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Note

Synthesis of 2,4-dinitrophenyl glycosides of D-xylobiose and D-mannobiose

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Abstract

D-Xylobiose hexaacetate and D-mannobiose octaacetate were obtained from xylan and mannan digests, respectively, by acetylation followed by chromatographic separation. Selective anomeric deacetylation of each peracetate, followed by 2,4-dinitrophenylation and subsequent de-protection gave 2,4-dinitrophenyl β-D-xylobioside and 2,4-dinitrophenyl α- and β-D-mannobiosides, respectively. The tetra-acetates of 2,4-dinitrophenyl α- and β-D-mannopyranoside were similarly obtained.

Keywords: Glycosides; 2,4-Dinitrophenyl glycosides; Xylobiosides; Mannosides; Mannobiosides; Xylobiose acetates; Mannobiose acetates; Hydrazine hydrate; 2,4-Dinitrofluorobenzene; conformation

In connection with enzyme studies [1,2], samples of 2,4-dinitrophenyl β-D-xylobioside ($DNPX_2$) (**4b**) and 2,4-dinitrophenyl β-D-mannobioside ($DNPM_2$) (**11b**) were required. The former compound **4b** has been reported [3] but no preparative details or properties were given other than the general methodology. This involved selective cleavage [4] of the anomeric acetate group of D-xylobiose hexaacetate (**1**) followed by arylation with 2,4-dinitrofluorobenzene [5] and finally deprotection with methanol–hydrogen chloride [6]. This approach was used in the present work for both **4b** and **11b**. Other recent publications have described syntheses of 2- and 4-nitrophenyl β-D-xylobiosides from penta-acetylxylobiosyl bromide [7] or penta-benzoylxylobiosyl bromide [8] and of 2,5- and 3,4-dinitrophenyl β-D-xylobiosides via glycosylation of the related 2,5- and 3,4-dinitrophenyl β-D-xylopyranosides [9].

Xylobiose hexaacetate (**1**) was obtained from a xylan digest (which contained xylose, xylobiose and higher molecular weight materials) by acetylation followed by chromatographic separation of the products. A similar method was used recently by Mechalloy et al. [7]. The hexaacetate fraction contained both **1a** (H-1: δ 6.22, $J_{1,2}$ 3.7 Hz) and **1b** (H-1: δ 5.65, $J_{1,2}$ 7.4 Hz) (**1a**:**1b**:1:6), **1b** [10] could be obtained from the mixture by crystallisation from ethanol. Treatment of either **1b** or the mixture **1** with hydrazine acetate in DMF gave the pentaacetate **2**. Reaction of **2** with 2,4-dinitrofluorobenzene gave **3b** whose ^{1}H NMR spectrum

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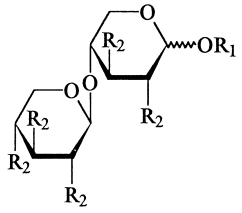
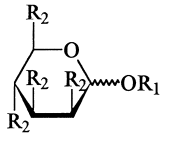
(see Table 1) showed that it was remarkable in having the terminal xylopyranose ring in the expected $^4C_1$ conformation ($J_{2',3'} \approx J_{3',4'} \approx J_{4',5'} \approx 8.5$ Hz) whereas the conformation of the ring attached to the dinitrophenyl group was an equilibrium of $^4C_1$ and $^1C_4$ forms ($J_{2,3} \approx J_{3,4} \approx J_{4,5} \approx 5$ Hz). The triacetate of 2,4-dinitrophenyl β-D-xylopyranoside, prepared as described previously [6], showed the same behaviour, the $^1C_4$ content of the ring conformation being even higher ($J_{2,3} \approx J_{3,4} \approx J_{4,5} \approx 4$ Hz). The strong anomeric effect of the 2,4-dinitrophenoxy group was also observed [9] in a chloro-analogue of **3b**.

Deacetylation of **3b** with hydrogen chloride in methanol gave a complex mixture from which the required 2,4-dinitrophenyl *β*-D-xylobioside (**4b**) was obtained by a combination of chromatography and crystallisation. Although its ^{1}H NMR spectrum was not completely resolved the coupling constants (Table 2) for the terminal pyranose ring were very similar to those of the acetate **3b** but values of 6.5 and 9.0 Hz for $J_{1,2}$ and $J_{4,5}$ suggested that the other ring had also adopted the $^1C_4$ conformation. The preference for the $^1C_4$ conformation in **3b** is probably also favoured by an attractive interaction between the syn-diaxial 2- and 4-acetoxy groups [11] in addition to the anomeric effect.

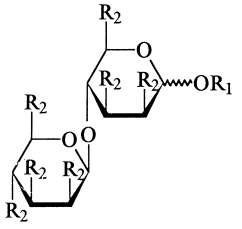
The synthesis of 2,4-dinitrophenyl *β*-D-mannobioside (**11b**) presented more of a challenge for *β*-mannopyranosides are notoriously difficult to synthesise [12]. However, a model experiment with D-mannose was encouraging. Even though selective deacetylation of an *αβ* mixture of D-mannopyranose penta-acetates (**5**) gave exclusively the *α*-tetraacetate **6a**, reaction of the latter with 2,4-dinitrofluorobenzene gave a separable mixture of



1 R_1=Ac; R_2=OAc
2 R_1=H; R_2=OAc
3 R_1=2,4-dinitrophenyl; R_2=OAc
4 R_1=2,4-dinitrophenyl; R_2=OH



5 R_1=Ac; R_2=OAc
6 R_1=H; R_2=OAc
7 R_1=2,4-dinitrophenyl; R_2=OAc



8 R_1=Ac; R_2=OAc
9 R_1=H; R_2=OAc
10 R_1=2,4-dinitrophenyl; R_2=OAc
11 R_1=2,4-dinitrophenyl; R_2=OH

a = α-anomer b = β-anomer

the *α*- and *β*-D-mannopyranosides **7** [13,14], albeit with the *α*-product **7a** in excess.

D-Mannobiose octaacetate (**8**) was obtained by acetylation of a mannose-mannobiose mixture (from a mannanase digest of ivory nut mannan) followed by chromatographic separation from mannose pentaacetate. Selective anomeric deacetylation as before gave the required D-mannobiose heptaacetate (**9**), dinitrophenylation of which gave a mixture of anomeric glycosides **10** from which pure samples of the *α*-anomer **10a** (34%) and the *β* anomeric **10b** (13%) were obtained by chromatography. These were de-acetylated as before with

Table 1
^{1}H NMR data: chemical shifts (ppm)

Compd	H-1	H-2	H-3	H-4	H-5a	H-5b	H-6a	H-6b	H-1′	H-2′	H-3′	H-4′	H-5′a	H-5′b	H-6′a	H-6′b	H-3 [a]	H-5 [a]	H-6 [a]
3b	5.53	5.07	5.22	3.86	4.13	3.68	—	—	4.63	4.92	5.16	4.95	4.12	3.41	—	—	8.70	8.42	7.44
4b	5.41	3.72		3.88	4.18	3.63	—	—	4.46	3.26	3.41	3.62	3.92	3.28	—	—	8.87	8.51	7.59
7a	5.83	5.50	5.54	5.44	4.10	—	4.29	4.08	—	—	—	—	—	—	—	—	8.84	8.46	7.51
7b	5.50	5.70	5.23	5.31	3.95	—	4.33	4.27	—	—	—	—	—	—	—	—	8.78	8.42	7.39
8a	6.03	5.21	5.41	4.05	3.98	—	4.31	4.25	4.76	5.44	5.05	5.22	3.65	—	4.32	4.11	—	—	—
9a	5.17	5.22	5.48	4.01	4.18	—	4.37	4.23	4.76	5.42	5.05	5.21	3.66	—	4.29	4.13	—	—	—
10a	5.74	5.44	5.64	4.14	4.08	—	4.32	4.27	4.82	5.41	5.07	5.24	3.68	—	4.24	4.15	8.82	8.44	7.48
10b	5.56	5.62	5.36	4.07	3.93	—	4.41	4.28	4.76	5.44	5.04	5.23	3.66	—	4.30	4.17	8.74	8.42	7.38
11a	5.96	4.28	4.19	4.02		3.72–3.78			4.74	4.03	3.64	3.54	3.42	—	3.92	3.73	8.88	8.51	7.68
11b	5.65	4.33	3.92			3.75–3.80			4.76	4.07	3.66	3.56	3.44	—	3.95	3.73	8.87	8.51	7.58

[a] Aromatic hydrogen.
Other signals: **3b**, 2.15 (2), 2.07, 2.06, 2.05 (5×Ac); **7a**, 2.23, 2.08, 2.05 (2) (4×Ac); **7b**, 2.25, 2.11, 2.08, 2.06 (4×Ac); **8a**, 2.18, 2.16, (2), 2.13, 2.10, 2.07, 2.06, 2.00 (8×Ac); **9a**, 2.17, 2.14 (2), 2.10, 2.07, 2.05, 2.00 (7×Ac), 3.91 (d, J=4.1 Hz) HO-1; **10a**, 2.20, 2.18, 2.11, 2.10, 2.05, 2.04, 1.99 (7×Ac); **10b**, 2.20, 2.18, 2.12, 2.10, 2.05 (2), 2.00 (7×Ac).

Table 2
^{1}H NMR data: coupling constants (Hz)

Compd	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5a}$	$J_{4,5b}$	$J_{5a,5b}$	$J_{5,6a}$	$J_{5,6b}$	$J_{6a,6b}$	$J_{1'2'}$	$J_{2'3'}$	$J_{3'4'}$	$J_{4,5'a}$	$J_{4'5'b'}$	$J_{5a',5b'}$	$J_{5,6a'}$	$J_{5,6b'}$	$J_{6a',6b'}$	$J^a_{3,5}$	$J^a_{5,6}$
3b	3.8	5.2	5.4	3.2	4.8	12.5	—	—	—	6.7	8.5	8.3	5.0	8.6	11.9	—	—	—	2.7	9.3
4b	6.5	?	?	5.0	9.0	12.0	—	—	—	7.6	9.6	8.9	5.3	10.7	11.7	—	—	—	2.8	9.4
7a	1.9	3.5	10.0	10.1	—	—	5.2	2.4	12.5	—	—	—	—	—	—	—	—	—	2.8	9.3
7b	1.8	3.1	8.9	7.9	—	—	6.2	3.6	12.2	—	—	—	—	—	—	—	—	—	2.8	9.3
8a	2.0	3.6	9.5	9.9	—	—	2.5	4.2	12.2	1.1	3.3	10.0	9.7	—	—	5.5	2.6	12.2	—	—
9a	1.7	3.5	9.8	9.8	—	—	2.2	4.4	12.0	0.7	2.3	10.0	9.7	—	—	5.5	2.6	12.2	—	—
10a	2.0	3.6	9.4	10.1	—	—	2.4	4.3	12.3	1.0	3.4	9.9	9.8	—	—	5.0	2.9	12.2	2.8	9.2
10b	1.9	3.6	8.4	8.0	—	—	3.4	6.1	12.1	1.0	3.3	10.0	9.7	—	—	5.4	2.6	12.3	2.8	9.3
11a	1.9	3.4	9.6	9.6	—	—	?	?	?	0	3.2	9.6	9.8	—	—	2.2	6.8	12.3	2.8	9.4
11b	0	1.9	?	?	—	—	?	?	?	0	3.2	9.6	9.8	—	—	2.2	6.9	12.3	2.8	9.4

[a] Aromatic hydrogen.

methanol–hydrogen chloride to give the crystalline 2,4-dinitrophenyl-α and β-D-mannobiosides (**11a**) and (**11b**); it is noteworthy that deacetylation of the α-anomer **10a** proceeded much more cleanly than that of the β-anomer **10b**.

1. Experimental

General methods.—Melting points are uncorrected. The petroleum ether (PE) used had boiling range 60–80 °C. ^{1}H NMR spectra were recorded at 200 or 500 MHz for solutions in $CDC1_3$ or D_2O. Kieselgel 60 was used for TLC (Merck 5554) and column chromatography (Prolabo, 200–400 mesh), elution was with EtOAc–PE (1:1 or 1:2) (for acetates) or $CHCl_3$–MeOH–H_2O (10:5:1) (for free sugars and glycosides). Optical rotations were measured at 22 °C.

*1,2,3,2′,3′,4′-Hexa-O-acetyl-*D*-xylobiose* (**1**).—Oak spelt xylan (5 g) was dissolved in 0.05 M–K_2HPO_4–0.01 M sodium citrate buffer (100 mL, pH 6.5) and after autoclaving was incubated for 16 h at 37 °C with xylanase [1] (10 mg). The resultant mixture was boiled (30 min) and centrifuged (30,000 ***g***, 10 min) to give a supernatant containing xylose, xylobiose and higher molecular weight compounds. This was evaporated under reduced pressure (bath temp. < 60 °C) and last traces of water were removed by adding PhMe–AcOH and re-evaporating. NaOAc (5 g), AcOH (20 mL) and Ac_2O (50 mL) were added to the flask and the mixture was heated (90 °C) for 1.5 h with vigorous stirring. The mixture was poured on to water (300 mL) and stirred for 30 min when CH_2Cl_2 (100 mL) was added and the mixture was filtered through Hyflo-supercel filter aid. The organic layer was further extracted with CH_2Cl_2 (2×50 mL). The total extract was dried ($MgSO_4$) and evaporated to a syrup from which last traces of AcOH were removed by azeotropic distillation with toluene. (An attempt to remove the AcOH by washing the CH_2Cl_2 extract with aqueous Na_2CO_3 resulted in emulsions.) The syrup (ca. 8 g) was dissolved in CH_2Cl_2 and decolourized by passage through a short silica column. Chromatography (column size: 40×40 mm) and elution with EtOAc–PE (1:2) gave a mixture of D-xylopyranose tetraacetates (2.2 g), from which the β-anomer (1.5 g) was crystallized (EtOH), m.p. 123–125 °C (lit., m.p. 126–128 °C [15]). Further elution with EtOAc–PE (1:1) gave the xylobiose hexa-acetates **1** (1.9 g) from which the β-anomer **1b** (1.3 g) was crystallised (EtOH), m.p. 152–153 °C, $[\alpha]_D$ −72° (*c*, 1.2, CH_2Cl_2) (lit., m.p. 155–156 °C, $[\alpha]_D$ −72.2° [10].

*2,4-Dinitrophenyl 2,3,2′,3′,4′-penta-*O*-acetyl-*β*-*D*-xylobioside* (**3b**). The hexa-acetate **1** (0.80 g, 1.40 mM) was dissolved in DMF (5 mL) containing hydrazine hydrate (0.10 mL, 103 mg, 2.06 mM) and AcOH (0.12 mL, 126 mg, 2.10 mM). After 40 min at room temperature, EtOAc (30 mL) was added and the solution was washed successively with M–HCl (2×10 mL) and aqueous $KHCO_3$ (1×10 mL) and finally dried ($MgSO_4$). Removal of solvents left the penta-acetate **2** (0.50 g, 66%) as a mixture of anomers (α:β:1:6). This was dissolved in DMF (8 mL) to which DABCO (0.44 g, 3.93 mM) and molecular sieves (4 A, 2 g) were added and the mixture was stirred for 1 h. 2,4-Dinitofluorobenzene (0.16 mL, 0.25 g, 1.35 mM) was added and stirring was continued overnight. The mixture was diluted with EtOAc (40 mL), filtered and washed successively with M–HCl (2×15 mL), aqueous Na_2CO_3 (3×15 mL) and aqueous $KHCO_3$ (1×15 mL)

and finally dried ($MgSO_4$). Removal of solvents and crystallisation of the residue from MeOH gave the penta-acetate **3b** (0.62 g, 63% based on **2**), m.p. 165–166 °C, $[\alpha]_D$ −84° (*c*, 0.78, CH_2Cl_2). Anal. Calcd for $C_{26}H_{30}O_{18}N_2$: C, 47.42; H, 4.59; N, 4.25. Found: C, 47.57; H, 4.25; N, 4.23.

2,4-Dinitrophenyl β-D-*xylobioside* (**4b**). A solution of the pentaacetate **3b** (0.16 g, 0.25 mM) in CH_2Cl_2 (2 mL) and MeOH (4 mL) containing HCl [(from acetyl chloride (0.08 mL)] was left at 4 °C until TLC showed the optimum yield of product (ca. 4 days). Solvents were removed under reduced pressure (bath temp < 15 °C). The residue was triturated with CH_2Cl_2 to remove 2,4-dinitrophenol and the residue (ca. 90 mg) was chromatographed quickly ($CHCl_3$–MeOH–H_2O, 10:5:1) to give the glycoside **4b** as a solid (35 mg, 31%) which crystallised from $CHCl_3$–MeOH–H_2O (60:10:1) when it had m.p. 150–152 °C (dec.), $[\alpha]_D$ −139° (*c*, 0.69, H_2O). Anal. Calcd for $C_{16}H_2N_{20}O_{13}.2H_2O$: C, 39.67; H 5.00; N, 5.78. Found: C, 39.73; H, 4.52: N, 5.51.

2,3,4,6-Tetra-O-*acetyl*-α-D-*mannopyranose* (**6a**).—1,2,3,4,6-Penta-*O*-acetyl-D-mannopyranose (**5**) (0.75 g, 1.9 mM) was dissolved in DMF (4.5 mL) containing hydrazine hydrate (0.1125 mL, 0.13 g, 2.6 mM) and AcOH (0.15 mL, 0.16 g, 2.6 mM). After 30 min at room temperature the reaction was worked up as described earlier to give the tetra-acetate (**6**) (0.45 g, 68%) as a syrup which eventually crystallised from ethanol, m.p. 93–95 °C (lit., 93–94 °C [15] for **6a**). However the syrup was sufficiently pure to be used in the following procedure.

2,4-Dinitrophenyl 2,3,4,6-tetra-O-*acetyl*-α- *and* β-D-*mannopyranosides* (**7**).—DABCO (0.45 g, 4.0 mM) and molecular sieves (4 A, 2 g) were added to a solution of the tetraacetate **6** (0.45 g, 1.30 mM) in DMF (4 mL) and the mixture was stirred at room temperature for 1 h when 2,4-dinitrofluorobenzene (0.18 mL, 0.28 g, 1.49 mM) was added and stirring was continued overnight. Work up as described earlier gave a solid (0.62 g) which crystallised from MeOH to yield the α-glycoside **7a** (0.31 g, 0.60 mM, 46%), m.p. 176–178 °C, $[\alpha]_D$ + 134° (*c*, 2.7, CH_2Cl_2) (lit., m.p. 175–176 °C, $[\alpha]_D$ + 137° [13]). The remaining material was chromatographed and elution with EtOAc–PE (1:1) gave first more of the α-glycoside **7a** (40 mg, 0.08 mM, 6%), further elution gave the β-glycoside **7b** (0.11 g, 0.21 mM, 16%) which, crystallised from EtOH, had m.p. 149–151 °C, $[\alpha]_D$ −133° (*c*, 1.5, CH_2Cl_2) (lit., m.p. 167–168 °C, $[\alpha]_D$ −102° [14]).

1,2,3,6,2,3′,4′,6′-Octa-O-*acetyl*-D-*mannobiose* (**8**).— Ivory nut mannan (4.5 g) was incubated with mannase A [2] (45,000 units) in 0.05 M-sodium phosphate buffer (360 mL, pH 7.0) at 37 °C for 64 h. The digest was worked up and acetylated [NaOAc (2.5 g) and Ac_2O (30 mL)] as described for the earlier xylan digestion. Chromatography gave, as syrups, both mannose pentaacetate **5** (1.5 g) and the title compound **8** (2.65 g), mass spectrum: *m*/*z* 619.1864 ($C_{28}H_{38}O_{19}$ calcd. *m*/*z* 619.1874 for M^+–CH_3CO).

2,4-Dinitrophenyl 2,3,6,2′,3′,4′,6′-hepta-O-*acetyl*-α *and* β-D-*mannobiosides* (**10**).—The above octaacetate **8** (1.60 g, 2.36 mM) was dissolved in DMF (8 mL) and a freshly prepared solution of hydrazine hydrate (0.17 mL, 0.175 g, 3.5 mM) and AcOH (0.20 mL, 0.21 g, 3.5 mM) in DMF (3 mL) was added. After 40 min at room temperature the reaction was worked up as described earlier to give the syrupy heptaacetate **9** (1.49 g, 2.34 mM, 99%). Dinitrophenylation of **9** in DMF (8.0 mL) with DABCO (0.78 g, 7.0 mM), molecular sieves (4 A, 2.0 g) and 2.4-dinitrofluorobenzene (0.52 mL, 0.50 g, 2.64 mM) as described earlier gave a solid (1.80 g). This was chromatographed on silica when elution with EtOAc–PE (1:1) gave first the β-anomer **10b** (0.38 g, 0.48 mM, 21%), m.p. 146–148 °C (dec) (from CH_2Cl_2–Et_2O), $[\alpha]_D$ −97° (*c*, 1.2, CH_2Cl_2). Anal. Calcd for $C_{32}H_{38}N_2O_{22}$: C, 47.88; H, 4.77; N, 3.49. Found: C, 47.28; H, 4.61; N, 3.46. Further elution gave a mixture (0.22 g) and then the α-anomer **10a** (1.03 g, 1.28 Mm, 55%) as a foam, $[\alpha]_D$ + 63° (*c*, 1.5, CH_2Cl_2). Anal. Found: C, 47.12; H, 4.56; N, 3.14.

2,4-Dinitrophenyl β–D-*mannobioside* (**11b**).—The β-heptaacetate **10b** (0.11 g, 0.14 mM) was dissolved in CH_2Cl_2 (1.3 mL) and MeOH (3.0 mL) containing HCl [from acetyl chloride (0.06 mL)] was added. The solution was left at 10 °C and the reaction was followed by TLC. After 4 days solvents were removed under reduced pressure (bath temp < 15 °C) to leave a syrup. On adding a mixture of $CHCl_3$–MeOH–H_2O (30:10:1) the syrup dissolved and deposited crystals of **11b** (47 mg, 0.093 mM, 67%), m.p. 162 °C (dec), $[\alpha]_D$ −52° (*c*, 1.0, H_2O). Anal. Calcd for $C_{18}H_{24}N_2O_{15}.2H_2O$: C, 39.71; H, 5.18; N, 5.15. Found: C, 39.62; H, 4.81; N, 4.99.

2,4-Dinitrophenyl α-D-*mannobioside* (**11a**).—The α-heptaacetate **10a** (0.17 g, 0.21 mM) was deacetylated as described for the β-anomer **10b** above. Crystallisation from MeOH gave the α-glycoside

11a (80 mg, 0.16 mM, 76%), m.p. 142 °C (dec.), $[\alpha]_D$ +87° (*c*, 0.86, H_2O). Anal. Calcd for $C_{18}H_{24}N_2O_{15}.2H_2O$: C, 39.71; H, 5.18; N, 5.15. Found: C, 39.45; H, 4.83; N, 4.91.

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