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Note

Synthesis of new methyl *O*-acetyl-α- and -β-D-xylopyranosides*

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Partially acetylated methyl glycosides of monosaccharides are important intermediates in synthetic carbohydrate chemistry. In the methyl α- and β-D-xylopyranoside series, only the 3-*O*-α- and 3-*O*-β compounds[2] and methyl di-*O*-acetyl-β-D-xylopyranosides[3–5] have been described. Studies of the correlation of the site of substitution and spectral properties required complete series of substances, and the syntheses of the title compounds were undertaken in this context.

Low regioselectivity is usually observed in the preparation of methyl *O*-acetyl-α- and -β-D-xylopyranosides by partial acetylation of the parent glycosides, and complex product mixtures are formed. A simpler approach involves unimolar acetylation of methyl mono-*O*-benzyl-α- and -β-D-xylopyranoside, and this has been explored.

Methyl 2-*O*- (**5**) and 3-*O*-acetyl-β-D-xylopyranoside (**6**) were prepared by partial acetylation of methyl 4-*O*-benzyl-β-D-xylopyranoside[4] (**1**) followed by chromatography and by synthesis. The acetyl groups in the methyl mono-*O*-acetyl-β-D-xylopyranosides **2** and **3**, as in other products of partial acetylation described herein, were readily located on the basis of ^{13}C-n.m.r. data (Table I), which showed clearly the upfield shift[6–8] of the signals for carbons at positions next to the COAc. Catalytic debenzylation of **2** and **3** then gave crystalline methyl 2-*O*- (**5**) and 3-*O*-acetyl-β-D-xylopyranoside (**6**). The synthesis of **5** involved cleavage of the epoxide ring in methyl 2,3-anhydro-4-*O*-benzyl-β-D-ribopyranoside[4] (**7**) with sodium benzyl oxide (see ref. 9). Acetylation of the resulting methyl 3,4-di-*O*-benzyl-β-D-xylopyranoside (**8**) and then debenzylation gave **5**. Compound **6** was also obtained by the following route. Treatment of methyl 2,3-anhydro-β-D-ribopyranoside (**10**) with sodium allyloxide gave methyl 3-*O*-allyl-β-D-xylopyranoside (**11**), which was benzylated (→**12**) and then deallylated[10], to give methyl 2,4-di-*O*-benzyl-β-D-xylopyranoside (**13**). Acetylation of **13** and debenzylation of the product **14** gave **6**.

Methyl 4-*O*-acetyl-β-D-xylopyranoside (**20**) was also synthesised from **10**. The 4-*O*-allyl derivative **15**, on alkaline hydrolysis, afforded methyl 4-*O*-allyl-β-D-xylopyranoside (**16**), which was benzylated to give **17**. Deallylation[10] of **17** and acetylation

*Alternative Syntheses of Methylated Sugars, Part XXV. For Part XXIV, see ref. 1.

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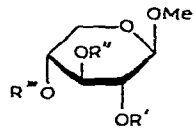
TABLE I

CHEMICAL SHIFTS FOR ^{13}C-N.M.R. SPECTRA OF **1–37**

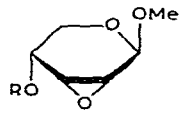
Compound	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*Me*	*CH_2*
1	104.0	73.0	74.7	77.1	63.1	56.7	73.0
2	101.7	72.8[b]	73.1[b]	77.3	62.8	56.5	72.9
3	103.8	71.3	74.0	74.5	62.5	56.9	72.7
4	101.9	71.4	73.6	75.0	63.5	56.7	72.8
5	102.3	73.5[b]	74.9[b]	70.1	65.4	56.9	
6	103.9	71.2	77.5	68.8	65.1	57.0	
7[a]	96.2	51.9	50.0	68.8	59.1	56.1	70.9
8	104.2	74.5	82.1	77.1	63.0	56.7	74.5, 73.0
9	102.1	72.2	80.8	77.5	63.3	56.5	74.5, 73.0
10[a]	95.6	51.9	51.9	61.8	61.8	55.7	
11	104.3	73.3	82.9	69.1	65.0	57.0	117.4, 73.5
12	105.1	81.8	83.4	77.6	63.8	56.9	116.6, 74.7, 74.3, 73.2
13	104.7	81.0	75.4	77.1	63.7	56.8	74.3, 73.0
14	104.9	78.9	75.4	74.5	63.5	56.9	73.8, 72.5
15	96.4	51.9	50.1	69.1	59.2	56.2	117.8, 70.1
16	103.2	71.2	71.7	76.4	60.8	56.5	117.8, 71.4
17	105.3	81.8	83.6	77.7	63.9	57.0	117.3, 75.6, 74.9, 72.3
18	104.1	80.1	81.6	68.9	64.1	56.7	74.4, 74.1
19	104.9	80.5	81.4	71.3	62.4	56.9	74.9, 74.7
20	104.1	73.3	73.3	71.5	62.5	57.1	
21	99.5	71.9	81.6	68.8	62.5	55.5	74.3
22	99.5	72.2	73.5	77.6	59.8	55.1	73.1
23	96.9	73.2	71.0	78.0	59.3	55.1	73.2
24	99.4	71.3	74.9[b]	75.1[b]	59.9	55.3	72.9
25	96.9	71.3	71.3	75.6	59.5	55.1	72.8
26	97.2	73.3	72.0	70.5	61.0	55.2	
27	99.4	70.6	76.6	68.4	61.7	55.4	
28	96.9	71.0	73.3	69.0	61.4	55.2	
29	99.5	72.1	79.4	71.0	58.8	55.3	74.6
30	97.1	72.9	76.7	71.1	58.4	55.2	74.8
31	99.6	71.5[b]	72.3[b]	71.5	58.6	55.4	
32	97.0	73.4	68.8	71.8	58.3	55.3	
33	97.8	77.1	71.2	69.5	58.2	55.4	73.0
34	97.9	79.3	73.2	70.0	61.1	55.2	73.2
35	99.3	71.1	72.8	68.9	58.6	55.6	
36[c]	101.6	70.8	71.6	69.0	62.0		
37[c]	96.4	70.5	69.1	68.8	57.7		

[a]Data for L enantiomorph, taken from ref. 14. [b]These assignments may be reversed. [c]Data taken from ref. 6; data for Me are not given.

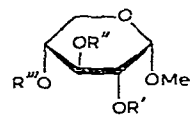
of the product **18** gave **19**, which was debenzylated to yield **20**. The methyl *O*-acetyl-α-D-xylopyranosides were synthesised from methyl 3-*O*- (**21**)[11] and 4-*O*-benzyl-α-D-xylopyranoside (**22**). The glycoside **22** was obtained by methyl glycosidation of 4-*O*-benzyl-D-xylose[12] followed by chromatography. The mono-*O*-acetyl-α-D-xylopyranosides **26**, **27**, and **31** were prepared by partial acetylation of **21** and **22**, isolation



	R′	R″	R‴
1	H	H	Bzl
2	Ac	H	Bzl
3	H	Ac	Bzl
4	Ac	Ac	Bzl
5	Ac	H	H
6	H	Ac	H
8	H	Bzl	Bzl
9	Ac	Bzl	Bzl
11	H	All	H
12	Bzl	All	Bzl
13	Bzl	H	Bzl
14	Bzl	Ac	Bzl
16	H	H	All
17	Bzl	Bzl	All
18	Bzl	Bzl	H
19	Bzl	Bzl	Ac
20	H	H	Ac
36	Ac	Ac	Ac



7 R = Bzl
10 R = H
15 R = All



	R′	R″	R‴
21	H	Bzl	H
22	H	H	Bzl
23	Ac	H	Bzl
24	H	Ac	Bzl
25	Ac	Ac	Bzl
26	Ac	H	H
27	H	Ac	H
28	Ac	Ac	H
29	H	Bzl	Ac
30	Ac	Bzl	Ac
31	H	H	Ac
32	Ac	H	Ac
33	Bzl	Ac	Ac
34	Bzl	H	H
35	H	Ac	Ac
37	Ac	Ac	Ac

of methyl mono-*O*-acetyl-4-*O*-benzyl- and -3-*O*-benzyl-α-D-xylopyranosides by chromatography, and subsequent catalytic debenzylation. Methyl 2,4-di-*O*-acetyl-3-*O*-benzyl- (**30**) and 2,3-di-*O*-acetyl-4-*O*-benzyl-α-D-xylopyranoside (**25**), also formed in the acetylations of **21** and **22**, were debenzylated to give methyl 2,3-di-*O*- (**28**) and 2,4-di-*O*-acetyl-α-D-xylopyranoside (**32**), respectively. The 3,4-diacetate **35** was obtained by debenzylation of **33**, isolated after the reaction[3] of 3,4-di-*O*-acetyl-2-*O*-benzyl-α-D-xylopyranosyl bromide with methanol.

A comparison of ^{13}C-n.m.r. chemical shifts for the title acetates with the data for methyl 2,3,4-tri-*O*-acetyl-α- (**37**) and -β-D-xylopyranoside (**36**) (Table I) shows that the shift effects of individual acetyl groups in methyl D-xylopyranosides are not such simple, additive parameters as those for acyl groups in the methyl D-glucopyranoside[7,8] and methyl L-rhamnopyranoside[13] series. Similar irregularities were also found[6] in other derivatives of D-xylose.

EXPERIMENTAL

General methods. — Melting points were determined on a Kofler hot-stage. Optical rotations (22°, *c* 1) were measured for solutions in chloroform, with a Perkin–Elmer Model 141 automatic polarimeter. T.l.c. was performed on Silica Gel G, and column chromatography on dry-packed Silica Gel 60, with *A*, 4:1 benzene–acetone; *B*, 8:1 heptane–acetone; *C*, 10:1 carbon tetrachloride–ethyl acetate; *D*, 4:1 heptane–

acetone; *E*, 1:1 carbon tetrachloride–methyl acetate; *F*, 8:1 benzene–acetone; and *G*, 16:1 chloroform–ethyl acetate. Detection was effected by charring with sulfuric acid. ^{13}C-N.m.r. spectra (internal Me_4Si) were measured at room temperature with a Jeol JNM FX-60 spectrometer in a deuterium-lock mode. Proton-decoupled F.t.-spectra were measured by using a repetition time of 2 s, a pulse width of 4 μs (45°), 4,000 Hz sweep-width, and 8 K real data-points. Solvents were dried with anhydrous sodium sulfate, and concentrated at 40°/2 kPa.

*Methyl 3,4-di-*O*-benzyl-β-*D*-xylopyranoside* (**8**). — Methyl 2,3-anhydro-4-*O*-benzyl-β-D-ribopyranoside[4] (**7**, 2.7 g) was added to a solution of sodium hydride (2.7 g) in benzyl alcohol (25 mL), and the solution was heated at 105° for 4 h, diluted with ethanol (50 mL), deionised with Dowex 50W (H^+) resin, and concentrated to dryness. Recrystallisation of the residue from ether–isopropyl ether yielded **8** (3.2 g, 82%), m.p. 99–99.5°, $[\alpha]_D$ −37° (Found: C, 69.80; H, 7.10. $C_{20}H_{24}O_5$ calc.: C, 69.74; H, 7.02%).

*Methyl 2,4-di-*O*-benzyl-β-*D*-xylopyranoside* (**13**). — Methyl 2,3-anhydro-β-D-ribopyranoside[15] (**10**, 5 g) was added to a freshly prepared solution of sodium hydride (2.4 g) in allyl alcohol (100 mL), and the mixture was heated at ~75° for 7 h. T.l.c. (solvent *A*) then showed that mainly **11** (R_F 0.3, *cf.* 0.5 for **10**) was present. The dark solution was processed as described for the preparation of **8**. Chromatography then gave methyl 3-*O*-allyl-β-D-xylopyranoside (**11**; 5 g, 72%), m.p. 84–85° (from ethyl acetate), $[\alpha]_D$ −71° (Found: C, 52.84; H, 7.67. $C_9H_{16}O_5$ calc.: C, 52.92; H, 7.89%).

A solution of **11** (4.3 g) in 1,2-dimethoxyethane (50 mL) was treated with sodium hydride (3 g) and benzyl bromide (5.8 mL), and the mixture was stirred at room temperature for 5 h. T.l.c. (solvent *B*) then showed that the reaction was almost complete, and conventional processing, followed by chromatography, gave methyl 3-*O*-allyl-2,4-di-*O*-benzyl-β-D-xylopyranoside (**12**) (7.2 g, 88.5%) as an oil.

1-Propanol (30 mL) was added to a solution of **12** (5.8 g) in acetic acid (17 mL), followed by water (17 mL) and 10% Pd/C (1.7 g), and the mixture was heated under reflux, with stirring, for 8 h. More catalyst (0.8 g) was then added and, after a further 20 h, the mixture, which still contained ~30% of **12** (t.l.c., solvent *C*), was filtered and concentrated, and the residue was chromatographed to give **12** (2.2 g) and then **13** (3 g, 93.7% based on the reacted **12**) as an oil, $[\alpha]_D$ +3° (Found: C, 70.02; H, 7.24. $C_{20}H_{24}O_5$ calc.: C, 69.74; H, 7.02%).

*Methyl 2,3-di-*O*-benzyl-β-*D*-xylopyranoside* (**18**). — Compound **10** (5 g) was treated with allyl bromide and sodium hydride, as described for the benzylation of **11**, and the product was distilled, to give methyl 4-*O*-allyl-β-D-ribopyranoside (**15**; 4.9 g, 77%), b.p. 50°/1.5 Pa, m.p. 39–39.5° (from hexane), $[\alpha]_D$ +5° (Found: C, 58.35; H, 7.81. $C_9H_{14}O_4$ calc.: C, 58.05; H, 7.57%).

A solution of **15** (4 g) in 10% aqueous potassium hydroxide (200 mL) was heated at 100° until t.l.c. showed that the reaction was complete (~5 h). Conventional processing gave methyl 4-*O*-allyl-β-D-xylopyranoside (**16**; 3 g, 68.5%), m.p. 106.5–107° (from 2-propanol–hexane), $[\alpha]_D$ −96° (Found: C, 52.82; H, 8.16. $C_9H_{16}O_5$ calc.: C, 52.92; H, 7.89%).

A solution of **16** (2.8 g) in *N*,*N*-dimethylformamide (60 mL) was treated at 80° with benzyl bromide (7 mL) and sodium hydride (2 g) for 5 h, to give methyl 4-*O*-allyl-2,3-di-*O*-benzyl-β-D-xylopyranoside [**17**; 3 g, 57%; R_F 0.4 (solvent *D*)], which was isolated by chromatography and had m.p. 39–40° (from 2-propanol), $[\alpha]_D$ +13° (Found: C, 71.62; H, 7.46. $C_{23}H_{28}O_5$ calc.: C, 71.85; H, 7.34%).

Compound **17** was deallylated as described for the preparation of **13**, and the crude product was chromatographed to give **17** (0.15 g) and **18** (0.9 g, 75% based on reacted **17**), m.p. 74–75° (from isopropyl ether), $[\alpha]_D$ −34° (Found: C, 69.95; H, 7.21. $C_{20}H_{24}O_5$ calc.: C, 69.74; H, 7.02%).

Methyl 4-O-benzyl-α-D-xylopyranoside (**22**). — 4-*O*-Benzyl-D-xylose (4 g) was heated at reflux in a mixture of methanol (80 mL) and acetyl chloride (3.2 mL) for 4 h. T.l.c. (solvent *E*) then showed that no starting material was present and that two products had been formed (R_F 0.3 and 0.4), of which the faster moving (minor product) was identical with methyl 4-*O*-benzyl-β-D-xylopyranoside (**1**). Conventional processing and chromatography yielded, first, **1** (1.1 g, 26%), m.p. 98–100°; lit.[4] m.p. 99–100°.

Eluted second was **22** (1.5 g, 35.5%), m.p. 74–75° (from ether), $[\alpha]_D$ +115° (Found: C, 61.27; H, 7.01. $C_{13}H_{18}O_5$ calc.: C, 61.40; H, 7.13%).

An ~1:2 mixture of **1** and **22** was also obtained.

Methyl 2-O-acetyl-β-D-xylopyranoside (**5**). — (*a*) Acetic anhydride (0.45 mL, 4.8 mmol) was added portionwise at 0° to a solution of **1** (1 g, 4 mmol) in pyridine (5 mL). Cooling was discontinued and, after 3 h, t.l.c. (solvent *F*) revealed a small proportion of **1** (R_F 0.1) together with **4**, **2**, and **3** (R_F 0.4, 0.25, and 0.2, respectively). Conventional processing and chromatography gave, first, the diacetate **4** (0.4 g, 30%), m.p. 73–75°; lit.[4] m.p. 73–74°.

Eluted second was the 2-acetate **2** (0.3 g, 25%), which was hydrogenolysed (methanol, room temperature, 5% Pd/C), to afford **5**, m.p. 96–96.5° (from ethyl acetate), $[\alpha]_D$ −55° (Found: C, 46.78; H, 7.19. $C_8H_{14}O_6$ calc.: C, 46.59; H, 6.84%).

Eluted third was the 3-acetate **3** (0.3 g, 25%), m.p. 162–163° (from ethyl acetate), $[\alpha]_D$ −48° (Found: C, 61.05; H, 7.13. $C_{15}H_{20}O_6$ calc.: C, 60.79; H, 6.80%).

(*b*) Compound **8** (2 g) was treated with an excess of acetic anhydride in pyridine, to give **9** which was hydrogenolysed, as described above, to give **5** (1.1 g, ~100%).

Methyl 3-O-acetyl-β-D-xylopyranoside (**6**). — (*a*) Hydrogenolysis of **3** (0.2 g), as described above, gave **6** in theoretical yield; m.p. 114–114.5° (from ethyl acetate), $[\alpha]_D$ −41°; lit.[2] m.p. 115–116°, $[\alpha]_D$ −49°.

(*b*) Compound **13** (2.2 g) was acetylated as described above, and the product was hydrogenolysed as described above, to give **6** (1.18 g, 90%).

Methyl 4-O-acetyl-β-D-xylopyranoside (**20**). — Compound **18** (0.7 g) was acetylated as described above, to give methyl 4-*O*-acetyl-2,3-di-*O*-benzyl-β-D-xylopyranoside (**19**; 0.66 g, 84.6%), m.p. 71–71.5° (from 1-propanol), $[\alpha]_D$ −28° (Found: C, 68.43; H, 7.00. $C_{22}H_{26}O_6$ calc.: C, 68.37; H, 6.78%).

Hydrogenolysis of **18**, as described above, gave **20** in theoretical yield; m.p.

113.5–114.5° (from ethyl acetate), $[\alpha]_D$ −92° (Found: C, 46.36; H, 6.93. $C_8H_{14}O_6$ calc.: C, 46.59; H, 6.84%).

Methyl 2-O-acetyl-α-D-xylopyranoside (**26**). — Compound **22** (1 g) was acetylated as described above. Chromatography afforded methyl 2,3-di-*O*-acetyl-4-*O*-benzyl-α-D-xylopyranoside (**25**; 0.16 g, 15%) as a syrup that was processed as described below; methyl 2-*O*-acetyl-4-*O*-benzyl-α-D-xylopyranoside (**23**; 220 mg, 22%), m.p. 121–122° (from ethanol), $[\alpha]_D$ +114° (Found: C, 60.64; H, 6.71. $C_{15}H_{20}O_6$ calc.: C, 60.79; H, 6.8%); methyl 3-*O*-acetyl-4-*O*-benzyl-α-D-xylopyranoside (**24**; 250 mg, 27%) as a syrup that was processed as described below.

A mixture of **23** and **24** was also obtained.

Hydrogenolysis of **23** (100 mg), as described above, gave chromatographically pure, syrupy **26** in theoretical yield, $[\alpha]_D$ +143° (Found: C, 46.68; H, 7.09. $C_8H_{14}O_6$ calc.: C, 46.59; H, 6.84%).

Methyl 3-O-acetyl-α-D-xylopyranoside (**27**). — Compound **24** (150 mg) was hydrogenolysed as described above, to give **27**, isolated in theoretical yield; m.p. 125–126° (from ether); lit.[2] m.p. 123–125°.

Methyl 4-O-acetyl-α-D-xylopyranoside (**31**). — Methyl 3-*O*-benzyl-α-D-xylopyranoside (**21**, 2 g) was acetylated as described for the preparation of **2** and **3**. T.l.c. (solvent *G*, triple development) of the crude product revealed the diacetate **30** (R_F 0.9), a small amount of **21** (R_F 0.3), and the products of partial acetylation (R_F ~0.5). Chromatography gave, first, syrupy **30** (0.7 g, 36.4%), which was processed as described below.

The product (0.4 g, 23.6%), m.p. 88.5–89.5° (from isopropyl ether, $[\alpha]_D$ +76°, isolated from the early fractions of zone having R_F ~0.5, was shown by ^{13}C-n.m.r. spectroscopy to be the 4-acetate **29** (Found: C, 60.83; H, 6.97. $C_{15}H_{20}O_6$ calc.: C, 60.79; H, 6.80%).

An unresolved mixture of **29** and the isomeric 2-acetate was also obtained.

Compound **29** (200 mg) was hydrogenolysed as described above, to give **31** in theoretical yield, m.p. 71–72° (from ether), $[\alpha]_D$ +127° (Found: C, 46.53; H, 6.79. $C_8H_{14}O_6$ calc.: C, 46.59; H, 6.84%).

Methyl 2,4-di-O-acetyl-α-D-xylopyranoside (**32**). — Compound **30** (0.4 g) was hydrogenolysed as described above, to afford, in theoretical yield, **32**, m.p. 66.5–67.5° (from isopropyl ether), $[\alpha]_D$ +132° (Found: C, 48.54; H, 6.61. $C_{10}H_{16}O_7$ calc.: C, 48.38; H, 6.50%).

Methyl 2,3-di-O-acetyl-α-D-xylopyranoside (**28**). — Hydrogenolysis of **25** (0.3 g) gave **28** in theoretical yield, m.p. 104–105° (from 2-propanol), $[\alpha]_D$ +120° (Found: C, 48.40; H, 6.27. $C_{10}H_{16}O_7$ calc.: C, 48.38; H, 6.50%).

Methyl 3,4-di-O-acetyl-α-D-xylopyranoside (**35**). — The crude product of the reaction[3] of 3,4-di-*O*-acetyl-2-*O*-benzyl-α-D-xylopyranosyl bromide with methanol contained, as the main component, methyl 3,4-di-*O*-acetyl-2-*O*-benzyl-β-D-xylopyranoside. The material in the mother liquors was chromatographed, and the substance that moved in t.l.c. slightly slower than methyl 3,4-di-*O*-acetyl-2-*O*-benzyl-β-D-xylopyranoside was isolated as a syrup and shown by ^{13}C-n.m.r. spectroscopy to be

methyl 3,4-di-*O*-acetyl-2-*O*-benzyl-α-D-xylopyranoside (**33**). The product **34** of deacetylation (Zemplén) of **33** was also amorphous. Catalytic hydrogenolysis of **33** gave **35** in theoretical yield, m.p. 94–95° (from ether–hexane), $[\alpha]_D$ +155° (Found: C, 48.24; H, 6.61. $C_{10}H_{16}O_7$ calc.: C, 48.38; H, 6.50%).

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