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Note

Synthesis of two isomeric methyl β-D-xylotriosides containing a (1→2)-β-linkage*

JÁN HIRSCH AND PAVOL KOVÁČ
Institute of Chemistry, Slovak Academy of Sciences, 809 33 Bratislava (Czechoslovakia)
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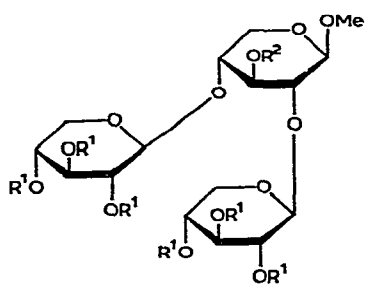
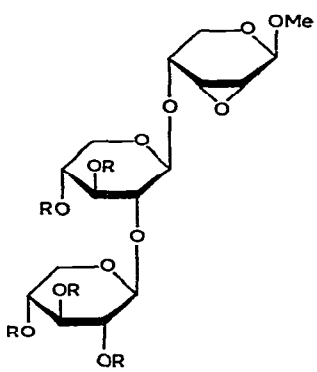
Isomeric xylo-oligosaccharides are model compounds for studies of branched xylans, and the syntheses of the methyl β-xylotriosides **3** and **8** were undertaken in this context.

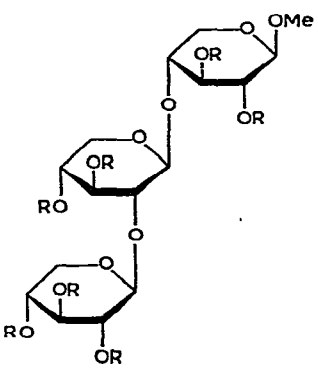
The reaction of methyl 3-*O*-benzyl-β-D-xylopyranoside[2] with 2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl bromide[3] in acetonitrile in the presence of mercuric cyanide afforded a good yield of crystalline **1**. Debenzylation and deacetylation of **1** effected the conversion **1**→**2**→methyl 2,4-di-*O*-β-D-xylopyranosyl-β-D-xylopyranoside (**3**), which gave a crystalline hepta-acetate **4** and hepta-*O*-methyl derivative **5**.



	R^1	R^2
1	Ac	Bzl
2	Ac	H
3	H	H
4	Ac	Ac
5	Me	Me



6 R = Ac
7 R = H



8 R = H
9 R = Ac
10 R = Me

Catalytic hydrogenolysis of the benzyl group from methyl 2,3-anhydro-(3,4-di-*O*-acetyl-2-*O*-benzyl-β-D-xylopyranosyl)-β-D-ribopyranoside[4] followed by reaction with ≈4 equiv. of 2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl bromide gave the trisaccharide

*Alternative Syntheses of Methylated Sugars: Part XXI. For Part XX, see Ref. 1.

derivative **6** which, in the higher-yielding procedure, was not isolated but deacetylated. Chromatography then gave **7**, alkaline hydrolysis[4] of which afforded crystalline methyl 4-*O*-(2-*O*-*β*-D-xylopyranosyl-*β*-D-xylopyranosyl)-*β*-D-xylopyranoside (**8**). The hepta-acetate **9** and hepta-*O*-methyl derivative **10** of **8** were also crystalline.

EXPERIMENTAL

M.p.s. were determined on a Kofler hot-stage. Optical rotations were measured with a Perkin–Elmer 141 polarimeter. T.l.c. was performed on Silica gel G, and column chromatography on dry-packed silica gel (Merck, 9385). Detection was effected with 5% sulphuric acid in ethanol. All reactions and the purity of the products were monitored by t.l.c. Solutions were dried over anhydrous sodium sulphate and concentrated at 40°/2 kPa.

Methyl 3-O-benzyl-2,4-di-O-(2,3,4-tri-O-acetyl-β-D-xylopyranosyl)-β-D-xylopyranoside (**1**). — A mixture of methyl 3-*O*-benzyl-*β*-D-xylopyranoside[2] (4 g, 15.7 mmol), mercuric cyanide (8 g, 31.6 mmol), and Drierite (5 g) in acetonitrile (150 ml) was stirred for 1 h. After the addition of 2,3,4-tri-*O*-acetyl-*α*-D-xylopyranosyl bromide (21.3 g, 62.8 mmol), stirring was continued at room temperature for 1 h. The reaction mixture was worked-up as previously described[5], and crystallisation of the crude product twice from ethanol gave **1** (5.5 g), m.p. 92–95° (sintered at 89°), $[\alpha]_D^{22}$ −82° (*c* 1, chloroform) (Found: C, 54.34; H, 5.86. $C_{35}H_{46}O_{19}$ calc.: C, 54.53; H, 6.01%).

Chromatography of the material in the mother liquor on a column of silica gel (600 g) gave more **1** (2.7 g; total yield, 67.6%).

Methyl 2,4-di-O-(2,3,4-tri-O-acetyl-β-D-xylopyranosyl)-β-D-xylopyranoside (**2**). — A solution of **1** (0.6 g) in methanol–acetone (1 : 1, 50 ml) was hydrogenolysed at room temperature and at atmospheric pressure over 5% palladium-on-charcoal until t.l.c. showed that the reaction was complete. The mixture was worked-up in the usual manner, and recrystallisation of the product from ethanol gave **2** (0.5 g, 94.3%), m.p. 161–163°, $[\alpha]_D^{22}$ −70.5° (*c* 1, chloroform) (Found: C, 49.31; H, 5.95. $C_{28}H_{40}O_{19}$ calc.: C, 49.40; H, 5.92%).

Methyl 2,4-di-O-β-D-xylopyranosyl-β-D-xylopyranoside (**3**). — Methanolic M sodium methoxide (1 ml) was added to a suspension of **2** (2 g) in methanol (50 ml), and the mixture was stirred until all starting material dissolved. After an additional 2 h, t.l.c. showed that the reaction was complete and that one product had been formed. The solution was deionised with Dowex-50W(H^+) resin, and concentrated. The residue, which crystallised on trituration with ethanol, was recrystallised from methanol (twice) to give **3** (0.75 g), m.p. 185–193°, $[\alpha]_D^{22}$ −79° (*c* 1, water). Those constants did not change significantly on recrystallisation and drying at 110°. The compound is dimorphous: a second crop of **3** (0.35 g; total yield, 87.3%), obtained from the concentrated mother liquor, had m.p. 160–168°, $[\alpha]_D^{22}$ −79° (Found: C, 44.63; H, 6.68. $C_{16}H_{28}O_{13}$ calc.: C, 44.85; H, 6.58%).

Acetylation of **2** or **3** with acetic anhydride in pyridine, in the usual manner, gave the hepta-acetate **4**, m.p. 130–132° (from ethanol–isopropyl ether, twice),

$[\alpha]_D^{22}$ +92° (*c* 1, chloroform) (Found: C, 49.68; H, 5.96. $C_{30}H_{42}O_{20}$ calc.: C, 49.86; H, 5.86%).

Conventional methylation of **3**, using sodium hydride, *N*,*N*-dimethylformamide, and methyl iodide, gave the hepta-*O*-methyl derivative **5** as long needles (from hexane) which changed to fibrous crystals (at 82–84°), m.p. 88–90°, $[\alpha]_D^{22}$ −89° (*c* 1, chloroform) (Found: C, 52.58; H, 7.98. $C_{23}H_{42}O_{13}$ calc.: C, 52.46; H, 8.04%).

Methyl 2,3-anhydro-4-O-(3,4-di-O-acetyl-β-D-xylopyranosyl)-β-D-ribopyranoside. — Catalytic hydrogenolysis of methyl 2,3-anhydro-4-*O*-(3,4-di-*O*-acetyl-2-*O*-benzyl-β-D-xylopyranosyl)-β-D-ribopyranoside[4] (2 g), as described above for the preparation of **2**, gave the title compound (1.4 g, 87.5%), m.p. 146–147° (from ethanol, twice), $[\alpha]_D^{22}$ −46.5° (*c* 1, chloroform) (Found: C, 49.62; H, 6.20. $C_{15}H_{22}O_{10}$ calc.: C, 49.72; H, 6.12%).

Methyl 2,3-anhydro-4-O-(2-O-β-D-xylopyranosyl-β-D-xylopyranosyl)-β-D-ribopyranoside (**7**). — (*a*) Treatment of the foregoing compound (4 g, 11 mmol) with 2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl bromide (15 g, 44.2 mmol), as described above for the preparation of **1**, gave, after chromatography of the crude product and crystallisation from ether–chloroform, the penta-acetate **6** (0.82 g, 12%), m.p. 157–158°, $[\alpha]_D^{22}$ −69° (*c* 1, chloroform). Acetylation of **7** gave the same product (Found: C, 50.14; H, 5.94. $C_{26}H_{36}O_{17}$ calc.: C, 50.32; H, 5.85%).

Deacetylation of **6**, as described above for the preparation of **3**, gave **7**, m.p. 223–224° (from methanol), $[\alpha]_D^{22}$ −47° (*c* 1, water) (Found: C, 46.85; H, 6.27. $C_{16}H_{26}O_{12}$ calc.: C, 46.83; H, 6.39%).

(*b*) Methyl 2,3-anhydro-4-*O*-(3,4-di-*O*-acetyl-β-D-xylopyranosyl)-β-D-ribopyranoside (4 g) was treated as described in (*a*), and the crude product was deacetylated and chromatographed to give **7** (2 g, 44.1%), m.p. 222–224°.

Methyl 4-O-(2-O-β-D-xylopyranosyl-β-D-xylopyranosyl)-β-D-xylopyranoside (**8**). — A mixture of **7** (2.8 g) and 10% aqueous potassium hydroxide (140 ml) was heated at 100–105° with the exclusion of atmospheric carbon dioxide for 4 h. T.l.c. then showed complete disappearance of **7**. The cooled, colourless solution was diluted with methanol (150 ml), deionised with Dowex-50W(H^+) resin, and concentrated, and a small amount of material insoluble in 95% ethanol was removed. Crystallisation of the product from ethanol gave **8** (2.5 g, 85.6%), m.p. 202–203°, $[\alpha]_D^{22}$ −80° (*c* 1, water) (Found: C, 44.79; H, 6.59%. $C_{16}H_{28}O_{13}$ calc.: C, 44.85; H, 6.58%).

The hepta-acetate **9** of **8** had m.p. 98–104° (from ether–ethyl acetate), $[\alpha]_D^{22}$ −94° (*c* 1, chloroform) (Found: C, 49.66; H, 5.90. $C_{30}H_{42}O_{20}$ calc.: C, 49.86; H, 5.86%).

The hepta-*O*-methyl derivative **10** of **8** had m.p. 105–106° (from isopropyl ether, twice), $[\alpha]_D^{22}$ −96° (*c* 1, chloroform) (Found: C, 52.51; H, 8.02. $C_{23}H_{42}O_{13}$ calc.: C, 52.46; H, 8.04%).

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