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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, ACR, and Carbosynth and were used without further purification. For purification via column chromatography silica gel from either Silicycle (Sil 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-d6, MeOD-d4 or D2O as solvent. Chemical shift values are reported in ppm with the solvent resonance as the internal standard (DMSO-d6: δ 2.50 for 1H, δ 39.51 for 13C; MeOD-d4: δ 3.31 for 1H, δ 49.15 for 13C; D2O: δ 4.80 for 1H; acetonitrile-d3: 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-*d₆*): 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-*d₆*): 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 νmax/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-*d₆*): 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 C$_{12}$H$_{12}$O$_6$Na ([M+Na]$^+$): 215.053, found: 215.052

IR $\nu_{\text{max}}$/cm$^{-1}$: 3382 (OH), 2953 (C-H), 1738 (C=O), 1036 (C-O)

Methyl-2-(acetylamino)-2-deoxy-$\alpha$-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($\mu$-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-$\alpha$-D-ribo-hexapyranosid-3-ulose (792 mg, 3.4 mmol) was isolated in 85% as a dark brown solid. $^1$H NMR (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 C$_9$H$_{15}$NO$_6$H ([M+H]$^+$): 234.0972, found: 234.0972, C$_9$H$_{15}$O$_6$Na ([M+Na]$^+$): 256.079, found: 256.079 IR $\nu_{\text{max}}$/cm$^{-1}$: 3296 (OH), 2878 (C-H), 1734 (C=O), 1035 (C-O)

Methyl-2-deoxy-$\alpha$-D-erythro-hexopyranosid-3-ulose (9)

Methyl-2-desoxy-$\alpha$-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($\mu$-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. $^1$H NMR (400 MHz, CD$_3$OD): $\delta$ 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$_3$OD): $\delta$ 207.39 (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 C$_7$H$_{13}$O$_5$ ([M+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°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 $^1$H-NMR, 0.30 mmol, 73%) of pure phenyl-α-D-ribo-hexapyranoside-3-ulose. $^1$H NMR (400 MHz, CD$_3$OD): $\delta$ = 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$_3$OD): $\delta$ = 206.9 (C$_{\text{quart.}}$), 158.2 (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 C$_{12}$H$_{16}$O$_6$Na ([M+Na]$^+$): 277.068, found: 277.068

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

Phenyithio- 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 μmol 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). 13C NMR (101 MHz, CD3OD): δ = 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 C23H30O6SiNa ([M+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/acetone (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, CD3OD): δ = 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). 13C NMR (101 MHz, CD3OD): δ = 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 C14H16O7Na ([M+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.\(^1\)H NMR (400 MHz, CD₃OD): \(\delta = 5.62\) (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).\(^1\)C NMR (101 MHz, CD₃OD): \(\delta = 207.2, 105.4, 104.8, 80.6, 78.0, 77.7, 76.6, 76.4, 74.8, 73.4, 62.6, 62.1, 57.5\). 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. \(^1\)H NMR (400 MHz, CD₃OD): \(\delta = 4.55\) (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). \(^1\)C NMR (101 MHz, CD₃OD): \(\delta = 206.8, 105.9, 105.4, 80.5, 78.4, 78.4, 76.6, 76.53, 75.0, 73.6, 62.5, 61.6, 57.5\). 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 $^1$H-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 $\sim$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.
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**

<table>
<thead>
<tr>
<th>Catalyst loading</th>
<th>Conversion after 30 min$^a$</th>
</tr>
</thead>
</table>
Oxidation of methyl-\(\alpha\)-glucopyranoside using benzoquinone as oxidant

Methyl-\(\alpha\)-glucopyranoside (1 mmol, 1.0 eq) and benzoquinone (3 mmol, 3.0 eq) were dissolved in DMSO (0.5 M). The catalyst \([(2,9\text{-dimethyl-1,10-phenanthroline})\text{-Pd(\(\mu\)-OAc)}]_2(\text{OTf})_2\) (0.1 mmol% or 0.5 mmol%) was added and the mixture was stirred at rt and followed by NMR.

<table>
<thead>
<tr>
<th>Catalyst loading</th>
<th>Conversion after 30 min</th>
<th>Conversion after 60 min</th>
<th>Conversion after 100 min</th>
<th>Conversion after 22 h([a])</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 mol%</td>
<td>33%</td>
<td>52%</td>
<td>66%</td>
<td>95%</td>
</tr>
<tr>
<td>0.5 mol%</td>
<td>Full</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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

Synthesis of methyl allopyranoside and aminoglucoside

Methyl-\(\alpha\)-allopyranoside (27)

Methyl-\(\alpha\)-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-\(\alpha\)-allopyranoside as
reddish sticky oil. $^1$H NMR$[^{[3]}]$ (400 MHz, CD$_3$OD): $\delta = 4.69$ (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). $^{13}$C NMR (101 MHz, CD$_3$OD) $\delta = 101.6$, 73.6, 69.6, 69.1, 68.4, 62.8, 56.2. HRMS (ESI) calculated for C$_7$H$_{14}$O$_6$Na ([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 NaHCO$_3$ (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 C$_8$H$_{15}$NO$_6$H ([M+H$^+$]): 222.097, found: 222.097, C$_9$H$_{15}$O$_6$Na ([M+Na$^+$]): 244.079, found: 244.079 IR $\nu_{max}$/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. $^1$H NMR (400 MHz, 298 K, DMSO-$d_6$) : $\delta = 5.21$ (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-\(\alpha\)-D-ribo-hexapyranoside (29b)

Methyl-3-amino-\(\alpha\)-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-\(\alpha\)-D-ribo-hexapyranoside (245 mg, 63%, 0.68 mmol) as a white solid.

\(^1\)H NMR\(^{[31]}\) (400 MHz, 298 K, DMSO-\(d_6\)):
\[\delta = 7.11 (d, J = 8.7 \text{ Hz}, 1H), \]
\[4.81 (d, J = 3.2 \text{ Hz}, 1H), 4.79 - 4.76 (m, 1H), 4.73 (d, J = 9.3 \text{ Hz}, 2H), 4.15 (d, J = 3.3 \text{ Hz}, 2H), 4.10 (dd, J = 9.0, 3.4 \text{ 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, CDCl\(_3\)):
\[\delta = 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-\(\alpha\)-D-ribo-hexapyranoside (29c)

Methyl-3-acetamido-2,4,6-tri-O-acetyl-3-deoxy-\(\alpha\)-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\textsuperscript{®} 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-\(\alpha\)-D-ribo-hexapyranoside (90 mg, 99%, 0.38 mmol) as a sticky slightly red solid.

\(^1\)H NMR (400 MHz, 298 K, DMSO-\(d_6\)):
\[\delta = 6.71 (d, J = 8.9 \text{ Hz}, 1H, NH), 4.52 (d, J = 3.0 \text{ Hz}, 1H, 1-H), 4.38 - 4.30 (m, 1H, 3-H), 3.63 (dd, J = 11.4, J = 1.6 \text{ 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, OCH\(_3\)), 1.88 (s, 3H, CH\(_3\)).

\(^{13}\)C NMR (101 MHz, 298 K, DMSO-\(d_6\)):
\[\delta = 170.9 (\text{NHCOCH}_3), 99.6 (\text{CH}, C-1), 68.8 (\text{CH}, C-4), 66.3 (\text{CH}, C-2), 66.0 (\text{CH}, C-5), 60.7 (\text{CH}, C-6), 54.8 (\text{OCH}_3), 52.8 (\text{CH}, C-3), 23.6 (\text{NHCOCH}_3).

\(g\)COSY (400 MHz, 298 K, DMSO-\(d_6\)):
\[\delta (\text{H}) / \delta (\text{H}) = 6.71 / 4.34 (\text{NH} / 3\text{-H}), 4.52 / 3.56 (1\text{-H} / 2\text{-H}), \]
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). \textbf{gHSQC (400 MHz, 298 K, DMSO-d$_6$)}: $\delta$ (1H) / $\delta$ (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 (OCH$_3$/ OCH$_3$), 1.88 / 54.81 (CH$_3$ / CH$_3$). \textbf{NOESY (400 MHz, 298 K, DMSO-d$_6$)}: $\delta$ (1H) / $\delta$ (1H) = 3.43 / 3.63, 3.56 (4-H / 6-H, 2-H), 3.43 / 6.71, 1.88 (5-H / NH, CH$_3$). \textbf{HRMS (ESI)} calculated for C$_9$H$_{18}$NO$_6$ ([M+H]$^+$): 236.113, found: 236.113, C$_9$H$_{17}$NO$_6$Na ([M+Na]$^+$): 258.095, found: 258.095

\textbf{Literature}

Spectroscopic data of keto-sugars 3-22

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

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Figure 33 COSY-NMR of phenyl-α-D-ribo-hexapyranoside-3-ulos in MeOD-d$_6$
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