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The Role of Hydrolases in a Synthesis of Some Epoxyalkyl β-*C*-Cellobiosides†

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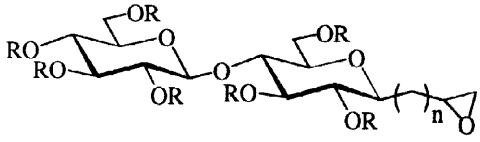
†This paper is dedicated to the memory of Professor Sir Derek Barton

Abstract: An endoglucanase from *Humicola insolens* has been used to glycosylate a range of alkenyl β-D-*C*-glucopyranosides with β-lactosyl fluoride. The resulting trisaccharides have been subjected to the action of a commercial β-galactosidase to form alkenyl β-*C*-cellobiosides. Oxidation of these has given a range of epoxyalkyl β-*C*-cellobiosides, putative inhibitors of cellobiohydrolases. © 1999 Elsevier Science Ltd. All rights reserved.

C-Glycosides, because of their tetrahydropyran rather than glycosidic nature, have the ability to survive the action of hydrolytic enzymes. In particular, epoxyalkyl β-*C*-cellobiosides (**1**) are attractive targets for use in inhibition studies of cellobiohydrolases because the mechanism of action of the enzyme precludes any hydrolysis of even the conventional glycosidic linkage that is present in the inhibitor.[1-3] We have previously reported a rather poor but general synthesis of the alkenyl β-*C*-cellobiosides (**2**), obvious precursors to the epoxyalkyl β-*C*-cellobiosides (**1**).[4] In that synthesis, the addition of alkenylmagnesium halides to the cellobionolactone (**3**) gave variable results and, after reduction of the intermediate hemiacetal, usually low yields of the desired *C*-cellobiosides (**2**). In an effort to provide a better synthesis of the desired putative inhibitors, we turned to an enzyme-mediated approach.



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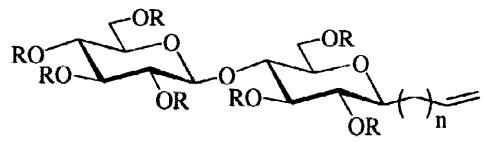
9 R = Ac



2 R = H
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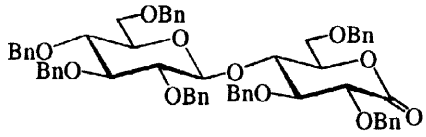
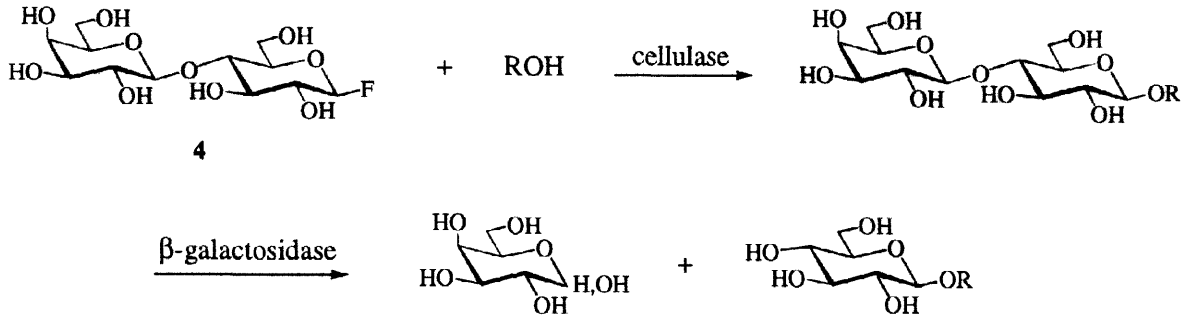
8 R = Bn



3

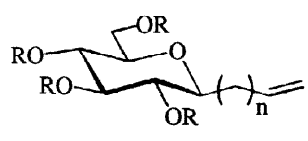
PII: S0040-4020(98)01177-6

Shoda *et al.* recently reported the effective D-glucosylation of an acceptor by a two-step procedure: (i) enzyme-mediated glycosylation of the acceptor using β-lactosyl fluoride (**4**) and a crude preparation of cellulases and (ii) selective removal of the D-galactose residue using a β-galactosidase (**Scheme 1**).[5] This paper reports on the application of this methodology to the alkenyl β-D-*C*-glucosides (**5**), resulting in a synthesis of the alkenyl β-*C*-cellobiosides (**2**) and thence the epoxyalkyl β-*C*-cellobiosides (**1**).

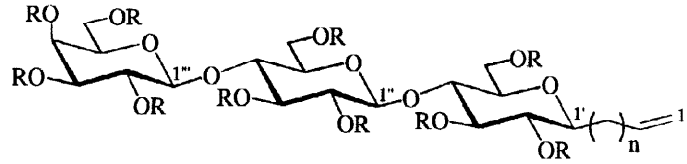


Scheme 1

The cellulase chosen for the initial glycosylation step was an endoglucanase (EG1) from the fungus, *Humicola insolens* which has previously been shown to exhibit a high trans-glycosylation activity.[6] Thus, β-lactosyl fluoride (**4**) and prop-2-enyl β-D-*C*-glucopyranoside (**5**, n = 1) in acetonitrile/maleate buffer[7] were subjected to the action of EG1. After denaturation of the enzyme and acetylation of the crude reaction mixture, the decaacetate (**6**, n = 1) was isolated in good yield. This yield could not be improved upon in the first step by adding more enzyme or changing the ratio of acetonitrile to buffer and reaction time. Indeed, longer reaction times resulted in lower yields, presumably owing to hydrolysis of the newly formed cellobiose linkage. Deacetylation of (**6**, n = 1), followed by treatment with a β-galactosidase from *Aspergillus oryzae*, gave a moderate yield of the desired prop-2-enyl β-*C*-cellobioside (**2**, n = 1), isolated and characterised as the heptaacetate (**7**, n = 1) or the heptabenzyl ether (**8**, n = 1).



5 R = H
10 R = Ac



6 R = Ac
11 R = H

The heptaacetate (**7**, n = 1) was best converted into the epoxide (**9**, n = 1) utilizing dimethyldioxirane[8] rather than the more traditional *m*-chloroperbenzoic acid.[9] The *per*-acetylated epoxide (**9**, n = 1) was indefinitely stable and a direct source of the putative inhibitor (**1**, n = 1) upon brief treatment with sodium methoxide in methanol. Similar procedures on the β-D-*C*-glucopyranosides (**5**, n = 2,3) provided the desired epoxides (**9**, n = 2,3).

It is our hope that the polyols (**1**, n = 1-3) will prove to be effective inhibitors of cellobiohydrolases.

Experimental

General experimental details have been given previously.[10] All n.m.r. spectra were recorded at 300 MHz (^{1}H) and 75.5 MHz (^{13}C) unless stated otherwise and deuterated methanol (CD_3OD) was used as solvent for the polyols. High-resolution mass spectra (h.r.m.s.) were recorded using the fast-atom-bombardment technique in a matrix of *p*-nitrobenzyl alcohol. Gel permeation chromatography was performed on a column of Sephadex LH-20 (90 x 2.6 cm), eluting (gravity) with MeOH.

The tetra-*O*-benzyl-D-glucono-1,5-lactone necessary for the preparation of the alkenyl β-D-*C*-glucosides (**5**)[2,4] was best prepared from methyl α-D-glucopyranoside *via* the sequence of benzylation (BnBr/NaH/DMF), hydrolysis (H_2O/TfOH, 9:1) and oxidation (DMSO/Ac_2O); this sequence was much preferred to that starting from sucrose.[11]

The lactosyl fluoride used, essentially of the β-configuration and containing small amounts of unreactive impurities, was prepared from lactose *via* acetylation (Ac_2O/pyridine), bromination (HBr/HOAc), fluorination (AgF/CH_3CN) and trans-esterification (cat. NaOMe/MeOH/CH_2Cl_2); zinc fluoride in refluxing CH_3CN containing 2,2'-bipyridine[12] was of no use in the fluorination step. ^{1}H n.m.r. δ 5.05, dd, $J_{1,2}$ 7.2, $J_{1,F}$ 53.4 Hz, H1. ^{13}C n.m.r. δ 106.71, d, $J_{C,F}$ 212 Hz, C1.

Humicola insolens endoglucanase I (EC 3.2.1.4) was cloned and expressed in *Aspergillus oryzae*,[13,14] purified according to the methods described by Armand *et al.*[7] and stored (4°) as a 6 mg/mL preparation in sodium maleate buffer (0.05 M, pH 7.0) prior to use. *Aspergillus oryzae* β-galactosidase (EC 3.2.1.23) was purchased from Sigma Aldrich Chemical Company (lyophilised powder) and stored (4°) as a 1500 U/mL preparation in potassium phosphate buffer (0.05 M, pH 7.3) prior to use.

General Procedure for the Preparation of the Alkenyl β-D-*C*-Glucosides (5, n = 1-3)

NaOMe (0.1 M in MeOH, 0.1 eq.) was added to a cooled (0°) solution of the tetraacetate (**10**)[4] in MeOH and the mixture was stirred (3 h). The solution was treated with Dowex 50X8–50 (H^+) resin, filtered and concentrated to afford the tetrol (**5**).

3-(β-D-Glucopyranosyl)prop-1-ene (**5**, n = 1)

The tetraacetate (**10**, n = 1) yielded the tetrol (**5**, n = 1) as fine, white needles (96%), $[\alpha]_D$ −5° (MeOH; lit.[2] −6°). ^{1}H n.m.r. (500 MHz) δ 2.22, dddt, $J_{1,3} \approx J_{1,3}$ 1.1, $J_{2,3}$ 6.8, $J_{3,3}$ 14.7, $J_{3,1'}$ 7.9 Hz, H3; 2.57, dddt, $J_{1,3} \approx J_{1,3}$ 1.5, $J_{2,3}$ 6.9, $J_{3,1'}$ 2.9 Hz, H3; 3.09, t, $J_{1',2'} \approx J_{2',3'}$ 9.3 Hz, H2′; 3.16-3.21, m, H1′,5′; 3.24, t, $J_{3',4'} \approx J_{4',5'}$ 8.8 Hz, H4′; 3.31, t, H3′; 3.63, dd, $J_{5',6'}$ 5.6, $J_{6',6'}$ 11.9 Hz, H6′; 3.82, dd, $J_{5',6'}$ 2.3 Hz, H6′; 5.02, ddt, $J_{1,1}$ 2.2, $J_{1,2}$ 10.2 Hz, H1; 5.08, ddt, $J_{1,2}$ 17.2 Hz, H1; 5.96, ddt, H2. ^{13}C n.m.r. (125.8 MHz) δ 37.00, C3; 63.04, C6′; 71.89, C4′; 74.80, C2′; 79.76, C3′; 80.54, 81.56, C1′,5′; 116.98, C1; 136.29, C2.

4-(β-D-Glucopyranosyl)but-1-ene (**5**, n = 2)

The tetraacetate (**10**, n = 2) yielded, after gel permeation chromatography, the tetrol (**5**, n = 2) as a colourless oil (97%), $[\alpha]_D$ −10.9° (MeOH). ^{1}H n.m.r. δ 1.31-1.41, 1.77-1.88, 1.97-2.29, 3m, 4H, H3,4; 2.93, dd, $J_{1',2'}$ 8.6, $J_{2',3'}$ 9.4 Hz, H2′; 3.00-3.20, m, H1′,5′; 3.11-3.20, m, H3′,4′; 3.52, dd, $J_{5',6'}$ 5.5, $J_{6',6'}$ 11.8 Hz, H6′; 3.72, dd, $J_{5',6'}$ 2.2 Hz, H6′; 4.82, ddt, $J_{1,1}$ 2.3, $J_{1,2}$ 10.2, $J_{1,3} \approx J_{1,3}$ 1.2 Hz, H1; 4.92, ddt, $J_{1,2}$ 17.2, $J_{1,3} \approx J_{1,3}$ 1.6 Hz, H1; 5.74, ddt, $J_{2,3}$ 6.4, 6.9 Hz, H2. ^{13}C n.m.r. δ 30.64, 32.19, C3,4; 63.15, C6′; 72.05, C4′; 75.46, C2′; 79.88, 80.10, 81.58, C1′,3′,5′; 114.89, C1; 139.90, C2. H.r.m.s. *m/z* 219.1238 [$C_{10}H_{19}O_5$ $(M+H)^{+\bullet}$ requires 219.1232].

5-(β-D-Glucopyranosyl)pent-1-ene (**5**, n = 3)

The tetraacetate (**10**, n = 3) yielded the *tetrol* (**5**, n = 3) as fine, white needles (98%), m.p. 92.5-94° (MeOH), $[\alpha]_D$ −11.8° (MeOH) (Found: C, 56.7; H, 8.5. $C_{11}H_{20}O_5$ requires C, 56.9; H, 8.7%). ^{1}H n.m.r. δ 1.24-1.42, 1.51-1.65, 1.69-1.79, 1.91-1.99, 4m, 6H, H3,4,5; 2.92, dd, $J_{1',2'}$ 8.4, $J_{2',3'}$ 9.4 Hz, H2′; 2.98-3.09, m, H1′,5′; 3.10-3.20, m, H3′,4′; 3.51, dd, $J_{5',6'}$ 5.4, $J_{6',6'}$ 11.8 Hz, H6′; 3.71, dd, $J_{5',6'}$ 2.2 Hz, H6′; 4.80, ddt, $J_{1,1}$ 2.3, $J_{1,2}$ 10.2, $J_{1,3} \approx J_{1,3}$ 1.2 Hz, H1; 4.89, ddt, $J_{1,2}$ 17.2, $J_{1,3} \approx J_{1,3}$ 1.6 Hz, H1; 5.74, ddt, $J_{2,3} \approx J_{2,3}$ 6.7 Hz, H2. ^{13}C n.m.r. δ 25.89, C3; 32.45, C5; 34.79, C4; 63.14, C6′; 72.05, C4′; 75.49, C2′; 79.89, C3′; 80.75, 80.57, C1′,5′; 114.83, C1; 140.06, C2. H.r.m.s. *m/z* 233.1370 [$C_{11}H_{21}O_5$ $(M+H)^{+\bullet}$ requires 233.1389].

General Procedure for the Preparation of the Trisaccharides (6, n = 1-3)

Humicola insolens endoglucanase I in maleate buffer (120 μL) was added to β-lactosyl fluoride (**4**) (4 eq.) and the tetrol (**5**) in a mixture of maleate buffer (0.05 M, pH 7.0) and CH_3CN (2:3). The solution was maintained (1 h) at constant temperature (40°) and fresh enzyme (120 μL aliquots) was added thereafter at fifteen minute intervals (45 min). Aqueous NH_3 (28% w/w) was added and the mixture was heated (100°, 10 min). The organic solvent was evaporated, the aqueous phase freeze-dried and the gummy residue acetylated [Ac_2O/pyridine/DMAP (0° → r.t., 24 h)]. Water was added and stirring continued (3 h). The

mixture was then subjected to standard workup ($CHCl_3$), flash chromatography (30-70% EtOAc/petrol) and gel permeation chromatography to yield the trisaccharide (**6**).

3-[O-(Tetra-O-acetyl-β-D-galactopyranosyl)-(1→4)-O-(tri-O-acetyl-β-D-glucopyranosyl)-(1→4)-tri-O-acetyl-β-D-glucopyranosyl]prop-1-ene (**6**, n = 1)

The tetrol (**5**, n = 1) yielded the *trisaccharide* (**6**, n = 1) as a white powder (48%), m.p. 93-95° (MeOH), $[\alpha]_D$ −11.1° (Found: C, 51.7; H, 6.1. $C_{41}H_{56}O_{25}$ requires C, 51.9; H, 6.0%). ^{1}H n.m.r. (500 MHz) δ 1.93, 1.94, 1.99, 2.00, 2.01, 2.02, 2.04, 2.09, 2.11, 2.12, 10s, 30H, Me; 2.21-2.27, m, 2H, H3; 3.42, ddd, $J_{3,1'}$ 4.0, 7.2, $J_{1',2'}$ 9.9 Hz, H1′; 3.49, ddd, $J_{4'',5''}$ 9.8, $J_{5'',6''}$ 1.9, 5.2 Hz, H5″; 3.56, ddd, $J_{4',5'}$ 9.8, $J_{5',6'}$ 2.0, 5.0 Hz, H5′; 3.67, t, $J_{3'',4''}$ 9.5 Hz, H4″; 3.76, t, $J_{3',4'}$ 9.1 Hz, H4′; 3.81-3.87, m, H5‴; 4.03-4.11, m, 4H, H6′,6″,6‴; 4.33, dd, $J_{6',6'}$ 12.1 Hz, H6′; 4.42, d, $J_{1''',2'''}$ 7.9 Hz, H1‴; 4.45, dd, $J_{6'',6''}$ 11.8 Hz, H6″; 4.46, $J_{1'',2''}$ 7.8 Hz, H1″; 4.78, t, $J_{2',3'}$ 9.6 Hz, H2′; 4.81, dd, $J_{2'',3''}$ 9.3 Hz, H2″; 4.90, dd, $J_{2''',3'''}$ 10.4, $J_{3''',4'''}$ 3.4 Hz, H3‴; 4.99-5.04, m, 2H, H1; 5.06, dd, H2‴; 5.09, t, H3″; 5.10, t, H3′; 5.31, dd, $J_{4''',5'''}$ 0.9 Hz, H4‴; 5.74, ddt, $J_{1,2}$ 10.6, 17.1, $J_{2,3} \approx J_{2,3}$ 6.9 Hz, H2. ^{13}C n.m.r. (125.8 MHz) δ 20.44, 20.53, 20.58, 20.59, 20.68, 20.72, 20.82, 10C, Me; 35.71, C3; 60.73, C6‴; 62.06, C6″; 62.22, C6′; 66.48, C4‴; 68.93, C2‴; 70.61, C5‴; 70.87, C3‴; 71.78, 71.81, C2′,2″; 72.55, C3′; 72.92, C5′; 73.96, C3″; 75.86, C4′; 76.46, C5″; 76.77, C4″; 76.83, C1′; 100.41, C1″; 101.01, C1‴; 117.59, C1; 132.84, C2; 169.07, 169.32, 169.72, 169.75, 169.90, 170.00, 170.09, 170.22, 170.32, 10C, CO. H.r.m.s. *m/z* 949.3214 [$C_{41}H_{57}O_{25}$ $(M+H)^{+\bullet}$ requires 949.3189].

4-[O-(Tetra-O-acetyl-β-D-galactopyranosyl)-(1→4)-O-(tri-O-acetyl-β-D-glucopyranosyl)-(1→4)-tri-O-acetyl-β-D-glucopyranosyl]but-1-ene (**6**, n = 2)

The tetrol (**5**, n = 2) yielded the *trisaccharide* (**6**, n = 2) as a colourless glass (52%), m.p. 88-90° (MeOH), $[\alpha]_D$ −13.3° (Found: C, 52.1; H, 5.9. $C_{42}H_{58}O_{25}$ requires C, 52.4; H, 6.1%). ^{1}H n.m.r. δ 1.40-1.60, m, 2H, H3; 1.94, 1.95, 1.99, 2.00, 2.01, 2.03, 2.04, 2.10, 2.11, 2.13, 10s, 30H, Me; 2.12-2.26, m, 2H, H4; 3.34, dt, $J_{4,1'} \approx J_{4,1'}$ 3.2, $J_{1',2'}$ 9.2 Hz, H1′; 3.48, ddd, $J_{4'',5''}$ 9.8, $J_{5'',6''}$ 1.8, 5.3 Hz, H5″; 3.57, ddd, $J_{4',5'}$ 9.8, $J_{5',6'}$ 1.8, 4.9 Hz, H5′; 3.67, t, $J_{3'',4''}$ 9.3 Hz, H4″; 3.77, t, $J_{3',4'}$ 9.1 Hz, H4′; 3.80-3.85, m, H5‴; 4.02-4.12, m, 4H, H6′,6″,6‴; 4.34, dd, $J_{6',6'}$ 12.0 Hz, H6′; 4.40-4.47, m, H1″,6″,1‴; 4.76, t, $J_{2',3'}$ 9.3 Hz, H2′; 4.82, dd, $J_{1'',2''}$ 7.8, $J_{2'',3''}$ 9.2 Hz, H2″; 4.90, dd, $J_{2''',3'''}$ 10.4, $J_{3''',4'''}$ 3.4 Hz, H3‴; 4.93-5.02, m, 2H, H1; 5.06, dd, $J_{1''',2'''}$ 7.9 Hz, H2‴; 5.10, t, H3″; 5.11, t, H3′; 5.31, dd, $J_{4''',5'''}$ 0.9 Hz, H4‴; 5.73, dddd, $J_{1,2}$ 10.1, 17.2, $J_{2,3}$ 6.1, 7.1 Hz, H2. ^{13}C n.m.r. δ 20.43, 20.57, 20.67, 20.71, 20.81, 10C, Me; 28.96, 30.32, C3,4; 60.73, C6‴; 62.24, 2C, C6′,6″; 66.49, C4‴; 68.95, C2‴; 70.03, C5‴; 70.88, C3‴; 71.80, C2′; 72.25, C2″; 72.55, C3′; 72.94, C5′; 73.99, C3″; 75.87, C4′; 76.50, 2C, C4″,5″; 76.94, C1′; 100.41, C1″; 101.02, C1‴; 115.21, C1; 137.47, C2;

169.06, 169.32, 169.70, 169.87, 169.99, 170.07, 170.21, 170.31, 10C, CO. H.r.m.s. *m/z* 963.3385 [$C_{42}H_{59}O_{25}$ $(M+H)^{+\bullet}$ requires 963.3345].

5-[O-(Tetra-O-acetyl-β-D-galactopyranosyl)-(1→4)-O-(tri-O-acetyl-β-D-glucopyranosyl)-(1→4)-tri-O-acetyl-β-D-glucopyranosyl]pent-1-ene (**6**, n = 3)

The tetrol (**5**, n = 3) yielded the *trisaccharide* (**6**, n = 3) as a white powder (53%), m.p. 85-87° (MeOH), $[\alpha]_D$ −14.1° (Found: C, 52.8; H, 6.1. $C_{43}H_{60}O_{25}$ requires C, 52.9; H, 6.2%). ^{1}H n.m.r. δ 1.34-1.61, 1.70-1.82, 2m, 4H, H3,4; 1.94, 1.95, 2.00, 2.01, 2.02, 2.03, 2.05, 2.10, 2.12, 2.13, 10s, 30H, Me; 2.12-2.26, m, 2H, H5; 3.29-3.36, m, H1′; 3.49, ddd, $J_{4'',5''}$ 9.9, $J_{5'',6''}$ 1.8, 5.2 Hz, H5″; 3.57, ddd, $J_{4',5'}$ 10.0, $J_{5',6'}$ 1.9, 4.9 Hz, H5′; 3.68, t, $J_{3'',4''}$ 9.7 Hz, H4″; 3.77, t, $J_{3',4'}$ 9.1 Hz, H4′; 3.80-3.86, m, H5‴; 4.02-4.12, m, 4H, H6′,6″,6‴; 4.34, dd, $J_{6',6'}$ 12.1 Hz, H6′; 4.42, d, $J_{1''',2'''}$ 7.9 Hz, H1‴; 4.43-4.47, m, H6″; 4.46, $J_{1'',2''}$ 7.8 Hz, H1″; 4.75, t, $J_{1',2'} \approx J_{2',3'}$ 9.6 Hz, H2′; 4.83, t, $J_{2'',3''}$ 7.9 Hz, H2″; 4.88-5.00, m, 3H, H1,3‴; 5.07, t, $J_{2''',3'''}$ 8.1 Hz, H2‴; 5.10, t, H3″; 5.11, t, H3′; 5.31, dd, $J_{3''',4'''}$ 3.4, $J_{4''',5'''}$ 0.8 Hz, H4‴; 5.74, ddt, $J_{1,2}$ 10.1, 17.2, $J_{2,3} \approx J_{2,3}$ 6.6 Hz, H2. ^{13}C n.m.r. δ 20.45, 20.57, 20.68, 20.82, 10C, Me; 24.13, C3; 30.54, C5; 33.23, C4; 60.76, C6‴; 62.26, C6′,6″; 66.53, C4‴; 68.99, C2‴; 70.67, C5‴; 70.91, C3‴; 71.84, C2′; 72.28, C2″; 72.59, C3′; 72.96, C5′; 74.05, C3″; 75.91, C4′; 76.51, C5″; 76.94, C4″; 77.35, C1′; 100.42, C1″; 101.04, C1‴; 114.73, C1; 138.26, C2; 169.07, 169.33, 169.72, 169.90, 170.01, 170.09, 170.23, 170.33, 10C, CO. H.r.m.s. *m/z* 977.3536 [$C_{43}H_{61}O_{25}$ $(M+H)^{+\bullet}$ requires 977.3502].

General Procedure for the Preparation of the Trisaccharides (11, n = 1-3)

A solution of the decaacetate (**6**) in MeOH was treated with NaOMe as described previously to yield the trisaccharide (**11**).

3-[O-(β-D-Galactopyranosyl)-(1→4)-(β-D-glucopyranosyl)-(1→4)-O-β-D-glucopyranosyl]prop-1-ene (**11**, n = 1)

The decaacetate (**6**, n = 1) yielded the *polyol* (**11**, n = 1) as a fine, white powder (98%), m.p. 133-136° (MeOH), $[\alpha]_D$ +2.3° (MeOH) (Found: C, 48.0; H, 7.1. $C_{21}H_{36}O_{15}$ requires C, 47.7; H, 6.9%). ^{1}H n.m.r. δ 2.05-2.15, 2.43-2.52, 2m, 2H, H3; 3.05, t, $J_{1',2'} \approx J_{2',3'}$ 9.5 Hz, H2′; 3.10, dt, $J_{3,1'} \approx J_{3,1'}$ 2.7, $J_{1',2'}$ 9.5 Hz, H1′; 3.15-3.21, m, H5′,2″; 3.32-3.52, m, H3′,4′,3″,4″,5″,2‴,3‴,5‴; 3.58, dd, $J_{5'',6''}$ 4.5, $J_{6'',6''}$ 11.5 Hz, H6″; 3.67, dd, $J_{5'',6''}$ 7.6 Hz, H6″; 3.69-3.76, m, 4H, H6′,4‴,6‴; 3.81, dd, $J_{5''',6'''}$ 2.4, $J_{6''',6'''}$ 12.1 Hz, H6‴; 4.24, d, $J_{1''',2'''}$ 7.3 Hz, H1‴; 4.33, d, $J_{1'',2''}$ 7.9 Hz, H1″; 4.90-5.02, m, 2H, H1; 5.84, ddt, $J_{1,2}$ 10.2, 17.1, $J_{2,3} \approx J_{2,3}$ 6.8 Hz, H2. ^{13}C n.m.r. (125.8 MHz) δ 39.43, C3; 64.04, C6‴; 64.57, C6′; 64.99, C6″; 72.77, C4‴; 74.99, C2‴; 77.04, C2″; 77.11, C5‴; 77.26, C2′; 78.68, 79.56, C4′,4″; 79.10, C3‴; 80.51, C3′; 82.57, C1′; 82.63, 82.96, C5′,5″;

83.50, C3″; 106.66, C1″; 107.54, C1‴; 119.54, C1; 138.73, C2. H.r.m.s. ***m/z*** **529.2148** [$C_{21}H_{37}O_{15}$ $(M+H)^{+\bullet}$ requires 529.2132].

4-[O-(β-D-Galactopyranosyl)-(1→4)-O-(β-D-glucopyranosyl)-(1→4)-β-D-glucopyranosyl]but-1-ene (**11**, n = 2)

The decaacetate (**6**, n = 2) yielded the *polyol* (**11**, n = 2) as a white powder (98%), m.p. 219-222° (MeOH), $[\alpha]_D$ –0.2° (MeOH) (Found: C, 48.6; H, 7.2. $C_{22}H_{38}O_{15}$ requires C, 48.7; H, 7.1%). ^{1}H n.m.r. (500 MHz) δ 1.48-1.52, 1.90-1.96, 2m, 2H, H4; 2.10-2.17, m, 2H, H3; 3.12, t, $J_{1',2'} \approx J_{2',3'}$ 9.5 Hz, H2′; 3.16, dt, $J_{4,1'} \approx J_{4,1'}$ 2.2, $J_{1',2'}$ 9.4 Hz, H1′; 3.26-3.31, m, H5′,2″; 3.45, t, $J_{3',4'}$ 8.7 Hz, H3′; 3.47-3.50, m, H3‴,5‴; 3.51-3.62, m, H4′,3″,4″,5″,2‴; 3.68, dd, $J_{5'',6''}$ 4.6, $J_{6'',6''}$ 11.5 Hz, H6″; 3.77, dd, $J_{5'',6''}$ 7.6 Hz, H6″; 3.81, dd, $J_{3''',4'''}$ 3.3, $J_{4''',5'''}$ 0.8 Hz, H4‴; 3.82-3.87, m, 3H, H6′,6‴; 3.91, dd, $J_{5''',6'''}$ 2.4, $J_{6''',6'''}$ 12.1 Hz, H6‴; 4.34, d, $J_{1''',2'''}$ 7.6 Hz, H1‴; 4.44, d, $J_{1'',2''}$ 7.9 Hz, H1″; 4.92, ddt, $J_{1,1}$ 2.1, $J_{1,2}$ 10.2, $J_{1,3} \approx J_{1,3}$ 1.1 Hz, H1; 5.02, ddt, $J_{1,2}$ 17.1, $J_{1,3} \approx J_{1,3}$ 1.6 Hz, H1; 5.84, dddd, $J_{2,3}$ 6.4, 6.8 Hz, H2. ^{13}C n.m.r. (125.8 MHz) δ 30.66, C3; 32.09, C4; 61.54, C6‴; 62.13, C6′; 62.50, C6″; 70.28, C4‴; 72.51, C2‴; 74.54, C2″; 74.76, C5‴; 75.23, C2′; 76.19, 77.08, C4′,4″; 76.62, C3‴; 78.07, C3′; 79.96, C1′; 80.06, 80.11, C5′,5″; 81.11, C3″; 104.39, C1″; 105.05, C1‴; 114.95, C1; 139.81, C2. H.r.m.s. *m/z* 543.2275 [$C_{22}H_{39}O_{15}$ $(M+H)^{+\bullet}$ requires 543.2289].

5-[O-(β-D-Galactopyranosyl)-(1→4)-O-(β-D-glucopyranosyl)-(1→4)-β-D-glucopyranosyl]pent-1-ene (**11**, n = 3)

The decaacetate (**6**, n = 3) yielded the *polyol* (**11**, n = 3) as a white powder (98%), m.p. >220° (MeOH), $[\alpha]_D$ –2.8° (MeOH) (Found: C, 49.8; H, 7.4. $C_{23}H_{40}O_{15}$ requires C, 49.6; H, 7.4%). ^{1}H n.m.r. δ 1.18-2.00, m, 6H, H3,4,5; 2.97-3.08, m, H1′,2′; 3.17-3.23, m, H5′,2″; 3.32-3.55, m, H3′,4′,3″,4″,5″,2‴,3‴,5‴; 3.59, dd, $J_{5'',6''}$ 4.5, $J_{6'',6''}$ 11.5 Hz, H6″; 3.68, dd, $J_{5'',6''}$ 7.6 Hz, H6″; 3.69-3.77, m, 4H, H6′,4‴,6‴; 3.82, dd, $J_{5''',6'''}$ 2.4, $J_{6''',6'''}$ 12.1 Hz, H6‴; 4.25, d, $J_{1''',2'''}$ 7.3 Hz, H1‴; 4.35, d, $J_{1'',2''}$ 7.9 Hz, H1″; 4.82, ddt, $J_{1,1}$ 2.1, $J_{1,2}$ 10.3, $J_{1,3} \approx J_{1,3}$ 1.1 Hz, H1; 4.89, ddt, $J_{1,2}$ 17.1, $J_{1,3} \approx J_{1,3}$ 1.6 Hz, H1; 5.72, ddt, $J_{2,3} \approx J_{2,3}$ 6.8 Hz, H2. ^{13}C n.m.r. (125.8 MHz) δ 25.91, C3; 32.33, C5; 32.91, C4; 61.56, C6‴; 62.16, C6′; 62.49, C6″; 70.27, C4‴; 72.49, C2‴; 74.53, C2″; 74.75, C5‴; 75.24, C2′; 76.18, 77.06, C4′,4″; 76.60, C3‴; 78.07, C3′; 80.09, 80.61, 3C, C1′,5′,5″; 81.18, C3″; 104.38, C1″; 105.04, C1‴; 114.87, C1; 140.00, C2. H.r.m.s. *m/z* 547.2413 [$C_{23}H_{41}O_{15}$ $(M+H)^{+\bullet}$ requires 547.2445].

General Procedure for the Preparation of the Disaccharides (7, n = 1-3)

Aspergillus oryzae β-galactosidase in phosphate buffer (100 μL) was added to a suspension of the trisaccharide (**11**) in phosphate buffer (0.05 M, pH 7.3) and the mixture was stirred (2 h) at constant

temperature (22°). CH_3CN was added and the mixture heated (100°, 10 min). The organic solvent was evaporated, the aqueous phase freeze-dried and the gummy residue was acetylated and subjected to standard workup ($CHCl_3$) as described previously. Flash chromatography (30-60% EtOAc/petrol) followed by gel permeation chromatography afforded the disaccharide (**7**).

3-[O-(Tetra-O-acetyl-β-D-glucopyranosyl)-(1→4)-tri-O-acetyl-β-D-glucopyranosyl]prop-1-ene (**7**, n = 1)

The trisaccharide (**11**, n = 1) yielded the heptaacetate (**7**, n = 1) as fine, white needles (43%), m.p. 159-160° (MeOH), $[\alpha]_D$ −5.9°. ^{1}H n.m.r. δ 1.97, 2.00, 2.01, 2.02, 2.08, 2.10, 6s, 21H, Me; 2.10-2.32, m, 2H, H3; 3.42-3.48, m, H1′; 3.52, ddd, $J_{4',5'}$ 9.9, $J_{5',6'}$ 2.0, 5.2 Hz, H5′; 3.63, ddd, $J_{4'',5''}$ 9.5, $J_{5'',6''}$ 2.2, 4.2 Hz, H5″; 3.71, t, $J_{3',4'}$ 9.8 Hz, H4′; 4.02, dd, $J_{6'',6''}$ 12.6 Hz, H6″; 4.07, dd, $J_{6',6'}$ 11.9 Hz, H6′; 4.38, dd, H6″; 4.47, dd, H6′; 4.49, d, $J_{1'',2''}$ 7.9 Hz, H1″; 4.82, t, $J_{1',2'} \approx J_{2',3'}$ 9.6 Hz, H2′; 4.93, dd, $J_{2'',3''}$ 9.1 Hz, H2″; 5.00-5.10, m, 3H, H1,4″; 5.10, t, $J_{3'',4''}$ 9.2 Hz, H3″; 5.12, t, H3′; 5.77, ddt, $J_{1,2}$ 9.9, 16.3, $J_{2,3} \approx J_{2,3}$ 6.9 Hz, H2. ^{13}C n.m.r. δ 20.52, 20.56, 20.63, 20.73, 20.83, 7C, Me; 35.76, C3; 61.54, C6″; 62.19, C6′; 67.77, C4″; 71.59, C2″; 71.81, C5″; 71.91, C2′; 72.93, C3′; 74.05, C3″; 76.52, C5′; 76.84, C4′; 76.92, C1′; 100.78, C1″; 117.64, C1; 132.90, C2; 169.05, 169.29, 169.83, 169.98, 170.23, 170.35, 170.50, 7C, CO.

4-[O-(Tetra-O-acetyl-β-D-glucopyranosyl)-(1→4)-tri-O-acetyl-β-D-glucopyranosyl]but-1-ene (**7**, n = 2)

The trisaccharide (**11**, n = 2) yielded the *heptaacetate* (**7**, n = 2) as fine, white needles (58%), m.p. 198.5-200.5° (MeOH), $[\alpha]_D$ −9.0° (Found: C, 53.5; H, 6.5. $C_{30}H_{42}O_{17}$ requires C, 53.4; H, 6.3%). ^{1}H n.m.r. δ 1.41-1.63, m, 2H, H3; 1.98, 2.00, 2.02, 2.03, 2.08, 2.12, 6s, 21H, Me; 2.00-2.20, m, 2H, H4; 3.37, dt, $J_{4,1'} \approx J_{4,1'}$ 3.3, $J_{1',2'}$ 9.7 Hz, H1′; 3.50, ddd, $J_{4',5'}$ 9.9, $J_{5',6'}$ 1.9, 5.4 Hz, H5′; 3.65, ddd, $J_{4'',5''}$ 9.4, $J_{5'',6''}$ 2.1, 4.4 Hz, H5″; 3.71, t, $J_{3',4'}$ 9.3 Hz, H4′; 4.03, dd, $J_{6'',6''}$ 12.5 Hz, H6″; 4.08, dd, $J_{6',6'}$ 11.9 Hz, H6′; 4.37, dd, H6″; 4.47, dd, H6′; 4.49, d, $J_{1'',2''}$ 7.9 Hz, H1″; 4.79, t, $J_{1',2'} \approx J_{2',3'}$ 9.6 Hz, H2′; 4.93, dd, $J_{2'',3''}$ 9.2 Hz, H2″; 4.95-5.04, m, 2H, H1; 5.06, t, $J_{3'',4''}$ 9.8 H4″; 5.12, t, H3″; 5.13, t, H3′; 5.76, dddd, $J_{1,2}$ 10.2, 17.3, $J_{2,3}$ 6.0, 7.3 Hz, H2. ^{13}C n.m.r. δ 20.53, 20.64, 20.72, 20.84, 7C, Me; 29.02, 30.39, C3,4; 61.55, C6″; 62.36, C6′; 67.78, C4″; 71.60, C2″; 71.91, C5″; 72.24, C2′; 72.94, C3′; 74.07, C3″; 76.58, C5′; 76.59, C4′; 77.01, C1′; 100.80, C1″; 115.26, C1; 137.53, C2; 169.05, 169.30, 169.96, 170.23, 170.36, 170.50, 7C, CO. H.r.m.s. *m/z* 675.2465 [$C_{30}H_{43}O_{17}$ $(M+H)^{+\bullet}$ requires 675.2500].

5-[O-(Tetra-O-acetyl-β-D-glucopyranosyl)-(1→4)-tri-O-acetyl-β-D-glucopyranosyl]pent-1-ene (**7**, n = 3)

The trisaccharide (**11**, n = 3) yielded the *heptaacetate* (**7**, n = 3) as fine, white needles (64%), m.p. 176-178° (MeOH), $[\alpha]_D$ −13.5° (Found: C, 53.9; H, 6.5. $C_{31}H_{44}O_{17}$ requires C, 54.1; H, 6.4%). ^{1}H n.m.r. (500 MHz) δ 1.35-1.42, 1.44-1.61, 2m, 4H, H4,5; 1.97, 2.00, 2.01, 2.02, 2.08, 2.09, 6s, 21H, Me; 1.98-2.08,

m, 2H, H3; 3.32-3.36, m, H1′; 3.52, ddd, $J_{4',5'}$ 9.8, $J_{5',6'}$ 2.0, 5.5 Hz, H5′; 3.64, ddd, $J_{4'',5''}$ 9.9, $J_{5'',6''}$ 2.4, 4.3 Hz, H5″; 3.69, t, $J_{3',4'}$ 9.4 Hz, H4′; 4.02, dd, $J_{6'',6''}$ 12.4 Hz, H6″; 4.07, dd, $J_{6',6'}$ 11.9 Hz, H6′; 4.37, dd, H6″; 4.45, dd, H6′; 4.48, d, $J_{1'',2''}$ 8.0 Hz, H1″; 4.77, t, $J_{1',2'} \approx J_{2',3'}$ 9.6 Hz, H2′; 4.92, dd, $J_{2'',3''}$ 9.3 Hz, H2″; 4.93, ddt, $J_{1,1}$ 3.0, $J_{1,2}$ 10.2, $J_{1,3} \approx J_{1,3}$ 1.2 Hz, H1; 4.97, ddt, $J_{1,2}$ 17.2, $J_{1,3} \approx J_{1,3}$ 1.8 Hz, H1; 5.06, t, $J_{3'',4''}$ 9.5 Hz, H4″; 5.12, t, H3″; 5.13, t, H3′; 5.75, ddt, $J_{2,3} \approx J_{2,3}$ 6.6 Hz, H2. ^{13}C n.m.r. (125.8 MHz) δ 20.54, 20.58, 20.65, 20.72, 20.86, 7C, Me; 24.16, C3; 30.50, C5; 33.27, C4; 61.52, C6″; 62.32, C6′; 67.73, C4″; 71.56, C2″; 71.88, C5″; 72.19, C2′; 72.92, C3′; 74.07, C3″; 76.49, C5′; 76.97, C4′; 77.39, C1′; 100.78, C1″; 114.76, C1; 138.30, C2; 169.07, 169.31, 169.99, 170.24, 170.39, 170.53, 7C, CO. H.r.m.s. *m/z* 689.2622 [$C_{31}H_{45}O_{17}$ $(M+H)^{+\bullet}$ requires 689.2598].

General Procedure for the Preparation of the Disaccharides (2, n = 1-3)

A solution of the heptaacetate (**7**) in MeOH was treated with NaOMe as described previously, and subjected to gel permeation chromatography to yield the heptaol (**2**).

3-[O-(β-D-Glucopyranosyl)-(1→4)-β-D-glucopyranosyl]prop-1-ene (**2**, n = 1)

The heptaacetate (**7**, n = 1) yielded the heptaol (**2**, n = 1) as a colourless oil (95%). ^{1}H n.m.r. δ 2.05-2.14, 2.41-2.51, 2m, 2H, H3; 3.01-3.28, m, H1′,2′,5′,2″,3″,4″,5″; 3.34, t, $J_{2',3'} \approx J_{3',4'}$ 8.7 Hz, H3′; 3.40, t, $J_{4',5'}$ 9.2 Hz, H4′; 3.54, dd, $J_{5'',6''}$ 5.3, $J_{6'',6''}$ 11.9 Hz, H6″; 3.68-3.77, m, 2H, H6′; 3.77, dd, $J_{5'',6''}$ 1.9 Hz, H6″; 4.28, d, $J_{1'',2''}$ 7.8 Hz, H1″; 4.88-5.02, m, 2H, H1; 5.84, ddt, $J_{1,2}$ 10.2, 17.1, $J_{2,3} \approx J_{2,3}$ 6.8 Hz, H2. ^{13}C n.m.r. δ 34.79, C3; 62.20, C6′; 62.47, C6″; 71.40, C4″; 74.66, C2″; 74.97, C2′; 77.89, C3″; 78.13, 2C, C3′,5″; 80.19, C5′; 80.48, C1′; 81.19, C4′; 104.63, C1″; 117.04, C1; 136.27, C2.

4-[O-(β-D-Glucopyranosyl)-(1→4)-β-D-glucopyranosyl]but-1-ene (**2**, n = 2)

The heptaacetate (**7**, n = 2) yielded the heptaol (**2**, n = 2) as a colourless oil (95%). ^{1}H n.m.r. δ 1.30-1.42, 1.77-1.87, 1.97-2.09, 2.12-2.25, 4m, 4H, H3,4; 2.97-3.05, m, H1′,2′; 3.11, dd, $J_{1'',2''}$ 7.8, $J_{2'',3''}$ 9.1 Hz, H2″; 3.12-3.28, m, H5′,3″,4″,5″; 3.33, t, $J_{2',3'} \approx J_{3',4'}$ 8.7 Hz, H3′; 3.40, t, $J_{4',5'}$ 9.2 Hz, H4′; 3.54, dd, $J_{5'',6''}$ 5.4, $J_{6'',6''}$ 11.7 Hz, H6″; 3.68-3.81, m, 3H, H6′,6″; 4.29, d, H1″; 4.75-4.94, m, 2H, H1; 5.73, dddd, $J_{1,2}$ 10.2, 17.1, $J_{2,3}$ 6.4, 6.9 Hz, H2. ^{13}C n.m.r. δ 30.67, 32.11, C3,4; 62.26, C6′; 62.47, C6″; 71.40, C4″; 74.97, C2″; 75.26, C2′; 77.89, C3″; 78.14, 2C, C3′,5″; 79.96, C5′; 80.16, C1′; 81.31, C4′; 104.64, C1″; 114.93, C1; 139.84, C2.

5-[O-(β-D-Glucopyranosyl)-(1→4)-β-D-glucopyranosyl]pent-1-ene (**2**, n = 3)

The heptaacetate (**7**, n = 3) yielded the heptaol (**2**, n = 3) as a colourless oil (95%). ^{1}H n.m.r. (500 MHz) δ 1.37-1.40, m, H4,5; 1.63-1.71, m, H4; 1.83-1.88, m, H5; 2.02-2.10, m, 2H, H3; 3.10, dd, $J_{1',2'}$ 8.1, $J_{2',3'}$ 9.4

Hz, H2′; 3.14, dt, $J_{5,1'} \approx J_{5,1'}$ 2.8 Hz, H1′; 3.22, dd, $J_{1'',2''}$ 7.9, $J_{2'',3''}$ 9.1 Hz, H2″; 3.27-3.31, m, H5′,4″; 3.33, ddd, $J_{4'',5''}$ 9.5, $J_{5'',6''}$ 2.0, 5.4 Hz, H5″; 3.36, t, $J_{3'',4''}$ 8.7 Hz, H3″; 3.44, t, $J_{3',4'}$ 8.7 Hz, H3′; 3.51, t, $J_{4',5'}$ 9.3 Hz, H4′; 3.65, dd, $J_{6'',6''}$ 11.9 Hz, H6″; 3.82, dd, $J_{5',6'}$ 3.9, $J_{6',6'}$ 12.1 Hz, H6′; 3.84, dd, $J_{5',6'}$ 2.7 Hz, H6′; 3.87, dd, H6″; 4.39, d, H1″; 4.92, ddt, $J_{1,1}$ 2.3, $J_{1,2}$ 10.2, $J_{1,3} \approx J_{1,3}$ 1.1 Hz, H1; 4.99, ddt, $J_{1,2}$ 17.1, $J_{1,3} \approx J_{1,3}$ 1.6 Hz, H1; 5.82, ddt, $J_{2,3} \approx J_{2,3}$ 6.7 Hz, H2. ^{13}C n.m.r. (125.8 MHz) δ 25.93, C3; 32.35, C5; 34.95, C4; 62.23, C6′; 62.44, C6″; 71.38, C4″; 74.95, C2″; 75.27, C2′; 77.86, C3″; 78.11, 78.14, C3′,5″; 80.13, C5′; 80.61, C1′; 81.26, C4′; 104.61, C1″; 114.87, C1; 140.02, C2. H.r.m.s. *m/z* 395.3532 [$C_{17}H_{31}O_{10}$ $(M+H)^{+\bullet}$ requires 395.1917].

General Procedure for the Preparation of the Disaccharides (8, n = 1-3)

Benzyl bromide (10 eq.) was added to a mixture of pre-washed (petrol) sodium hydride (55% oil suspension, 14 eq.) and the heptaol (**2**) in DMF under an atmosphere of nitrogen and the mixture was stirred (r.t., 12 h). Water was added to the cooled (0°) suspension and stirring continued (3 h). The mixture was twice extracted ($CHCl_3$) and the combined extracts were washed with water and brine and dried. Flash chromatography (5-10% EtOAc/petrol) afforded the heptabenzyl *C*-cellobioside (**8**).

3-[O-(Tetra-O-benzyl-β-D-glucopyranosyl)-(1→4)-tri-O-benzyl-β-D-glucopyranosyl]prop-1-ene (**8**, n = 1)

The heptaol (**2**, n = 1) yielded the heptabenzyl *C*-cellobioside (**8**, n = 1) as a white powder (85%), m.p. 114-116° (lit.[4] 117-119°). H.r.m.s. *m/z* 997.4844 [$C_{64}H_{69}O_{10}$ $(M+H)^{+\bullet}$ requires 997.4891].

4-[O-(Tetra-O-benzyl-β-D-glucopyranosyl)-(1→4)-tri-O-benzyl-β-D-glucopyranosyl]but-1-ene (**8**, n = 2)

The heptaol (**2**, n = 2) yielded the heptabenzyl *C*-cellobioside (**8**, n = 2) as a colourless oil (75%). The ^{1}H- and ^{13}C- n.m.r. spectra were similar to those already reported in the literature.[4]

5-[O-(Tetra-O-benzyl-β-D-glucopyranosyl)-(1→4)-tri-O-benzyl-β-D-glucopyranosyl]pent-1-ene (**8**, n = 3)

The heptaol (**2**, n = 3) yielded the *heptabenzyl C-cellobioside* (**8**, n = 3) as a white solid (90%), m.p.122-123° (EtOH/petrol; lit.[4] 123-125°) (Found: C, 77.4; H, 7.0. $C_{66}H_{72}O_{10}$ requires C, 77.3; H, 7.1%).

General Procedure for the Preparation of the Epoxides (9, n = 1-3)

Freshly prepared dimethyldioxirane[8] (0.1 M in acetone, 4 eq.) was added to a cooled (0°), stirred solution of the alkene (**7**) in CH_2Cl_2 under an atmosphere of argon. The solution was allowed to warm (r.t., 4 h) and then the solvent was evaporated to afford a mixture of the diastereoisomeric epoxides (**9**) (1:1).

1,2-Epoxy-3-[O-(tetra-O-acetyl-β-D-glucopyranosyl)-(1→4)-tri-O-acetyl-β-D-glucopyranosyl]propane (**9**, n = 1)

The disaccharide (**7**, n = 1) yielded the epoxides (**9**, n = 1) as a white powder, m.p. 154-157°. ^{1}H n.m.r. δ 1.41-2.10, m, 2H, H3; 1.98, 2.00, 2.01, 2.02, 2.03, 2.08, 2.11, 7s, 21H, Me; 2.47, 2.49, 2dd, $J_{1,1}$ 4.9, $J_{1,2}$ 2.7 Hz, H1; 2.73, 2.79, 2dd, $J_{1,2}$ 4.0 Hz, H1; 3.02-3.11, m, H2; 3.49-3.67, m, H1′,5′,5″; 3.74, 3.75, 2t, $J_{3',4'} \approx J_{4',5'}$ 9.8 Hz, H4′; 4.04, dd, $J_{5'',6''}$ 2.2, $J_{6'',6''}$ 12.5 Hz, H6″; 4.05-4.12, m, H6′; 4.38, dd, $J_{5'',6''}$ 4.2 Hz, H6″; 4.49, 4.53, 2dd, $J_{5',6'}$ 2.0, $J_{6',6'}$ 11.8 Hz, H6′; 4.52, d, $J_{1'',2''}$ 7.9 Hz, H1″; 4.81, t, $J_{1',2'} \approx J_{2',3'}$ 9.6 Hz, H2′; 4.90, 4.94, 2dd, $J_{2'',3''}$ 9.8 Hz, H2″; 5.07, 5.08, 2t, $J_{3'',4''} \approx J_{4'',5''}$ 9.7 Hz, H4″; 5.04, 5.06, 2t, H3″; 5.07, t, H3′. ^{13}C n.m.r. δ 20.53, 20.65, 20.83, 7C, Me; 33.84, 35.28, C3; 46.38, 47.42, 48.60, 2C, C1,2; 61.55, C6″; 62.05, 62.17, C6′; 67.78, C4″; 71.60, 71.95, 72.10, 72.92, 73.83, 73.97, 74.92, 75.17, 5C, C2′,3′,2″,3″,5″; 76.62, 76.70, 3C, C1′,4′,5′; 100.76, C1″; 169.02, 169.30, 169.86, 170.05, 170.25, 170.31, 170.51, 7C, CO.

1,2-Epoxy-4-[O-(tetra-O-acetyl-β-D-glucopyranosyl)-(1→4)-tri-O-acetyl-β-D-glucopyranosyl]butane (**9**, n = 2)

The disaccharide (**7**, n = 2) yielded the epoxides (**9**, n = 2) as a white powder, m.p. 179-182°. ^{1}H n.m.r. δ 1.35-1.90, m, 3H, H3,4; 1.97, 2.00, 2.02, 2.02, 2.04, 2.08, 2.10, 7s, 21H, Me; 2.10-2.20, m, H3; 2.45, 2.46, 2dd, $J_{1,1}$ 5.0, $J_{1,2}$ 2.9 Hz, H1; 2.75, dd, $J_{1,2}$ 4.0 Hz, H1; 2.85-2.94, m, H2; 3.36-3.44, m, H1′; 3.52, ddd, $J_{4',5'}$ 9.9, $J_{5',6'}$ 1.9, 5.0 Hz, H5′; 3.65, ddd, $J_{4'',5''}$ 9.6, $J_{5'',6''}$ 2.2, 4.1 Hz, H5″; 3.70, 3.71, 2t, $J_{3',4'} \approx J_{4',5'}$ 9.9 Hz, H4′; 4.03, dd, $J_{6'',6''}$ 12.5 Hz, H6″; 4.05, 4.07, 2dd, $J_{6',6'}$ 11.9 Hz, H6′; 4.37, dd, H6″; 4.47, 4.49, 2dd, H6′; 4.49, d, $J_{1'',2''}$ 7.8 Hz, H1″; 4.78, 4.79, 2t, $J_{1',2'} \approx J_{2',3'}$ 9.6 Hz, H2′; 4.92, dd, $J_{2'',3''}$ 9.1 Hz, H2″; 5.07, t, $J_{3'',4''}$ 9.7 Hz, H4″; 5.14, t, H3′,3″. ^{13}C n.m.r. δ 20.52, 20.63, 20.72, 20.83, 7C, Me; 27.30, 27.69, 28.03, 28.31, C3,4; 46.93, 47.01, C1; 51.50, 52.02, C2; 61.55, C6″; 62.22, C6′; 67.78, C4″; 71.60, C2″; 71.92, C5″; 72.13, C2′; 72.92, 73.96, C3′,3″; 76.58, C5′; 76.85, C4′; 77.16, C1′; 100.78, C1″; 169.05, 169.30, 169.94, 170.23, 170.34, 170.52, 7C, CO. H.r.m.s. *m/z* 691.2460 [$C_{30}H_{43}O_{18}$ $(M+H)^{+\bullet}$ requires 691.2460].

1,2-Epoxy-5-[O-(tetra-O-acetyl-β-D-glucopyranosyl)-(1→4)-tri-O-acetyl-β-D-glucopyranosyl]pentane (**9**, n = 3)

The disaccharide (**7**, n = 3) yielded the epoxides (**9**, n = 3) as fine white needles, m.p. 176-178°. ^{1}H n.m.r. (500 MHz) δ 1.40-1.65, m, 5H, H3,4,5; 1.97, 1.99, 2.02, 2.03, 2.07, 2.10, 2.11, 7s, 21H, Me; 2.00-2.12, m, H3; 2.44, dd, $J_{1,1}$ 5.0, $J_{1,2}$ 2.7 Hz, H1; 2.72, 2.73, 2dd, $J_{1,2}$ 3.5 Hz, H1; 2.85-2.88, m, H2; 3.33-3.57, m, H1′; 3.48-3.53, m, H5′; 3.64, ddd, $J_{4'',5''}$ 9.9, $J_{5'',6''}$ 2.3, 4.2 Hz, H5″; 3.70, t, $J_{3',4'} \approx J_{4',5'}$ 9.4 Hz, H4′; 4.03, dd, $J_{6'',6''}$ 12.5 Hz, H6″; 4.06, 4.07, 2dd, $J_{5',6'}$ 1.9, $J_{6',6'}$ 11.9 Hz, H6′; 4.36, dd, H6″; 4.44-4.47, m, H6′; 4.48, d, $J_{1'',2''}$ 8.0 Hz, H1″; 4.77, t, $J_{1',2'} \approx J_{2',3'}$ 9.6 Hz, H2′; 4.92, dd, $J_{2'',3''}$ 9.3 Hz, H2″; 5.05, t, $J_{3'',4''}$ 9.7 Hz, H4″;

5.12, t, H3″; 5.13, t, H3′. ^{13}C n.m.r. (125.8 MHz) δ 20.52, 20.57, 20.64, 20.72, 7C, Me; 21.53, 21.67, C3; 30.84, 30.97, C5; 31.95, 32.20, C4; 46.81, 46.98, C1; 51.99, 52.08, C2; 61.53, C6″; 62.28, C6′; 67.74, C4″; 71.87, C2″; 71.89, C5″; 72.10, 72.12, C2′; 72.91, 74.01, C3′,3″; 76.53, C5′; 76.88, C4′; 77.39, C1′; 100.77, C1″; 169.06, 169.70, 169.96, 170.00, 170.23, 170.38, 170.51, 7C, CO.

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