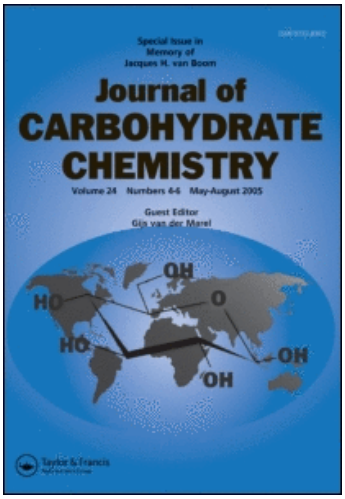

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Application of Dichlorovinyl Xyloside for the Novel Synthesis of 2,3,4-Tri-*O*-methyl-D-xylono-1,5-lactone

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A novel synthesis of 2,3,4-tri-*O*-methyl-D-xylopyranose, **4**, and its oxidation product 2,3,4-tri-*O*-methyl-D-xylono-1,5-lactone, **5**, are reported. The new synthesis applies a regioselective Wittig-like reaction of tetra-O-acetyl-D-xylopyranase, **1**, with triphenylphosphine and carbon tetrachloride to yield an *O*-dichlorovinyl xyloside protected at C-1, **2**. The protecting group facilitates the permethylation of xylose and is removed under the methylation conditions, to yield tetra-O-acetyl-D-xylopyranase, **3**. The anomeric methyl group was removed under mildly acidic conditions to give 2,3,4-tri-*O*-methyl-D-xylopyranose, **4**, in good yield. Compound **4** was oxidized using pyridinium chlorochromate to give the title compound, **5**, in 95% yield.

Keywords Carbohydrates, Protecting groups, Wittig reactions, Lactones, Oxidations

INTRODUCTION

Carbohydrates are important in many biological processes and structures. They regulate intercellular interactions and play essential roles in cell–cell, cell–pathogen, and cell-signaling events. Their use in therapeutics or as model compounds to study biological processes is attracting much attention. Carbohydrates are also abundant and inexpensive renewable resources but have received much less attention as alternative reagents to petrochemicals, for example, in polymer synthesis. As an example of their potential, it is noteworthy that glucose is produced at 5 million metric tons per annum and at a cost of \$0.76 kg^{-1}, which compares with methyl methacrylate production at 2.1 million tons per annum and a cost of \$1.32 kg^{-1}.[1,2] Two major challenges

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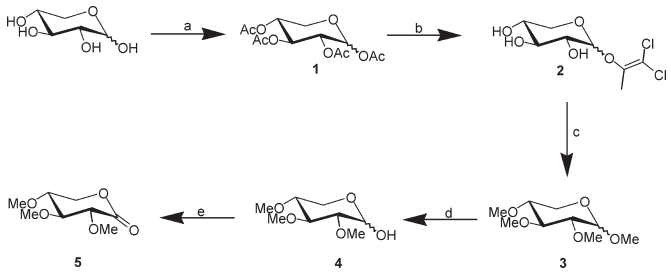
for polymer applications are the development of efficient and selective protection strategies for the hydroxyl functionalities and the selection of a monomer class that will undergo general, high-yielding polymerizations. Carbohydrate δ-lactones are attractive precursors due to the reactivity of the lactone, for example, in selective ring-opening reactions, although to date they have received limited attention as monomers themselves.[3,4] Galbis and coworkers have carried out extensive investigations using carbohydrate-derived diacids, diols, and diamines to make condensation polyamides, polyesters, and polycarbonates.[5–11] Their syntheses sometimes use carbohydrate δ-lactones as starting materials in the diacid or diamine synthesis.[12,13] Fleet et al. have also recently reported a number of routes starting from δ- and γ-lactones to make tetrahydroxylated 6-amino hexanoic acids or 4-aminomethyl-tetrahydrofuran-2-carboxylates, which were subsequently transformed into well-defined oligoamides.[14–16] We are researching the synthesis of aliphatic polyesters directly from carbohydrate-derived lactones.[17] Therefore, the efficient, selective, and scaleable synthesis of hydroxyl-protected carbohydrate 1,5-lactones is required; herein we present a novel synthesis of 2,3,4-tri-*O*-methyl-D-xylono-1,5-lactone and full analytical data.

RESULTS AND DISCUSSION

The synthesis of 2,3,4-tri-*O*-methyl-D-xylonolactone has been known since the 1920s when both the δ- and γ-lactones were prepared as part of studies to elucidate the structure of carbohydrates.[18,19] As part of these studies, Haworth reported the first synthesis by bromine oxidation of 2,3,4-tri-*O*-methyl-D-xylose. Although the yield for the oxidation was excellent, the method to prepare the xylose precursors was low yielding and inefficient.[20] Furthermore, the analytical data presented were limited to specific rotations and melting points. Galbis has reported an alternative synthesis from benzyl-α-D-xylopyranoside, by methylation, selective hydrogenolysis, and oxidation, producing the title compound in excellent yield.[13] However, the synthesis of benzyl-α-D-xylopyranoside itself is low yielding.[21] The alternative synthetic scheme applied here is outlined in Scheme 1 and takes advantage of a protecting group recently identified by Cleophax et al. for selective anomeric protection of hexoses.[22]

Tetra-*O*-acetyl-D-xylopyranose **1** was prepared according to the literature procedure by reaction of D-xylose with acetic anhydride and a catalytic quantity of trifluoroacetic acid.[23] The second step involved a Wittig-type condensation between the anomeric acetyl group of **1** and carbon tetrachloride to yield an *O*-dichlorovinylxylopyranoside. This reaction has been previously used by Cleophax et al. to prepare 2,3,4,6-tetra-*O*-benzyl-glycopyranosides.[22] The condensation was highly regioselective, and only occurred at the anomeric acetyl group. The 1-*O*-dichlorovinyl-2,3,4-tri-*O*-acetyl-D-xylopyranoside was



Scheme 1: Synthesis of 2,3,4-tri-*O*-methyl-D-xylono-1,5-lactone Reagents and conditions: (a) CF_3CO_2H, $(CH_3CO)_2O$, 20 h, 25°C, 100%; (b) (i) 3 KCl, CCl_4, py, 1 h, 90°C; (ii) NaOMe, MeOH, 2 h, 25°C, (i) and (ii) 50%; (c) NaH, MeI, DMF, 4 h, 0°C, 60%; (d) CF_3CO_2H (aq), 4 h, 65°C, 65%; (e) PCC, CH_2Cl_2, 12 h, 50°C, 95%.

not isolated but was reacted in situ under the Zemplen deacetylation conditions, with sodium methoxide in methanol, to yield 1-*O*-dichlorovinyl-D-xylopyranose **2** in 50% yield as a mixture of anomers. The compound showed elemental analysis in good agreement with calculated values and an isotope distribution pattern for the molecular ion consistent with two chlorides being present. Furthermore, the ^{13}C {1H} NMR spectrum showed characteristic signals at 148, 104, and 14 ppm, indicative of the *O*-dichlorovinyl group. Compound **2** was methylated by reaction with sodium hydride in DMF, followed by the addition of methyl iodide, and this produced tetra-*O*-methyl-D-xylopyranose **3** in 60% yield and as a mixture of anomers. Compound **3** showed analytical values in agreement with the literature,[20] its ^1H and $^{13}C\{^1H\}$ NMR spectra were also fully assigned. The removal of the anomeric methyl group was accomplished in improved yield by heating **3** with trifluoroacetic acid for 4 h to produce 2,3,4-tri-*O*-methyl-D-xylopyranose **4** in 66% yield, as a mixture of anomers. Compound **4** showed analytical values in agreement with the literature,[20] and was further characterized using NMR spectroscopy, mass spectrometry, and elemental analysis. The route to **4** was accomplished in straightforward steps and in 20% overall yield from D-xylose. The route is an improvement over alternative permethylation and selective anomeric *O*-methyl hydrolysis routes, which only yielded **4** in 10% from D-xylose.[20] Compound **4** was oxidized to 2,3,4-tri-*O*-methyl-D-xylono-1,5-lactone **5** in 95% yield by reaction with pyridinium chlorochromate. Compound **5** showed analytical data in agreement with the literature[19] and in addition was fully characterized, including by NMR spectroscopy, with the characteristic carbonyl C-1 resonance at 169.57 ppm and by IR spectroscopy where absorption at 1765 cm^{-1} was characteristic of the carbonyl group in a δ-lactone.

In conclusion, a new synthesis of 2,3,4-tri-*O*-methyl-D-xylono-1,5-lactone was achieved in five steps from D-xylose in an overall yield of 15%. The synthesis applied a novel C-1 protecting group strategy, previously described for the hexoses, to facilitate the synthesis and purification of permethylated xylose.

The anomeric methyl group was cleaved in reasonable yield using a dilute trifluoroacetic acid solution and the oxidation of the permethylated xylopyranose was accomplished in excellent yield by using pyridinium chlorochromate.

EXPERIMENTAL SECTION

Toluene and THF were dried by distillation over sodium metal; methylene chloride was dried by distillation from calcium hydride. All other reagents and chemicals were purchased from Aldrich Chemical Co. and used as received. All manipulations were carried out under a dry nitrogen atmosphere. NMR spectra collected at 400 MHz were performed on a Bruker AV400 instrument. NMR spectra collected at 500 MHz and $^{13}C\{^1H\}$ NMR spectra were carried out on a Bruker AV500 instrument. $CDCl_3$ was used as the NMR solvent and reference compound. Chemical ionization mass spectrometry was performed on a Fison's VG Platform, a quadrapole mass spectrometer. The ionization gas was ammonia and the source temperature was 150°C. IR absorbances were determined using a Satellite FTIR instrument using KBr plates and processed using WinFIRST lite 1.02. Specific rotations were measured using an Optical Activity Ltd Instrument with a cell path length of 0.5 dm. Melting points were measured using a Reichert instrument and are uncorrected. Elemental analyses were determined by Mr Stephen Boyer at London Metropolitan University.

Tetra-*O*-acetyl-D-xylopyranose (α- and β-anomers) (1)

D-(+)-Xylose (9.38 g, 62.50 mmol, 1 eq) was suspended in a solution of trifluoroacetic acid (6 mL) in acetic anhydride (120 mL) for 3 h and until all the solid had been consumed. The reaction mixture was filtered and concentrated in vacuo, and toluene (3 × 20 mL) was then distilled from the residue to form a white semi-solid, that was dissolved in methanol and washed with hexane (3 × 20 mL). The solvent was removed in vacuo to form the product as a pale yellow semi-solid and as a mixture of α- and β-anomers in the ratio 1:0.8, respectively (19.80 g, 62.20 mmol, quantitative).

α-anomer: ^1H NMR (500 MHz, $CDCl_3$): $\delta = 6.18$ (d, $^3J_{HH} = 3.63$ Hz, 1H, H-1), 5.14 (m, 1H, H-3), 4.99–4.93 (m, 2H, H-2, H-4), 4.08 (dd, $^2J_{HH} = 11.97$, $^3J_{HH} = 4.88$ Hz, 1H, H-5), 3.65 (m, 1H, H-5), 2.15–1.95 (4 × s, 12H, OAc). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta = 170.00$ (m, 4 × C=O), 88.96 (C-1), 70.64 (C-3), 69.09, 68.39 (C-2, C-4), 60.37 (C-5), 20 (m, 4 × CH_3).

β-anomer: ^1H NMR (500 MHz, $CDCl_3$) $\delta = 5.66$ (d, $^3J_{HH} = 6.76$ Hz, 1H, H-1), 5.43–5.37 (m, 1H, H-3), 4.99–4.93 (m, 2H, H-2, H-4), 4.08 (dd, $^2J_{HH} = 11.97$, $^3J_{HH} = 4.88$ Hz, 1H, H-5), 3.48 (dd, $^2J_{HH} = 12.06$, $^3J_{HH} = 8.33$ Hz, 1H, H-5), 2.15–1.95 (4 × s, 12H, OAc).

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) : $\delta = 170.00$ (m, 4 × C═O), 91.74 (C-1), 69.18 (C-3), 69.06, 68.03 (C-2, C-4), 62.47 (C-5), 20 (m, 4 × CH_3).

MS (CI, ammonia): m/z (%): 336 (100) $[M + NH_4^+]$.
Anal. Calcd. for $C_{13}H_{18}O_9$: C, 49.06; H, 5.70; Found: C, 48.88; H, 5.63.

(2′,2′-Dichloro-1′-methyl)-ethenyl-D-xylopyranoside (α- and β-anomers) (2)

Tetra-*O*-acetyl-D-xylopyranose (20.00 g, 62.80 mmol, 1 eq), PPh_3 (49.40 g, 189 mmol, 3 eq), and KCl (42.20 g, 566 mmol, 9 eq) were dried in vacuo for 1 h and suspended in dry toluene (55 mL), dry pyridine (30 mL), and dry CCl_4 (45 mL) and stirred at 90°C for 50 min. The resulting black heterogeneous mixture was filtered through a plug of silica gel eluted with CH_2Cl_2-EtOAc (1:1) and concentrated to dryness to yield a yellow semi-solid, which was purified by column chromatography (EtOAc:Hexane, 1:1, $R_f = 0.6$) to yield a yellow semi-solid (2′,2′-dichloro-1′-methyl)-ethenyl-D-xylopyranose (15.25 g, 40.82 mmol, 63%). To a solution of (2′,2′-dichloro-1′-methyl)-ethenyl-2,3,4-tri-*O*-acetyl-D-xylopyranoside (5.00 g, 13 mmol, 1 eq.) in absolute MeOH (50 mL) was added MeONa (0.37 g, 6.90 mmol, 0.5 eq). After 2 h, the solution was neutralized with ion exchange resin (Amberlite IRC 50 S H^+ form). The reaction mixture was concentrated and washed with acetone (30 mL) to yield the product as a semi-solid (2.49 g, 9.60 mmol, 80%).

$^{13}C\{^{1}H\}$NMR (75 MHz, DMSO-d_6): $\delta = 148.38$, 148.11 (C-1′), 104.38, 103.59 (C-2′), 97.73, 92.43 (C-1), 76.66, 74.62 (C-3), 73.1, 72.26 (C-2), 70.1, 69.75 (C-4), 65.62, 61.51 (C-5), 14.78, 14.33 (C-3′).

MS (CI, ammonia): m/z (%) = 276 (100) $[M + NH_4^+, {}^{35}Cl)$, 278 (65), $[M + NH_4^+, {}^{35}Cl, {}^{37}Cl]$, 280 (15) $[M + NH_4^+, {}^{37}Cl]$.
Anal. Calcd. for $C_8H_{12}Cl_2O_5$: C, 37.09; H, 4.67. Found: C, 37.05; H, 4.70.

Tetra-*O*-methyl-D-xylopyranose (3)[20]

(2′,2′-Dichloro-1′-methyl)ethenyl-D-xylopyranoside [**2**] (0.74 g, 2.90 mmol, 1 eq) was dissolved in dry DMF (15 mL), under nitrogen. NaH (1.5 g, 60% dispersion in mineral oil, 31 mmol, 13 eq) was added at 0°C with stirring, followed by MeI (1.42 mL, 23 mmol, 8 eq). After 4 h at room temperature, the reaction was quenched by addition of MeOH (20 mL). The mixture was diluted with CH_2Cl_2 (50 mL) and water (50 mL). The organic phase was separated and the aqueous layer extracted with $CHCl_3$ (350 mL). The organic layer was dried ($MgSO_4$) and concentrated in vacuo and residual DMF was removed by distillation under vacuum (5 mbar, 35°C). The resulting residue was purified by flash chromatography (EtOAc-Hexane; 1:1) to yield the product as a mixture of the α- and β-anomers in the ratio 1:3, respectively (0.36 g, 1.74 mmol, 60%).

Mp 44–45°C [lit.[20] Mp 46–48°C, β-anomer].
$[\alpha]_D^{25}$ −16.1° (c, 0.31, $CHCl_3$) [lit. $[\alpha]_D^{20}$ −66°, β-anomer (c, 1.16, MeOH)[20]].

α-anomer: ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 4.75$ (1H, d, $^3J_{HH} = 3.5$ Hz, H-1), 3.98 (1H, dd, $^2J_{HH} = 11.5$ Hz, $^3J_{HH} = 4.7$ Hz, H-2), 3.61 (3H, s, OMe), 3.50 (3H, s, OMe), 3.47 (3H, s, OMe), 3.40 (3H, s, OMe), 3.62–2.93 (4H, m, H-3, H-4, H-5).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 97.59$ (C-1), 82.65 (C-2), 81.69 (C-3), 79.74 (C-4), 60.90 (C-5), 59.33, 59.02, 58.90 (OMe), 55.1 (C-1 - OMe).

β-anomer: ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 4.13$ (1H, d, $^3J_{HH} = 7.2$ Hz, H-1), 3.69 (1H, dd, $^2J_{HH} = 10.90$ Hz, $^3J_{HH} = 5.60$ Hz, H-2), 3.59 (3H, s, OMe), 3.55 (3H, s, OMe), 3.50 (3H, s, OMe), 3.46 (3H, s, OMe), 3.62–2.93 (4H, m, H-3, H-4, H-5).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 104.70$ (C-1), 85.01 (C-2), 83.17 (C-3), 79.35 (C-4), 63.03 (C-5), 60.55, 60.34, 58.63 (OMe), 56.76 (C-1- OMe).

MS (CI, ammonia) m/z (%) = 224 (100) $[M + NH_4^+]$.
Anal. Calcd. for $C_9H_{18}O_5$: C 52.43, H 8.74. Found: C, 53.43; H, 8.84.

2,3,4-Tri-*O*-methyl-D-xylopyranoside (4)[20]

Tetra-*O*-methyl-D-xylopyranose [**3**] (0.26 g, 1.26 mmol) was dissolved in a solution of trifluoroacetic acid (2.5 mL) and water (1.0 mL) and heated at 65°C for 4 h. The mixture was concentrated to yield the product as an oil (0.16 g, 0.83 mmol, 66%). The oil was composed of a 2:1 ratio of α:β anomers.
$[\alpha]_D^{25}$ +18.8° (c, 0.64, $CHCl_3$) [lit $[\alpha]_D^{25}$ +20.1° (c, 1.095, MeOH)[20]].

α-anomer (66%): ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 5.24$ (1 H, d, $^3J_{HH} = 3.44$ Hz, H-1), 3.76–3.72 (1 H, m, H-5), 3.62 (3 H, s, OMe), 3.55 (3 H, s, OMe), 3.49 (3 H, s, OMe), 3.45 (1 H, d, $^3J_{HH} = 8.44$ Hz, H-3), 3.28–3.16 (2 H, m, H-2, H-4).

$^{13}C\{^1H\}$ (125 MHz, $CDCl_3$) $\delta = 90.90$ (C-1), 81.45 (C-2 or C-4), 81.36 (C-3), 79.01 (C-2 or C-4), 60.67 (OMe), 59.89 (C-5), 58.93, 58.71 (OMe).

β-anomer (33%): ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 4.62$ (1 H, d, $^3J_{HH} = 6.83$ Hz, H-1), 4.02 (1 H, dd, $^2J_{HH} = 11.09$, $^3J_{HH} = 4.23$ Hz, H-5), 3.62 (6 H, s, OMe), 3.46 (3 H, s, OMe), 3.31–3.17 (2 H, m, H-3, H-4), 2.99 (1 H, dd, $^3J_{H2H3} = 8.01$ Hz, $^3J_{H1H2} = 6.91$ Hz, H-2).

$^{13}C\{^1H\}$ (125 MHz, $CDCl_3$) $\delta = 97.10$ (C-1), 84.17 (C-3 or C-4), 83.46 (C-2), 78.80 (C-3 or C-4), 62.64 (C-5), 60.52, 60.36, 58.65 (OMe).

MS (CI, ammonia): m/z (%) = 210 (100) $[M + NH_4^+]$.
Anal. Calcd. for $C_8H_{16}O_5$: C, 50.00; H, 8.33. Found: C, 50.08; 7.24.

2,3,4-Tri-*O*-methyl-D-xylono-1,5-lactone (5)[19]

Pyridinium chlorochromate (0.36 g, 1.70 mmol, 2.0 eq) in dichloromethane (3 mL) was added to 2,3,4-tri-*O*-methyl-D-xylopyranoside [**4**] (0.20 g, 1 mmol) dissolved in CH_2Cl_2 (3 mL), and the mixture was refluxed for 7 h. It was then cooled, diluted with diethyl ether (30 mL), decanted, filtered through celite, and concentrated to yield the product as an oil (0.15 g, 0.80 mmol, 95%).

$[\alpha]_D^{25}$ +16.8° (c, 0.95, CH_2Cl_2).

IR ($CDCl_3$): 1765 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): $\delta = 4.44$ (1 H, ddd, $^2J_{HH} = 12.26$, $^3J_{HH} = 2.99$, 1.66 Hz, H-5 axial), 4.29 (1 H, dd, $^2J_{HH} = 12.41$, $^3J_{HH} = 1.75$ Hz, H-5 equatorial), 3.84 (1 H, d, $^3J_{HH} = 6.53$ Hz, H-2), 3.63 (3 H, s, CH_3), 3.53 (3 H, s, CH_3), 3.43 (3 H, s, CH_3), 3.57–3.55 (1 H, m, H-4), 3.50 (1 H, m, H-3).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta = 169.57$ (C-1), 82.91 (C-3), 80.49 (C-2), 77.00 (C-4), 64.93 (C-5), 59.47, 58.02, 56.22 (3 × CH_3).

MS (CI, ammonia): m/z (%) = 208 (100), $[M + MH_4^+]$.

Anal Calcd. for $C_8H_{14}O_5$: C 50.52, H 7.42. Found: C 50.68, H 7.51.

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