxy- α -D-erythro-hexopyranosid-3-ulose (9)

Methyl-2-desoxy- α -glucopyranoside (150 mg, 0.84 mmol, 1.0 eq) and 2,6-dichloro-1,4-benzoquinone (447 mg, 2.53 mmol, 3.0 eq) were dissolved in 2.5 mL dioxane/DMSO mixture (4:1, 0.3 M) and [(2,9-dimethyl-1,10-phenanthroline)-Pd(μ -OAc)] $_2$ (OTf) $_2$ (22 mg, 2.5 mol%) was added. The mixture was stirred at rt for 30 min. The reaction was quenched by adding water (12 mL) and the resulting precipitate was filtered. The filter was washed with 3 x 2.25 mL of water and the combined water layers were passed over a charcoal column (12 g of charcoal). The charcoal column was washed with 4 column volumes of water and subsequently the product was eluted with

water/acetonitrile 1:1 (2.5 column volumes). Methyl-2-deoxy- α -D-erythro-hexopyranosid-3-ulose (89 mg, 0.50 mmol, 60%) was obtained pure, after freeze drying, as greenish oil. **^1H NMR (400 MHz, CD_3OD):** δ 5.14 (d, J = 4.3 Hz, 1H), 4.18 (dd, J = 9.9, 1.1 Hz, 1H), 3.88 (dd, J = 12.0, 2.3 Hz, 1H), 3.81 (dd, J = 12.0, 4.7 Hz, 1H), 3.69 (ddd, J = 9.9, 4.7, 2.3 Hz, 1H), 3.34 (s, 3H), 2.88 (ddd, J = 14.1, 4.5, 1.1 Hz, 1H), 2.50 (dd, J = 14.1, 1.1 Hz, 1H). **^{13}C NMR (101 MHz, CD_3OD):** δ 207.39 ($\text{C}_{\text{quart.}}$), 101.34 (CH), 76.53 (CH), 74.27 (CH), 62.79 (CH_2), 55.18 (CH_3), 46.80 (CH_2). **HRMS (APCI)** calculated for $\text{C}_7\text{H}_{13}\text{O}_5$ ($[\text{M}+\text{H}]^+$): 177.076, found: 177.075

Phenyl- α -D-ribo-hexapyranoside-3-ulose (11)

Phenyl- α -D-glucopyranoside (108 mg, 0.42 mmol, 1.0 eq) was dissolved in a dioxane/DMSO mixture (4:1, 1.3 mL, 0.32 M) and dichlorobenzoquinone (223 mg, 1.26 mmol, 3.0 eq) and [(2,9-dimethyl-1,10-phenanthroline)-Pd(μ -OAc)]₂(OTf)₂ (11 mg, 2.5 mol%) were added. The reaction was stirred for 30 min and was quenched by addition of 8 mL water. The mixture was filtered and the precipitates were washed with water (3 x 2 mL). The water layer was concentrated using a Genevac ($T < 40^\circ\text{C}$), which gave 230 mg of crude product. The crude product was purified by column chromatography (21 g silica gel (SG2), eluent: DCM/MeOH 20/1, DCM was saturated with water), which gave 89 mg (contains about 13% DMSO according to ^1H -NMR, 0.30 mmol, 73%) of pure phenyl- α -D-ribo-hexapyranoside-3-ulose. **^1H NMR (400 MHz, CD_3OD):** δ = 7.29 (t, J = 7.9 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 7.03 (t, J = 7.4 Hz, 1H), 5.83 (d, J = 4.2 Hz, 1H), 4.58 (dd, J = 4.2, 1.1 Hz, 1H), 4.38 (dd, J = 9.0, 1.1 Hz, 1H), 3.85 – 3.74 (m, 3H). **^{13}C NMR (101 MHz, CD_3OD):** δ = 206.9 ($\text{C}_{\text{quart.}}$), 158.2 ($\text{C}_{\text{quart.}}$), 130.7 (CH), 124.0 (CH), 118.2 (CH), 101.9 (CH), 77.7 (CH), 76.0 (CH), 73.3 (CH), 62.3 (CH_2). **HRMS (ESI)** calculated for $\text{C}_{12}\text{H}_{14}\text{O}_6\text{Na}$ ($[\text{M}+\text{Na}]^+$): 277.068, found: 277.068

Thiophenyl- β -D-ribo-hexopyranoside-3-ulose (13)

Phenylthio- β -glucopyranoside (229 mg, 0.84 mmol, 1.0 eq) and 2,6-dichloro-1,4-benzoquinone (446 mg, 2.53 mmol, 3.0 eq) were dissolved in 2.8 mL dioxane/DMSO mixture (4:1, 0.3 M)

and [(2,9-dimethyl-1,10-phenanthroline)-Pd(μ -OAc)]₂(OTf)₂ was added portions wise over time (6.5 mol%, 57.2 mg 54.6 μ mol in total, 4x1 mol% every 2 h then 2x1.0 mol% every 1 h and 1x0.5 mol% after 1 h). The mixture was stirred at rt for an additional 1 h (12 h in total), no more starting material was observed by NMR-spectroscopy. NMR-spectroscopy of the untreated reaction mixture showed no indication for oxidation, elimination or hydrolyzation of the thiophenyl group. The reaction was quenched by adding water (17 mL) and the resulting precipitate was filtered. The filter was washed with 3 x 2 mL of water and the combined water layers were passed over a charcoal column (10 g charcoal). The charcoal column was washed with 6 column volumes of water and subsequently with acetonitrile/water mixtures (25%, 50%, 75%, 100% acetonitrile, 200 ml each, 50% acetonitrile eluted the product) to elute the product. The fractions containing the product were freeze dried to give 107 mg (0.39 mmol, 47%) of pure product as white fluffy solid. **¹H NMR (400 MHz, CD₃OD):** δ 7.64 – 7.49 (m, 2H), 7.37 – 7.20 (m, 3H), 4.68 (d, J = 10.0, 1H), 4.24 (dd, J = 10.1, 1.4 Hz, 1H), 4.06 (dd, J = 10.0, 1.4 Hz, 1H), 3.93 (dd, J = 12.3, 2.0 Hz, 1H), 3.79 (dd, J = 12.3, 4.9 Hz, 1H), 3.43 (ddd, J = 10.1, 4.9, 2.0 Hz, 1H). **¹³C NMR (101 MHz, CD₃OD):** δ = 207.4, 134.0, 133.9, 130.1, 129.1, 91.0, 84.0, 76.1, 73.9, 62.8. **HRMS (ESI)** calculated for C₁₂H₁₄O₅SNa ([M+Na]⁺): 293.045, found: 293.045

(6-O-*tert*-butyl-diphenylsilyl)-methyl- α -D-ribo-hexapyranoside-3-ulose (16)

Methyl-C6-TBDPS- α -glucopyranoside (364 mg, 0.84 mmol, 1.0 eq) and 2,6-dichloro-1,4-benzoquinone (447 mg, 2.53 mmol, 3.0 eq) were dissolved in DMSO (0.93 mL, 0.9 M) and [(2,9-dimethyl-1,10-phenanthroline)-Pd(μ -OAc)]₂(OTf)₂ (22 mg, 2.5 mol%) was added. The mixture was stirred at rt for 30 min. The reaction was quenched by adding water (12 mL) and the resulting precipitate was decanted. The precipitate was dissolved in MeOH/Et₂O to transfer it. Concentration of the dissolved precipitate *in vacuo* gave 774 mg of crude product, which was purified by silica column chromatography (eluent: gradient of acetone/MeOH 1:1 in DCM 0%-3%). 239 mg of pure (6-O-*tert*-butyl-diphenylsilyl)-methyl- α -D-ribo-hexapyranoside-3-ulose (0.56 mmol, 66%) was isolated as a white foam. **¹H NMR (400 MHz, CD₃OD):** δ = 7.82 – 7.64 (m, 4H), 7.54 – 7.28 (m, 6H), 5.08 (d, J = 4.3 Hz, 1H), 4.40 (dd, J = 4.3,

1.4 Hz, 1H), 4.34 (dd, $J = 9.8$, 1.4 Hz, 1H), 4.00 (d, $J = 3.3$ Hz, 2H), 3.74 (dt, $J = 9.7$, 3.3 Hz, 1H), 3.40 (s, 3H), 1.07 (s, 9H). ^{13}C NMR (101 MHz, CD_3OD): $\delta = 207.2$, 136.9, 136.9, 134.8, 134.7, 131.0, 131.0, 128.9, 103.8, 77.0, 76.3, 73.6, 64.8, 55.8, 27.4, 20.3. HRMS (ESI) calculated for $\text{C}_{23}\text{H}_{30}\text{O}_6\text{SiNa}$ ($[\text{M}+\text{Na}]^+$): 453.170, found: 453.164

(6-O-benzoyl)-methyl- α -D-ribo-hexapyranoside-3-ulose (18)

(6-O-benzoyl)-methyl- α -D-glucopyranoside (251 mg, 0.84 mmol, 1.0 eq) and 2,6-dichloro-1,4-benzoquinone (447 mg, 2.53 mmol, 3.0 eq) were dissolved in DMSO (0.93 mL, 0.9 M) and [(2,9-dimethyl-1,10-phenanthroline)-Pd(μ -OAc)]₂(OTf)₂ (22 mg, 2.5 mol%) was added. The mixture was stirred at rt for 1 h. The reaction was quenched by adding water (10 mL), the resulting precipitate was filtered and the filter was washed with water (1x10 mL, 1x5 mL). The water layer was passed over a charcoal column (10 g charcoal). The charcoal column was washed with 4.5 column volumes of water, 3 column volumes of water/acetonitrile (3:1) and subsequently the product was eluted with 3 column volumes of DCM/acetone/MeOH/water (56/20/20/4) which gave 409 mg of crude product. The crude product was purified by silica column chromatography (automated, eluent: gradient of DCM/MeOH 0-10%). 113 mg of pure (6-O-benzoyl)-methyl- α -D-ribo-hexapyranoside-3-ulose (45%) was isolated as a white foam. ^1H NMR (400 MHz, CD_3OD): $\delta = 8.09 - 8.03$ (m, 2H), 7.65 – 7.58 (m, 1H), 7.52 – 7.46 (m, 2H), 5.08 (d, $J = 4.3$ Hz, 1H), 4.72 (dd, $J = 11.9$, 2.2 Hz, 1H), 4.57 (dd, $J = 11.9$, 5.7 Hz, 1H), 4.48 (dd, $J = 4.3$, 1.5 Hz, 1H), 4.34 (dd, $J = 10.0$, 1.4 Hz, 1H), 3.99 (ddd, $J = 9.9$, 5.6, 2.1 Hz, 1H), 3.42 (s, 3H). ^{13}C NMR (101 MHz, CD_3OD): $\delta = 206.3$, 167.8, 134.6, 131.3, 130.7, 129.8, 103.8, 76.2, 74.2, 74.0, 65.3, 55.9. HRMS (ESI) calculated for $\text{C}_{14}\text{H}_{16}\text{O}_7\text{Na}$ ($[\text{M}+\text{Na}]^+$): 319.079, found: 319.074

Methyl- β -3-ketomaltoside (20)

Methyl- β -maltoside (150 mg, 0.42 mmol, 1.0 eq) was dissolved in a dioxane/DMSO mixture (4:1, 1.3 mL, 0.32 M), benzoquinone (137 mg, 1.26 mmol, 3.0 eq) and [(2,9-dimethyl-1,10-

phenanthroline)-Pd(μ -OAc)]₂(OTf)₂ (2.2 mg, 0.5 mol%) were added. The reaction was stirred for 4.5 h and was quenched by addition of 8 mL water. The mixture was filtered and the precipitates were washed with water (3 x 2 mL). The water layer was concentrated by Genevac (T <40°C), which gave 246 mg of crude product. The crude product was purified by column chromatography (10 g silica gel (SG2), eluent: DCM/acetone/MeOH/water 56/20/20/4) which gave 103 mg (0.29 mmol, 69%) of pure methyl- β -3-ketomaltoside. **¹H NMR (400 MHz, CD₃OD):** δ = 5.62 (d, *J* = 4.5 Hz, 1H), 4.45 (dd, *J* = 4.5, 1.6 Hz, 1H), 4.25 (dd, *J* = 9.6, 1.5 Hz, 1H), 4.15 (d, *J* = 7.8 Hz, 1H), 3.92 – 3.70 (m, 5H), 3.60 – 3.55 (m, 2H), 3.51 (s, 3H), 3.34 – 3.31 (m, 1H), 3.21 – 3.15 (m, 1H). **¹³C NMR (101 MHz, CD₃OD):** δ = 207.2, 105.4, 104.8, 80.6, 78.0, 77.7, 76.6, 76.4, 74.8, 73.4, 62.6, 62.1, 57.5. **HRMS (ESI)** calculated for C₁₃H₂₂O₁₁Na ([M+Na]⁺): 377.105, found: 377.105

Methyl- β -3-ketocellobioside (22)

Methyl- β -cellobioside (150 mg, 0.42 mmol, 1.0 eq) was in dissolved dioxane/DMSO mixture (4:1, 1.3 mL, 0.32 M) and benzoquinone (137 mg, 1.26 mmol, 3.0 eq) and [(2,9-dimethyl-1,10-phenanthroline)-Pd(μ -OAc)]₂(OTf)₂ (2.2 mg, 0.5 mol%) were added. The reaction was stirred for 3 h and was quenched by addition of 6 mL water. The mixture was filtered and the precipitates were washed with water (3 x 2 mL). The water layer was concentrated by Genevac (T <40°C), which gave 275 mg of crude product. The crude product was purified by column chromatography (10 g silica gel (SG2), eluent: DCM/acetone/MeOH/water 56/20/20/4), which gave 79 mg (0.22 mmol, 53%) of pure methyl- β -3-ketomaltoside. **¹H NMR (400 MHz, CD₃OD):** δ = 4.55 (d, *J* = 7.9 Hz, 1H), 4.25 (dd, *J* = 10.2, 1.5 Hz, 1H), 4.22 (d, *J* = 7.8 Hz, 1H), 4.19 (dd, *J* = 8.0, 1.6 Hz, 1H), 3.95 (dd, *J* = 12.1, 2.0 Hz, 1H), 3.88 (qd, *J* = 12.2, 3.1 Hz, 3H), 3.78 (dd, *J* = 12.1, 5.0 Hz, 1H), 3.66 (t, *J* = 9.2 Hz, 1H), 3.56 (t, *J* = 9.0 Hz, 1H), 3.53 (s, 3H), 3.44 – 3.34 (m, 2H), 3.24 (dd, *J* = 9.0, 8.0 Hz, 1H). **¹³C NMR (101 MHz, CD₃OD):** δ = 206.8, 105.9, 105.4, 80.5, 78.4, 78.4, 76.6, 76.53, 75.0, 73.6, 62.5, 61.6, 57.5. **HRMS (ESI)** calculated for C₁₃H₂₂O₁₁Na ([M+Na]⁺): 377.105, found: 377.100.

Selectivity based on NMR-spectroscopy

The selectivity of the reaction is deduced from the ^1H -NMR spectra which were taken either during the reaction or from the crude product before any purification or separation.

Figure 1 Crude reaction mixture of **16**

The crude spectrum of **16** shows no additional oxidation products as can be seen from the region from ~3.5 to 5 ppm. Oxidation at C3 is the only product.

Figure 2 Crude reaction mixture of **18**

The crude spectrum of **18** shows only minor byproducts as can be seen in the region from 3.2 – 5 ppm, **18** is at least 95% pure with respect to other oxidation products.

Figure 3 Crude reaction mixture of **20**

The crude spectrum of **20**, shows only minor byproducts in the region from 3 - 5.8 ppm. **20** is more than 90% pure with respect to other oxidation products.

Figure 4 Crude reaction mixture of 22

The spectrum of crude **22** shows byproducts at 4.5 -4.3 ppm, but the byproducts do not exceed 5% per oxidation product.

Optimization of the catalyst loading

Oxidation of methyl- α -glucopyranoside using dichlorobenzoquinone as oxidant

Methyl- α -glucopyranoside (1 mmol, 1.0 eq) and 2,6-dichlorobenzoquinone (3 mmol, 3.0 eq) were dissolved in DMSO (0.5 M). The catalyst [(2,9-dimethyl-1,10-phenanthroline)-Pd(μ -OAc) $_2$ (OTf) $_2$ (0.5 mol%, 1 mol% or 1.1 mmol%) was added and the mixture was stirred at rt and followed by NMR.

Table 1 Catalyst loading using dichlorobenzoquinone as oxidant

Catalyst loading	Conversion after 30 min ^[a]

0.5 mol%	47%
1 mol%	95%
1.1 mol%	Full

[a] no further conversion was observed after prolonged reaction time

Oxidation of methyl- α -glucopyranoside using benzoquinone as oxidant

Methyl- α -glucopyranoside (1 mmol, 1.0 eq) and benzoquinone (3 mmol, 3.0 eq) were dissolved in DMSO (0.5 M). The catalyst [(2,9-dimethyl-1,10-phenanthroline)-Pd(μ -OAc)]₂(OTf)₂ (0.1 mmol% or 0.5 mmol%) was added and the mixture was stirred at rt and followed by NMR.

Table 2 Catalyst loading using benzoquinone as oxidant

Catalyst loading	Conversion after 30 min	Conversion after 60 min	Conversion after 100 min	Conversion after 22 h ^[a]
0.1 mol%	33%	52%	66%	95%
0.5 mol%	Full			

[a] no further conversion was observed after prolonged reaction time

Synthesis of methyl allopyranoside and aminoglucoside

Methyl- α -allopyranoside (27)

Methyl- α -D-ribo-hexapyranosid-3-ulose (200 mg, 1.04 mmol, 1.0 eq) was dissolved in MeOH (8.5 mL) and the mixture was cooled to 0 °C. Sodium borohydride (118 mg, 3.12 mmol, 3.0 eq) was added and the mixture stirred for 30 min at rt. Excess borohydride was destroyed by addition of acidic ion exchange resin (Amberlite® 120 H⁺-form), the mixture was filtered over celite and concentrated *in vacuo*. The residue was co-evaporated with MeOH (3x 10 mL) to give 193 mg (0.99 mmol, 95%) of methyl- α -allopyranoside as

reddish sticky oil. **¹H NMR**^[3] (400 MHz, CD₃OD): δ = 4.69 (d, *J* = 3.8 Hz, 1H), 3.98 (appears as t, *J* = 3.2 Hz, 1H), 3.88 – 3.82 (m, 1H), 3.74 – 3.67 (m, 2H), 3.60 (appears as t, *J* = 3.6 Hz, 1H), 3.47 (dd, *J* = 9.7, 3.1 Hz, 1H), 3.43 (s, 3H). **¹³C NMR** (101 MHz, CD₃OD) δ = 101.6, 73.6, 69.6, 69.1, 68.4, 62.8, 56.2. **HRMS (ESI)** calculated for C₇H₁₄O₆Na ([M+Na]⁺): 217.068, found: 217.068.

***E/Z*-Methyl-3-*O*-methyloxime- α -D-ribo-hexapyranoside (28)**

Methyl- α -D-ribo-hexapyranosid-3-ulose (330 mg, 1.70 mmol, 1.0 eq), *O*-methylhydroxylamine hydrochloride (215 mg, 2.58 mmol, 1.5 eq) and NaHCO₃ (218 mg, 2.58 mmol, 1.5 eq) were heated at reflux for 2 h in methanol (13 mL). After filtration to remove salts, and evaporation of the solvent, the residue was extracted with hot ethyl acetate. The extract was passed over a short silica gel column and was concentrated *in vacuo*, to give methyl-3-*O*-methyloxime- α -D-ribo-hexapyranoside (344 mg, 1.55 mmol, 92% as a mixture of *E/Z* isomers) as a sticky yellow solid. **HRMS (ESI)** exact mass calculated for C₈H₁₅NO₆H ([M+H]⁺): 222.097, found: 222.097, C₉H₁₅O₆Na ([M+Na]⁺): 244.079, found: 244.079 **IR** ν_{max} /cm⁻¹: 3454 (OH), 2946 (C-H), 1034 (C-O)

Methyl-3-amino- α -D-ribo-hexapyranoside (29a)

E/Z-Methyl-3-*O*-methyloxime- α -D-ribo-hexapyranoside (**26**; 240 mg, 1.08 mmol, 1.0 eq) in acetic acid (5 mL) was hydrogenated over platinum(IV) oxide (25 mg, 0.11 mmol, 10 mol%) under hydrogen pressure (5 bar) for 24 h. The mixture was passed over a short celite column and concentrated *in vacuo*, to give methyl-3-amino- α -D-ribo-hexapyranoside (208 mg, 1.08 mmol, 99%) as a sticky slightly yellow solid. The product was directly used in a subsequent per-acetylation reaction. **¹H NMR (400 MHz, 298 K, DMSO-*d*₆)** : δ = 5.21 (d, *J* = 3.1 Hz, 1H), 4.31 – 4.26 (m, 2H), 4.23 (dd, *J* = 9.9, 4.1 Hz, 1H), 4.15 (dd, *J* = 11.0, 4.9 Hz, 2H), 4.00 (appears as t, *J* = 3.7 Hz, 1H), 3.90 (s, 3H).

Methyl-3-acetamido-2,4,6-tri-*O*-acetyl-3-deoxy- α -D-ribo-hexapyranoside (29b)

Methyl-3-amino- α -D-ribo-hexapyranosid (**26a**; 208 mg, 1.08 mmol, 1.0 eq) was dissolved in dry pyridine (2.4 mL) and acetic anhydride (1 mL, 9.9 mmol, 8 eq). The reaction mixture was stirred overnight. The mixture was co-evaporated with toluene (1 mL) and purified by automated silicagel column chromatography (GRACE) with a solvent gradient of pentane/EtOAc (1:1 to pure EtOAc) to give methyl-3-acetamido-2,4,6-tri-*O*-acetyl-3-deoxy- α -D-ribo-hexapyranoside (245 mg, 63%, 0.68 mmol) as a white solid. ^1H NMR^[31] (400 MHz, 298 K, DMSO-*d*₆): δ = 7.11 (d, J = 8.7 Hz, 1H), 4.81 (d, J = 3.2 Hz, 1H), 4.79 – 4.76 (m, 1H), 4.73 (d, J = 9.3 Hz, 2H), 4.15 (d, J = 3.3 Hz, 2H), 4.10 (dd, J = 9.0, 3.4 Hz, 1H), 3.30 (s, 3H), 2.00 (s, 3H), 1.97 (s, 3H), 1.89 (s, 3H), 1.88 (s, 3H). ^{13}C NMR (50 MHz, 298 K, CDCl₃): δ = 170.9, 170.8, 169.8, 169.6, 98.1, 66.7, 66.5, 64.1, 62.5, 56.2, 47.9, 23.8, 20.9, 20.9.

Synthesis of methyl-3-acetamido- α -D-ribo-hexapyranoside (29c)

Methyl-3-acetamido-2,4,6-tri-*O*-acetyl-3-deoxy- α -D-ribo-hexapyranoside (**26b**; 141 mg, 0.39 mmol, 1.0 eq) was dissolved in dry methanol (1.4 mL). To this mixture, sodium methanolate (1 M, 0.1 mL) was added and the reaction mixture was stirred overnight at rt upon which the reaction had finished as indicated by TLC (pentane/EtOAc 1:1). The reaction was quenched with acidic ion exchange resin (Amberlite® 120 H⁺-form) and stirred for an additional 10 min. After passing over a short silica gel column, the solvent was removed *in vacuo* to give methyl-3-amido- α -D-ribo-hexapyranoside (90 mg, 99%, 0.38 mmol) as a sticky slightly red solid. ^1H NMR (400 MHz, 298 K, DMSO-*d*₆) : δ = 6.71 (d, J = 8.9 Hz, 1H, NH), 4.52 (d, J = 3.0 Hz, 1H, 1-H), 4.38 – 4.30 (m, 1H, 3-H), 3.63 (dd, J = 11.4, J = 1.6 Hz, 1H, 6-H), 3.56 (dd, J = 5.2, 2.7 Hz, 1H, 2-H), 3.46 (m, 1H, 6'-H), 3.43 (m, 2H, 4-H, 5-H), 3.32 (s, 3H, OCH₃), 1.88 (s, 3H, CH₃). ^{13}C NMR (101 MHz, 298 K, DMSO-*d*₆) : δ = 170.9 (NHCOCH₃), 99.6 (CH, C-1), 68.8 (CH, C-4), 66.3 (CH, C-2), 66.0 (CH, 5-C), 60.7 (CH₂, C-6), 54.8 (OCH₃), 52.8 (CH, C-3), 23.6 (NHCOCH₃). gCOSY (400 MHz, 298 K, DMSO-*d*₆) : δ (^1H) / δ (^1H) = 6.71 / 4.34 (NH / 3-H), 4.52 / 3.56 (1-H / 2-H),

4.38-4.30 / 6.71, 3.56, 3.43 (3-H / NH, 2-H, 4-H), 3.63 / 3.46, 3.43 (6-H / 6'-H, 5-H), 3.56 / 4.52, 4.34 (2-H / 1-H, 3-H), 3.46 / 3.63, 3.43 (6'-H / 6-H, 5-H), 3.43 / 4.34, 3.43 (4-H / 3-H, 5-H), 3.43 / 3.63, 3.46 (5-H / 6-H, 6'-H). **gHSQC (400 MHz, 298 K, DMSO-*d*₆)** : δ (¹H) / δ (¹³C) = 4.52 / 99.63 (1-H / C-1), 4.38 – 4.30 / 52.75 (3-H, C-3), 3.63 / 60.73 (6-H / C-6), 3.56 / 66.34 (2-H / C-2), 3.46 / 60.73 (6'-H / C-6), 3.43 / 68.83 (4-H / C-4), 3.43 / 66.00 (5-H / C-5), 3.32 / 23.58 (OCH₃ / OCH₃), 1.88 / 54.81 (CH₃ / CH₃). **NOESY (400 MHz, 298 K, DMSO-*d*₆)**: δ (¹H) / δ (¹H) = 3.43 / 3.63, 3.56 (4-H / 6-H, 2-H), 3.43 / 6.71, 1.88 (5-H / NH, CH₃). **HRMS (ESI)** calculated for C₉H₁₈NO₆ ([M+H]⁺): 236.113, found: 236.113, C₉H₁₇NO₆Na ([M+Na]⁺): 258.095, found: 258.095

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Spectroscopic data of keto-sugars 3-22

Methyl- α -D-ribo-hexapyranoside-3-ulose (3)

Figure 5 ^1H -NMR of methyl- α -D-ribo-hexapyranoside-3-ulose in DMSO-d_6

Figure 6 ^{13}C -NMR of methyl- α -D-ribo-hexapyranoside-3-ulose in DMSO-d_6

Figure 7 APT-NMR of methyl- α -D-ribo-hexapyranoside-3-ulose in MeOD- d_4

Figure 8 COSY-NMR of methyl- α -D-ribo-hexapyranoside-3-ulose in DMSO- d_6

Figure 9 HSQC-NMR of methyl- α -D-ribo-hexapyranoside-3-ulose in DMSO-d_6

Figure 10 NOESY-NMR of methyl- α -D-ribo-hexapyranoside-3-ulose in DMSO- d_6

NL:
1.14E8
MH_008#2-17
RT: 0.01-0.42
AV: 16 T:

NL:
9.13E5
C₇H₁₂O₆Na:
C₇H₁₂O₆Na:
pa Chrg 1

Figure 11 HR/MS of methyl-α-D-ribo-hexapyranoside-3-ulose

Methyl-β-D-ribo-hexapyranoside-3-ulose (5)

Figure 12 ¹H-NMR of methyl-β-D-ribo-hexapyranoside-3-ulose in DMSO-d₆

Figure 13 COSY-NMR of methyl- β -D-ribo-hexapyranoside-3-ulose in DMSO-d_6

Figure 14 NOESY-NMR of methyl- β -D-ribo-hexapyranoside-3-ulose in DMSO- d_6

Figure 15 HSQC-NMR of methyl- β -D-ribo-hexapyranoside-3-ulose in DMSO-d_6

Figure 16 ^{13}C -NMR of methyl- β -D-ribo-hexapyranoside-3-ulose in DMSO-d_6

Methyl-2-(acetylamino)-2-deoxy- α -D-ribo-hexapyranoside-3-ulose (7)

Figure 17 $^1\text{H-NMR}$ of methyl-2-(acetylamino)-2-deoxy- α -D-ribo-hexapyranoside-3-ulose in DMSO-d_6

Figure 18 ¹³C-NMR of methyl-2-(acetylamino)-2-deoxy-α-D-ribo-hexapyranoside-3-ulose in DMSO-d₆

Figure 19 APT-NMR of methyl-2-(acetylamino)-2-deoxy- α -D-ribo-hexapyranoside-3-ulose in MeOD- d_4

Figure 20 COSY-NMR of methyl-2-(acetylamino)-2-deoxy- α -D-ribo-hexapyranoside-3-ulose in DMSO- d_6

Figure 21 NOESY-NMR of Methyl-2-(acetylamino)-2-deoxy- α -D-ribo-hexapyranoside-3-ulose in DMSO-d₆

Figure 22 HSQC-NMR of Methyl-2-(acetylamino)-2-deoxy- α -D-ribo-hexapyranoside-3-ulose in DMSO- d_6

Figure 23 HR/MS of methyl-2-(acetylamino)-2-deoxy-α-D-ribo-hexapyranoside-3-ulose

Methyl-2-deoxy- α -D-erythro-hexopyranoside-3-ulose (9)

Figure 24 ¹H-NMR of methyl-2-deoxy- α -D-erythro-hexopyranoside-3-ulose in MeOD-d₄

Figure 25 ¹³C-NMR of methyl-2-deoxy- α -D-erythro-hexopyranoside-3-ulose in MeOD-d₄

Figure 26 APT-NMR of methyl-2-deoxy- α -D-erythro-hexopyranoside-3-ulose in MeOD- d_6

Figure 27 COSY-NMR of methyl-2-deoxy- α -D-erythro-hexopyranoside-3-ulose in MeOD- d_6

Figure 28 HSQC-NMR of methyl-2-deoxy- α -D-erythro-hexopyranoside-3-ulose in MeOD- d_6

Figure 29 HR/MS of methyl-2-deoxy- α -D-erythro-hexopyranoside-3-ulose

Phenyl- α -D-ribo-hexapyranoside-3-ulose (11)

Figure 30 ¹H-NMR of phenyl- α -D-ribo-hexapyranoside-3-ulose in MeOD-d₆

Figure 31 ¹³C-NMR of phenyl- α -D-ribo-hexapyranoside-3-ulose in MeOD-d₆

Figure 32 APT-NMR of phenyl- α -D-ribo-hexapyranoside-3-ulose in MeOD- d_6

Figure 33 COSY-NMR of phenyl- α -D-ribo-hexapyranoside-3-ulose in MeOD- d_6

Figure 34 HMQC-NMR of phenyl- α -D-ribo-hexapyranoside-3-ulose in MeOD- d_6

Figure 35 pESI-HRMS of phenyl- α -D-ribo-hexapyranoside-3-ulose

Thiophenyl- β -D-ribo-hexopyranoside-3-ulose (13)

Figure 36 $^1\text{H-NMR}$ of thiophenyl- β -D-ribo-hexopyranoside-3-ulose in MeOD-d_6

Figure 37 ¹³C-NMR of thiophenyl-β-D-ribo-hexopyranoside-3-ulose in MeOD-d₆

Figure 38 APT-NMR of thiophenyl- β -D-ribo-hexopyranoside-3-ulose in MeOD- d_6

Figure 39 COSY-NMR of thiophenyl-β-D-ribo-hexopyranoside-3-ulose in MeOD-d₆

Figure 40 HMQC-NMR of thiophenyl- β -D-ribo-hexopyranoside-3-ulose in MeOD- d_6

Figure HRMS of thiophenyl-β-D-ribo-hexopyranoside-3-ulose 13

(6-O-tert-butyl-diphenylsilyl)-methyl- α -D-ribo-hexapyranoside-3-ulose (16)

Figure 41 ¹H-NMR of (6-O-tert-butyl-diphenylsilyl)-methyl- α -D-ribo-hexapyranoside-3-ulose in MeOD-d₆

Figure 42 ¹³C-NMR of (6-O-tert-butyl-diphenylsilyl)-methyl-α-D-ribo-hexapyranoside-3-ulose in MeOD-d₆

Figure 43 APT-NMR of (6-O-tert-butyl-diphenylsilyl)-methyl- α -D-ribo-hexapyranoside-3-ulose in MeOD- d_6

Figure 44 COSY-NMR of (6-O-tert-butyl-diphenylsilyl)-methyl- α -D-ribo-hexapyranoside-3-ulose in MeOD- d_6

Figure 45 HSQC-NMR of (6-O-tert-butyl-diphenylsilyl)-methyl- α -D-ribo-hexapyranoside-3-ulose in MeOD- d_6

Figure 46 HR/MS of (6-O-tert-butyl-diphenylsilyl)-methyl-α-D-ribo-hexapyranoside-3-ulose

(6-O-benzoyl)-methyl- α -D-ribo-hexapyranoside-3-ulose (18)

Figure 47 ¹H-NMR of (6-O-benzoyl)-methyl- α -D-ribo-hexapyranoside-3-ulose in MeOD-D₄

Figure 48 ¹³C-NMR of (6-O-benzoyl)-methyl-α-D-ribo-hexapyranoside-3-ulose in MeOD-D₄

Figure 49 APT-NMR of (6-O-benzoyl)-methyl- α -D-ribo-hexapyranoside-3-ulose in MeOD-D₄

Figure 50 HSQC-NMR of (6-O-benzoyl)-methyl- α -D-ribo-hexapyranoside-3-ulose in MeOD- D_4

Figure 51 NOESY-NMR of (6-O-benzoyl)-methyl- α -D-ribo-hexapyranoside-3-ulose in MeOD-D₄

Figure 52 HR/MS of (6-O-benzoyl)-methyl- α -D-ribo-hexapyranoside-3-ulose

Methyl- β -3-ketomaltoside (20)

Figure 53 ¹H-NMR of methyl- β -3-ketomaltoside in MeOD-d₄

Figure 54 ¹³C-NMR of methyl-β-3-ketomaltoside in MeOD-d₄

Figure 55 APT-NMR of methyl- β -3-ketomaltoside in MeOD- d_4

Figure 56 COSY-NMR of methyl-β-3-ketomaltoside in MeOD-d₄

Figure 57 HMQC-NMR of methyl-β-3-ketomaltoside in MeOD-d₄

Figure 58 HR/MS of methyl-β-3-ketomaltoside

Methyl- β -3-cellobioside (22)

Figure 59 $^1\text{H-NMR}$ of methyl- β -3-ketocellobioside in MeOD-d_4

Figure 60 ¹³C-NMR of methyl-β-3-ketocellobioside in MeOD-d₄

Figure 61 APT-NMR of methyl-β-3-ketocellobioside in MeOD-d₄

Figure 62 COSY-NMR of methyl- β -3-ketocellobioside in MeOD- d_4

Figure 63 HMQC-NMR of methyl-β-3-ketocellobioside in MeOD-d₄

Figure 64 NOESY-NMR of methyl- β -3-ketocellobioside in MeOD- d_4

Figure 65 HR/MS of methyl-β-3-ketocellobioside

Spectroscopic data of compound 27, 28 and 29

Methyl- α -allopyranoside (27)

Figure 66 ¹H-NMR of Methyl- α -allopyranoside in MeOD-d₄

Figure 67 ¹³C-NMR of Methyl-α-allopyranoside in MeOD-d₄

Figure 68 APT-NMR of Methyl- α -allopyranoside in MeOD- d_4

Figure 69 COSY-NMR of Methyl- α -allopyranoside in MeOD- d_4

Figure 70 HMQC-NMR of Methyl- α -allopyranoside in MeOD- d_4

Figure 71 HR/MS of Methyl-α-allopyranoside

E/Z-Methyl-3-O-methyloxime- α -D-ribo-hexapyranoside (28)

Figure 72 ¹H-NMR of E/Z-methyl-3-O-methyloxime- α -D-ribo-hexapyranoside in DMSO-d₆

Figure 73 HR/MS of E/Z-methyl-3-O-methyloxime-α-D-ribo-hexapyranoside

Methyl-3-amino- α -D-ribo-hexapyranoside (29a)

Figure 74 ¹H-NMR of methyl-3-amino- α -D-ribo-hexapyranoside in DMSO-d₆

Methyl-3-acetamido-2,4,6-tri-O-acetyl-3-deoxy- α -D-ribo-hexapyranoside (29b)

Figure 75 $^1\text{H-NMR}$ Methyl-3-acetamido-2,4,6-tri-O-acetyl-3-deoxy- α -D-ribo-hexapyranoside in DMSO-d_6

Figure 76 ^{13}C -NMR methyl-3-acetamido-2,4,6-tri-O-acetyl-3-deoxy- α -D-ribo-hexapyranoside in CDCl_3

Figure 77 APT-NMR methyl-3-acetamido-2,4,6-tri-O-acetyl-3-deoxy- α -D-ribo-hexapyranoside in CDCl_3

Methyl-3-acetamido- α -D-ribo-hexapyranoside (29c)

Figure 78 ¹H-NMR of methyl-3-acetamido- α -D-ribo-hexapyranoside in DMSO- d_6

Figure 79 ^{13}C -NMR of methyl-3-acetamido- α -D-ribo-hexapyranoside in DMSO-d_6

Figure 80 APT-NMR of methyl-3-acetamido- α -D-ribo-hexapyranoside in DMSO- d_6

Figure 81 COSY-NMR of methyl-3-acetamido- α -D-ribo-hexapyranoside in DMSO-d_6

Figure 82 HSQC-NMR of methyl-3-acetamido- α -D-ribo-hexapyranoside in DMSO- d_6

Figure 83 NOESY-NMR of methyl-3-acetamido- α -D-ribo-hexapyranoside in DMSO-d₆

Figure 84 HR/MS of methyl-3-acetamido- α -D-ribo-hexapyranoside