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THE STEPWISE SYNTHESIS OF A METHYL β-XYLOTETRAOSIDE RELATED TO BRANCHED XYLANS*

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ABSTRACT

3,4-Di-*O*-acetyl-2-*O*-benzyl-α-D-xylopyranosyl bromide (**1**) reacts with methyl 2,3-anhydro-β-D-ribopyranoside (**2**) to afford, in high yield, methyl 2,3-anhydro-4-*O*-(3,4-di-*O*-acetyl-2-*O*-benzyl-β-D-xylopyranosyl)-β-D-ribopyranoside (**3**). Deacetylation of **3** gave **4**, which reacted with 2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl bromide to give the branched tetrasaccharide derivative **5**, which, in turn, was converted by a series of conventional reactions into methyl 4-*O*-[3,4-di-*O*-(β-D-xylopyranosyl)-β-D-xylopyranosyl]-β-D-xylopyranoside. The reaction of **1** with its hydrolysis product gave 3,4-di-*O*-acetyl-2-*O*-benzyl-α-D-xylopyranosyl 3,4-di-*O*-acetyl-2-*O*-benzyl-β-D-xylopyranoside, which was also isolated after the reaction of **1** with **2**.

INTRODUCTION

The main chain of wood (4-*O*-methylglucurono)xylans is slightly branched, and some of the (1→4)-linked β-D-xylosyl residues bear a β-D-xylopyranosyl group or a short-chain xylose oligosaccharide[2] at position 3. Only linear, neutral oligosaccharides have been isolated from the products of partial hydrolysis of this type of polysaccharide, and higher oligosaccharides representing sequences around the site of branching are model compounds in studies of various properties of natural polysaccharides. We have an interest in methyl β-glycosides of oligosaccharides, where the aglycon imitates the situation in the main polysaccharide backbone and have described[3–7] syntheses of several substances of this class. We now report a stepwise synthesis of a methyl β-xylotetraoside related to branched xylans.

RESULTS AND DISCUSSION

Unambiguous chemical synthesis of a higher oligosaccharide requires the stereo-controlled reaction of, for example, an appropriately substituted glycosyl halide and partially substituted sugar derivative. In the series of xylose oligosaccharides, only xylobiose[8–11] (4-*O*-β-D-xylopyranosyl-D-xylopyranose) and its methyl[5] and benzyl[9] β-glycosides have been chemically synthesised. Because the preparation

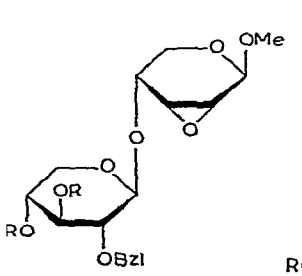
*Alternative Syntheses of Methylated Sugars: Part XIX. For Part XVIII, see Ref. 1.

of a D-xylose derivative having only HO-4 unsubstituted is difficult[8,10], methyl 2,3-anhydro-β-D-ribopyranoside (**2**) or its benzyl analogue have been used[5,7,9,11] as nucleophiles in the formation of (1→4)-β-linkages, since alkaline hydrolysis[12] of alkyl 2,3-anhydro-β-D-ribosides gives derivatives of D-xylose in high yield.

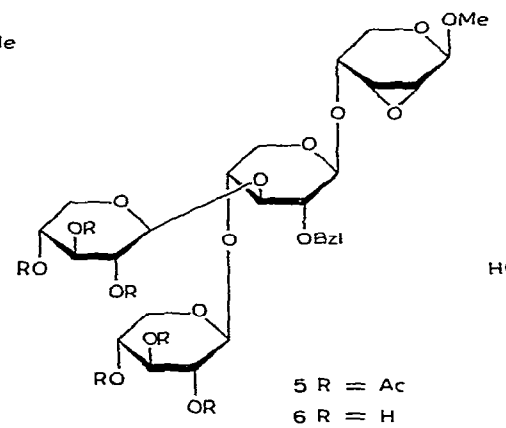
A D-xylotriose derivative representing the branch point at C-3 can be synthesised[6] by the reaction of 2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl bromide (acetobromoxylose) with methyl 2-*O*-benzyl-β-D-xylopyranoside[13]. The title methyl β-xylotetraoside (**8**) was synthesised by condensation of 3,4-di-*O*-acetyl-2-*O*-benzyl-α-D-xylopyranosyl bromide (**1**) with **2** and deacetylation of the product **3** to give the diol **4**. The reaction of **4** with acetobromoxylose[14] then gave the tetrasaccharide derivative **5**, which was treated in sequence with sodium methoxide, potassium hydroxide, and hydrogen (over palladium) to give the desired glycoside **8**.

The condensation of **1** with **2** occurred with marked stereoselectivity, to give **3** in high yield. The structure **3** was established by conversion (*via* **4**, **15**, and **16**) into the known[5,15] xylobiose derivative **17**.

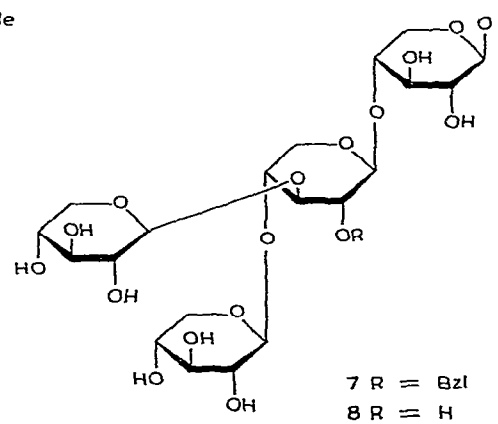
In addition to **3**, another disaccharide derivative **11** was isolated by chromatography after the reaction of **1** and **2**. The p.m.r. spectrum of **11** did not contain signals



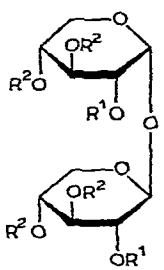
3 R = Ac
4 R = H



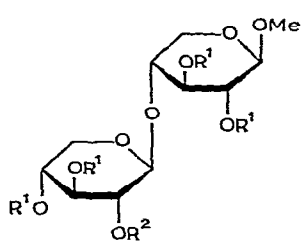
5 R = Ac
6 R = H



7 R = Bzl
8 R = H



	R^1	R^2
11	Bzl	Ac
12	Bzl	H
13	H	H
14	Ac	Ac



	R^1	R^2
15	H	Bzl
16	H	H
17	Ac	Ac

for methoxyl protons, but contained signals for aromatic and *O*-acetyl protons in the ratio ~10:12 (precise determination was prevented by partial overlapping of signals). The structure was confirmed by the conversion of **11** into the known[16], non-reducing disaccharide **13** and its hexa-acetate **14**. The mass spectrum of **14** was much simpler than expected by analogy with those of acetylated sugar glycosides[17,18] or acetates of sugars having HO-1 unsubstituted[17]. Apart from the peak for Ac^+, the mass spectrum of **14** showed[19] only peaks of Series A at *m/e* 259, 199, 157, 139, 97, and 69. The peak for fragments O-*a* (or O-*b*), at *m/e* 275, was also present.

When promoted by mercuric bromide and mercuric oxide, the reactions of 2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl bromide with simple alcohols in chloroform yield[14] β-D-xylopyranosides. These reactions involved substrate concentrations much higher than is practicable in oligosaccharide syntheses. By the above method, the reaction of **4** with acetobromoxylose (up to a 50% excess over the theoretical amount for the substitution of both hydroxyl groups), followed by deacetylation of the product **5**, yielded only 15–20% of **6**. When mercuric cyanide was used, the yield of **6** (isolated by chromatography) was elevated to 45%. Moreover, other tetrasaccharide derivatives were formed, showing that the glycosylation reaction was not very stereoselective. The low stereoselectivity may be due, at least in part, to the special properties of the complex nucleophile **4** and its relatively low concentration in the reaction system. Hanessian and Banoub[20] have noted the diversity of factors upon which glycosylation reactions depend. Reactions performed with mercuric cyanide variously in chloroform and acetonitrile gave almost identical yields of **6**, although the reaction performed in the more polar solvent (acetonitrile) would be expected[20,21] to be less stereoselective. The reaction in acetonitrile was much faster than those in less-polar solvents, and 2,3,4-tri-*O*-acetyl-D-xylopyranose, the formation of which from acetobromoxylose could not be prevented, reacted in acetonitrile almost completely with the excess of acetobromoxylose to give **14**. When the glycosylation was performed in chloroform, the extent of this further reaction of 2,3,4-tri-*O*-acetyl-D-xylose was much less (see Experimental) than in acetonitrile. The formation of **11** during preparation of **3** can be rationalised in a similar manner.

Hydrolysis of **8** gave (p.c.) only xylose, and acetylation and methylation gave amorphous derivatives (**9** and **10**). The mass spectrum of **10** showed features consistent with the expected structure. For convenience of interpretation, the component sugars in **10** are designated $a \rightarrow b \rightarrow c$. The molecular weight (686) of **10** was calculated[19,22]

$$\begin{matrix} & & \uparrow \\ & & d \end{matrix}$$

from the peaks of the A series, according to the equation $M = cabdA_1 + 31$ or $M = badA_1 + cA_1 + 16$ ($M = 655 + 31$, and $M = 495 + 175 + 16$). The observed molecular weight together with the ion peaks A_1 (*m/e* 175, 495, and 655) and J_1 (*m/e* 235 and 555) were in agreement with the compound's being a methyl nona-*O*-methylpentotetraoside. The branching at *b* could be deduced from the absence in the mass spectrum of peak A_1 (*m/e* 335) containing two sugar residues.

EXPERIMENTAL

Melting points were determined on a Kofler hot-stage. Optical rotations (*c* 1, chloroform; unless stated otherwise) were measured with a Perkin–Elmer Model 141 polarimeter. P.m.r. spectra ($CDCl_3$, internal Me_4Si) were recorded at 80 MHz with a Tesla-478-B spectrometer. Mass spectra (74 eV) were obtained with a JMS-100D instrument at an emission of 300 μA. The evaporation temperature was, according to the volatility of the samples, 160–300°, and that of the ionising chamber was 180°.

T.l.c. was performed on Silica Gel G, and column chromatography on dry-packed silica gel (Merck, 9385), with *A*, benzene–acetone (8:1); *B*, chloroform–methanol (15:1); *C*, benzene–acetone (5:1); *D*, chloroform–methanol (6:1); *E*, chloroform–methanol (4:1); *F*, chloroform–methanol (3:1); and *G*, chloroform–acetone (10:1). Detection was effected by charring with 5% sulfuric acid in ethanol. Descending paper chromatography was performed on Whatman No. 1 paper with pyridine–ethyl acetate–water (2:8:1) as the mobile phase, and detection with aniline hydrogen phthalate.

Microanalyses were performed with a Perkin–Elmer Model 240 automatic analyser. Solutions were dried with anhydrous sodium sulfate and concentrated, unless stated otherwise, at 40°/2 kPa.

*Methyl 2,3-anhydro-4-*O*-(3,4-di-*O*-acetyl-2-*O*-benzyl-β-*D*-xylopyranosyl)-β-*D*-ribopyranoside* (**3**). — A solution of bromide **1** [freshly prepared[13] from 1,3,4-tri-*O*-acetyl-2-*O*-benzyl-D-xylose (20 g, 54.6 mmol)] in the minimum amount of acetonitrile was added to a mixture of **2** (5.3 g, 36.3 mmol), mercuric cyanide (7.5 g, 29.7 mmol), and Drierite (10 g) in acetonitrile (150 mL), and the mixture was stirred with the exclusion of moisture at room temperature for 1 h. T.l.c. (solvent *A*) then showed complete disappearance of the starting materials (R_F 0.8 and 0.25), and that **3** (R_F 0.45) was the main product. The reaction mixture was worked-up as recommended[16], and crystallisation from ethanol afforded **3** (10.2 g), m.p. 150.5–151.5°. The material in the mother liquor was chromatographed on a column of silica gel to give, first, the dimer **11** (1.8 g), m.p. 172.5–174.5° (from ethanol, twice), $[\alpha]_D^{22}$ +76.7° (Found: C, 60.84; H, 6.06. $C_{32}H_{38}O_{13}$ calc.: C, 60.94; H, 6.07%).

Eluted next was **3** (1.55 g; total yield, 71.6%), m.p. 150.5–151.5°, $[\alpha]_D^{22}$ +3° (Found: C, 58.50; H, 6.31. $C_{22}H_{28}O_{10}$ calc.: C, 58.40; H, 6.24%).

*Methyl 2,3-anhydro-4-*O*-(2-O-benzyl-β-D-xylopyranosyl)-β-D-ribopyranoside* (**4**). — Compound **3** (2 g) was added to a mixture of dry methanol (100 mL) and M methanolic sodium methoxide (1 mL), and stirred at room temperature. One hour after dissolution of the starting material (total of 2–3 h), t.l.c. showed that the reaction was complete and that one product (R_F 0.4, solvent *B*) had been formed. The solution was deionised with Dowex-50W(H^+) resin, filtered, and concentrated to give chromatographically pure **4** (1.6 g, 98%), which was crystallised from ethyl acetate–hexane. Recrystallisation from ethyl acetate afforded the analytical sample, m.p. 119.5–120.5°, $[\alpha]_D^{22}$ −41.6° (Found: C, 58.73; H, 6.43. $C_{18}H_{24}O_8$ calc.: C, 58.68; H, 6.57%).

*Methyl 2,3-anhydro-4-*O-[*2-*O-*benzyl-3,4-di-*O-(*2,3,4-tri-*O-*acetyl-β-*D-*xylopyranosyl*)-*β-*D-*xylopyranosyl*]-*β-*D-*ribopyranoside* (**5**). — (*a*) Compound **6** (0.1 g, m.p. 215–216°) was treated at room temperature with acetic anhydride–pyridine (1:2, 1.5 mL) for 18 h. The reaction mixture was worked-up in the usual manner, and the product was crystallised from chloroform–ether to give **5** (0.128 g, 91.4%), m.p. 88–92°, $[\alpha]_D^{22}$ −75.3° (Found: C, 54.26; H, 5.94. $C_{40}H_{52}O_{22}$ calc.: C, 54.29; H, 5.92%).

(*b*) Acetobromoxylose (5.52 g, 16.3 mmol) was added to a mixture of **4** (2 g, 5.43 mmol), mercuric cyanide (2.1 g, 8.3 mmol), and Drierite (6 g) in acetonitrile (20 mL), and the mixture was stirred at room temperature and with the exclusion of air for 1 h. T.l.c. (solvent *C*) then showed the absence of both starting materials, and the formation of a major product (R_F 0.4) and two minor products (ratio ~4:1, R_F 0.5 and 0.35) having mobilities indistinguishable from those of authentic samples[16] of **14** and 2,3,4-tri-*O*-acetyl-D-xylopyranose. The reaction mixture was worked-up[16], and the crude product was crystallised from ethanol–ether with seeding. Recrystallisation of the product (1.41 g) gave **5**, m.p. 90–93°, $[\alpha]_D^{22}$ −74°. The product in the mother liquor was chromatographed on a column of silica gel to give more **5** (2.6 g; 0.52 g after recrystallisation, total yield 40.2%).

*Methyl 2,3-anhydro-4-*O-[*2-*O-*benzyl-3,4-di-*O-(*β-*D-*xylopyranosyl*)-*β-*D-*xylopyranosyl-*]-*β-*D-*ribopyranoside* (**6**). — (*a*) Acetobromoxylose (5.52 g, 16.3 mmol) was added to a mixture of **4** (2 g, 5.43 mmol), Drierite (6 g), yellow mercuric oxide (1.8 g, 8.3 mmol), and mercuric bromide (0.5 g) in dry, alcohol-free chloroform (80 mL), and the reaction mixture was stirred at room temperature and with the exclusion of air for 24 h. The crude product was isolated in the usual manner and deacetylated (Zemplén). The fraction (2.5 g) having R_F 0.4 was obtained by elution of the products from a column of silica gel, and crystallisation from methanol yielded **6** (0.6 g, 17.5%), m.p. 212–215°, $[\alpha]_D^{22}$ −71° (*c* 1.1, water).

(*b*) A mixture of **4** (2 g, 5.43 mmol), acetobromoxylose (5.52 g, 16.3 mmol), dry, alcohol-free chloroform (80 mL), mercuric cyanide (2.1 g), mercuric bromide (0.5 g), and Drierite (6 g) was kept at room temperature for 24 h, and then processed as described above. T.l.c. (solvent *D*) revealed that **6** (R_F 0.4) and D-xylose (R_F 0.2) were the main products; a small proportion of **13** (R_F 0.1) was also present. Column chromatography gave the product (2.1 g) having R_F 0.4 (solvent *D*), and crystallisation from methanol afforded **6** (1.45 g, 42.3%), m.p. 213–216°.

(*c*) The reaction in benzene (80 mL), performed with the same amounts of reagents as in (*b*), gave, after deacetylation of the crude product and chromatography, 1.4 g of material having R_F 0.4, and crystallisation from methanol yielded **6** (0.9 g, 26.2%), m.p. 212–215°.

(*d*) Compound **4** (2 g, 5.43 mmol) was treated as described for the preparation (*b*) of **5**, and the crude product was deacetylated. T.l.c. (solvent *D*) then showed that material having R_F 0.4 and **13** (R_F 0.1) were the main products; a small proportion of D-xylose was also present. Column chromatography gave 2.7 g of material having R_F 0.4, and crystallisation from methanol yielded **6** (1.5 g, 43.7%), m.p. 212–215°.

Recrystallisation from the same solvent afforded the analytical sample, m.p. 215–216°, $[\alpha]_D^{22}$ −71.8° (*c* 1, water) (Found: C, 53.09; H, 6.32. $C_{28}H_{40}O_{16}$ calc.: C, 53.16; H, 6.37%).

Methyl 4-O-[2-O-benzyl-3,4-di-O-(β-D-xylopyranosyl)-β-D-xylopyranosyl]-β-D-xylopyranoside (**7**). — Compound **6** (4 g) was treated with 10% aqueous potassium hydroxide (200 mL) at 105°, with the exclusion of atmospheric carbon dioxide, for 4 h. T.l.c. (solvent *E*) then showed the absence of **6** (R_F 0.5). The colourless solution was diluted with ethanol (200 mL), cooled (0°), neutralised with Dowex-50W(H^+) resin, filtered, and concentrated. The solid residue was crystallised from 70% ethanol to give chromatographically pure **7** (3.68 g, 89.7%; R_F 0.3, solvent *E*), m.p. 259–260°. Recrystallisation from methanol gave material with m.p. 260–261°, $[\alpha]_D^{22}$ −87.4° (*c* 1, water) (Found: C, 51.82; H, 6.44. $C_{28}H_{42}O_{17}$ calc.: C, 51.69; H, 6.51%).

Methyl 4-O-[3,4-di-O-(β-D-xylopyranosyl)-β-D-xylopyranosyl]-β-D-xylopyranoside (**8**). — Compound **7** (2 g) in water (200 mL) was hydrogenated at room temperature over 5% palladium-on-charcoal (0.5 g) until the starting material disappeared (~6 h), as shown by t.l.c. (solvent *F*). The product **8** (R_F 0.2), isolated in the usual manner, could not be induced to crystallise and, after being dried at 50°/2 kPa for 8 h, was obtained as a colourless, solid foam (1.7 g, 98.8%) having $[\alpha]_D^{22}$ −87.7° (*c* 1, water) (Found: C, 44.87; H, 6.53. $C_{21}H_{36}O_{17}$ calc.: C, 45.0; H, 6.47%).

Compound **8** (5 mg) was treated in a sealed vial with 10% aqueous trifluoroacetic acid (1 mL) at 95° for 1 h. The solution was then concentrated, with co-distillation with water to remove trifluoroacetic acid. Paper chromatography of the residue revealed only xylose.

Compound **8** (100 mg) was treated, with occasional shaking, with acetic anhydride–pyridine (4:1, 2.5 mL) for 18 h at room temperature. The peracetate **9**, isolated in the usual manner, was chromatographically homogeneous (R_F 0.4, solvent *C*) and could not be induced to crystallise. On drying at 50°/2 kPa for 8 h, it formed a colourless, solid foam, $[\alpha]_D^{22}$ −105° (Found: C, 49.66; H, 5.76. $C_{39}H_{54}O_{24}$ calc.: C, 49.89; H, 5.79%).

Sodium hydride (0.3 g) was added to a solution of **8** (250 mg) in *N,N*-dimethylformamide (8 mL), followed, after cooling (0°), by methyl iodide (0.4 mL), and the mixture was stirred at 20° with the exclusion of atmospheric moisture and carbon dioxide for 2 h. After addition of water (10 mL) and neutralisation with dilute acetic acid to pH 7.5, the solution was partitioned between chloroform and water. The chloroform solution was concentrated, with co-distillation with xylene to remove *N,N*-dimethylformamide, and t.l.c. then revealed only traces of undermethylated material (R_F <0.25). The product was purified by chromatography and, after drying at 50°/2 kPa for 8 h, the permethyl ether **10** was obtained as a glassy solid (0.27 g, 88.2%), $[\alpha]_D^{22}$ −107° (Found: C, 52.30; H, 8.11. $C_{30}H_{54}O_{17}$ calc.: C, 52.46; H, 7.92%).

Methyl 4-O-(2-O-benzyl-β-D-xylopyranosyl)-β-D-xylopyranoside (**15**). — Compound **4** (1 g) was treated with 10% aqueous potassium hydroxide (50 mL) for 5 h at 105° with the exclusion of atmospheric carbon dioxide. T.l.c. (solvent *B*) then

showed that the starting material (R_F 0.5) was absent, and the reaction mixture was worked-up as described for the preparation of **7**; the ion exchanger used for the neutralisation was washed by stirring at room temperature with water (3 × 100–150 mL) for 5 min. The combined filtrates were concentrated, the solid residue was digested with methanol, and a small amount of insoluble material was removed by filtration of the hot solution. Concentration of the filtrate to a small volume gave 0.8 g (76.2%) of chromatographically pure **15**, m.p. 202–203°. Recrystallisation from methanol afforded the analytical sample, m.p. 202.5–203°, $[\alpha]_D^{22}$ −73.5° (*c* 0.6, water) (Found: C, 56.07; H, 7.00. $C_{18}H_{26}O_9$ calc.: C, 55.95; H, 6.78%).

*Methyl 2,3-di-*O*-acetyl-4-*O*-(2,3,4-tri-*O*-acetyl-β-*D*-xylopyranosyl)-β-*D*-xylopyranoside* (**17**). — Compound **15** (0.2 g) in ethanol (100 mL) was hydrogenated over 5% palladium-on-charcoal (50 mg) at room temperature until the reaction was complete, as shown by t.l.c. (solvent *B*). After isolation in the usual manner, the product **16** (R_F 0.5, solvent *D*) was dissolved in pyridine (0.5 mL), and acetic anhydride (1 mL) was added. After 18 h, the usual work-up gave **17** (0.22 g, 84%), which was obtained by crystallisation from ethanol. Recrystallisation from ethanol afforded material having m.p. 145–146°; lit.[15] m.p. 145–146°.

α-D-Xylopyranosyl β-D-xylopyranoside (**13**). — A mixture of **11** (1 g) and M methanolic sodium methoxide (1 mL) in methanol (50 mL) was stirred at room temperature for 2 h. T.l.c. (solvent *A*) then showed that the reaction was complete and that one product (R_F 0.2 solvent *B*) had been formed. Neutralisation with Dowex-50W(H^+) resin, filtration, and concentration gave crude **12** (0.73 g, ~100%), a solution of which in ethanol (50 mL) was hydrogenated at room temperature over 5% palladium-on-charcoal (0.2 g) until t.l.c. showed complete conversion of **12** into **13** (R_F 0.1, solvent *D*). The mixture was worked-up in the usual manner, and crystallisation from methanol gave **13** (0.39 g, 88.5%), m.p. 208–210°; lit.[16] m.p. 208.5–210.5°. A portion of **13**, when acetylated with acetic anhydride in pyridine, gave **14**, m.p. 175–176° (from methanol); lit.[16] m.p. 175–176.5°.

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