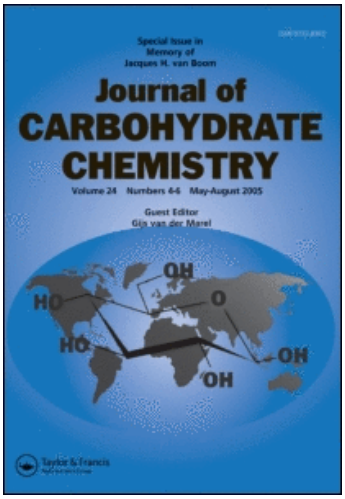


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# Syntheses of Methyl 2-*O*-, 3-*O*- and 6-*O*-(2'-Hydroxypropyl)-α-D-Glucopyranosides

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# SYNTHESES OF METHYL 2-*O*-, 3-*O*- AND 6-*O*-(2'-HYDROXYPROPYL)-α-D-GLUCOPYRANOSIDES[1]

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## ABSTRACT

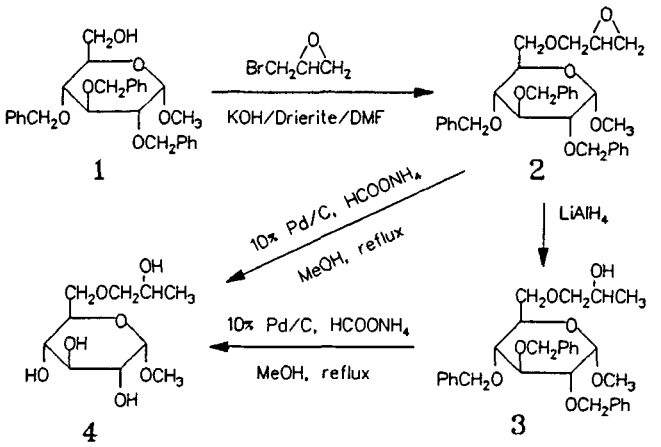
Methyl 6-*O*-, 3-*O*- and 2-*O*-(2'-hydroxypropyl)-α-D-glucopyranosides (**4**, **8**, and **12**) were synthesized starting from methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (**1**), methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (**5**), and methyl 3-*O*-benzyl-4,6-*O*-benzylidene-D-glucopyranoside (**9**), respectively. Overall yields were 88%, 6% and 26% of **4**, **8** and **12**, respectively, with the 2-ether (**12**) being crystalline and the 3-ether (**8**) a single diastereomer.

## INTRODUCTION

To determine the position of substitution of hydroxypropyl groups in lightly modified starch by $^1$H NMR spectroscopy,[2] we needed the three mono-(2'-hydroxypropyl) ethers (**4**, **8** and **12**). We report here their syntheses.

## RESULTS AND DISCUSSION

Compound **1** was etherified by epibromohydrin in the presence of potassium hydroxide to give the 6-epoxypropyl ether (**2**) (Scheme 1). The epoxy ring of **2** was opened with lithium aluminium hydride to yield methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2'-



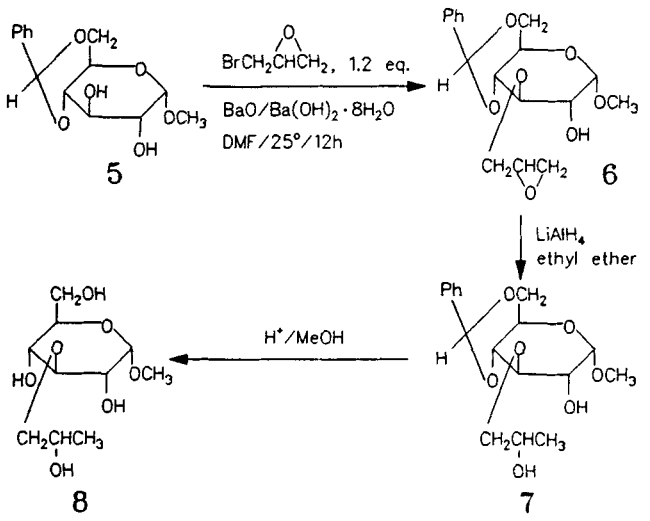

Scheme 1



hydroxypropyl)-α-D-glucopyranoside (**3**), which was debenzylated by catalytic hydrogenation[3] using palladium on carbon in methanol containing ammonium formate to obtain syrupy **4** in 65% yield from **1**. Compound **2** was converted directly to **4** using palladium on carbon in methanol containing ammonium formate, which increased the yield of **4** from **1** to 88%. The methyl signals of the *R* and *S* forms of the 2'-hydroxypropyl groups in **4** appeared in acetone at either δ 1.080 (d, *J* 6.5 Hz) or 1.075 (d, *J* 6.5 Hz) ppm.

Methyl 3-*O*-(2'-hydroxypropyl)-α-D-glucopyranoside (**8**) was synthesized from methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (**5**) (Scheme 2), which was etherified with epibromohydrin using a mixture of barium oxide-barium hydroxide octahydrate as catalyst. When epichlorohydrin was used as the etherifying agent,[4] it was necessary to increase the reaction temperature, and complex reaction products were obtained. The same was true if **5** was reacted with epibromohydrin using sodium hydroxide or sodium hydride as catalyst.

In the presence of barium oxide-barium hydroxide octahydrate, reaction of **5** with 1.2 equiv epibromohydrin at 25 °C for 12 h gave, after column chromatography on silica gel, methyl 4,6-*O*-benzylidene-3-*O*-(2',3'-epoxypropyl)-α-D-glucopyranoside (**6**) in 11% yield. Increasing reaction time did not improve the yield of **6**. TLC of the reaction




Scheme 2

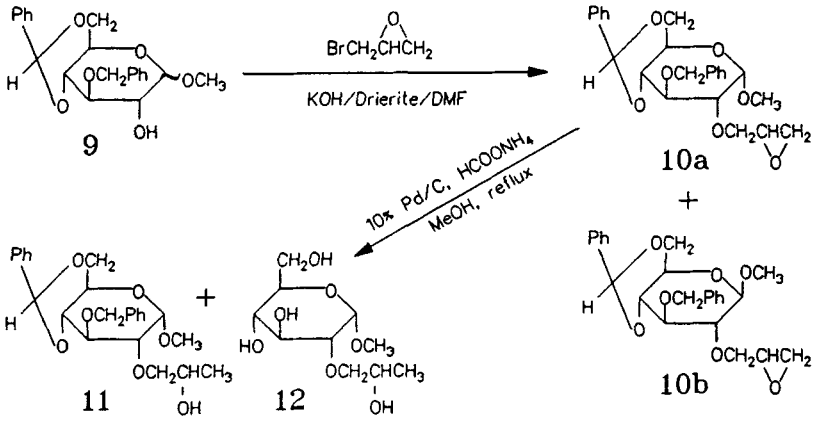


mixture at 12 h showed three components, which were unreacted **5** (approximately 50%), compound **6** and complex products.

The NMR spectra of compounds **6, 7**, and **8** indicated **6** was one diastereomer. The structure of **6** was established by $^1$H NMR spectroscopy. Irradiation of H-1 at δ 4.80 (d, *J* 3.7 Hz) collapsed the H-2 signal at δ 3.69 (dddd, *J* 3.7, 7.3, 9.2 Hz) from 8 to 4 lines (dd, *J* 7.3, 9.2 Hz), confirming the assignment of H-2. Irradiation of the OH doublet (*J* 7.3 Hz) at δ 2.69, which was exchangeable with deuterium oxide, also simplified H-2 to a doublet of doublets (*J* 3.7, 9.2 Hz).

The epoxy ring of **6** was opened by reduction with lithium aluminium hydride to give **7**, which was treated with $H^+$ cation exchange resin to give the final product (**8**) in 6% overall yield.

The last model compound (**12**) was synthesized starting with the anomeric mixture of methyl 3-*O*-benzyl-glycosides produced by acid-catalyzed methanolysis of the 3-benzyl ether of diacetone glucose. Reaction of the glucosides with benzaldehyde in the presence of zinc chloride gave in 72% yield a 3:2 mixture of methyl 3-*O*-benzyl-4,6-*O*-benzylidene-α- and β-D-glucopyranosides (**9**, Scheme 3) as determined from its $^1$H NMR spectrum. Fleet *et al.*[5] obtained 85% of the pure α-anomer of **9** from 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranoside essentially by the same procedure.




Scheme 3



Treatment of **9** with epibromohydrin in the presence of potassium hydroxide gave a mixture of **10a** ($R_F$ 0.19) and **10b** ($R_F$ 0.39), which were resolved by column chromatography. Compound **10a** was directly converted to the target ether (**12**) in boiling methanol in the presence of ammonium formate and 10% palladium on carbon, even though a small amount of methyl 4,6-*O*-benzylidene-2-*O*-(2'-hydroxypropyl)-α-D-glucopyranoside (**11**) was also isolated from the reaction mixture. Some of the $^1$H- and $^{13}$C-signals in the NMR spectra of **10a**, **10b** and **12** showed closely paired chemical shifts and when the differences (Δδ) were ≥0.01 ppm, they are reported in the experimental. The paired NMR signals indicate either mixed crystals in **12** with *R* and *S* hydroxypropyl groups, or one of the two configurations with restricted rotation in aqueous solution at 25 °C .

## EXPERIMENTAL

**General methods and materials.** Solutions were concentrated below 40 °C under diminished pressure. Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Specific rotations were determined in a 10-cm polarimeter tube on a Perkin-Elmer 241 polarimeter. Column chromatography was carried out at 25 °C on silica gel (230-425 mesh, Fisher Scientific Co.). Thin layer chromatography was performed at 25 °C on aluminium sheets coated with silica gel 60 $F_{254}$ (Whatman Ltd.) with detection either by

viewing under short-wavelength UV or by heating after spraying with a solution of *p*-anisaldehyde. Both $^1H$ (400 Mhz) and $^{13}C$ (100.6 Mhz) NMR spectra were recorded on a Bruker WM-400 instrument. Chemical shifts in chloroform-*d* were referenced to tetramethylsilane, and those in $D_2O$ to the sodium salt of 3-(trimethylsilyl)-propanoic-*2,2,3,3-d*$_4$ acid. HPLC-MS spectra were recorded on a Hewlett Packard 5989A MS apparatus.

Methyl α-D-glucopyranoside, lithium aluminium hydride and epibromohydrin were from Sigma Chemical Co. Benzaldehyde and benzyl chloride were from Fisher Scientific Co. Dimethylformamide (DMF), 10% palladium on activated carbon, ammonium formate and 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose were from Aldrich Chemical Co. Drierite (non-indicating) was from W. A. Hammond Drierite Co., Xenia, Ohio.



**Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-(2',3'-epoxypropyl)-α-D-glucopyranoside (2).** Tritylation[6] of methyl α-D-glucopyranoside followed by benzylation and detritylation[7,8] gave crude **1** that was chromatographed on a column of silica gel with petroleum ether-acetone (9:1 and 5:1, v/v) as eluent. The product (**1**) (58% yield) showed one component ($R_F$ 0.4) on TLC with petroleum ether/chloroform/acetone (10/4/1) and gave $[\alpha]_D^{25}$ +24.7°(*c* 0.5, $CHCl_3$). Lit.[7] mp 54-55 °C, $[\alpha]_D^{15}$ +23.8°(*c* 1.0, $CHCl_3$). To a solution of syrupy **1** (4.64 g, 10 mmol) in DMF (60 mL) was added ground potassium hydroxide (1.18 g, 30 mmol) and ground Drierite (5.0 g), followed by epibromohydrin (4.11 g, 30 mmol). The mixture was stirred at 25 °C for 5 h, and then filtered by suction and the solids washed with chloroform. The filtrate was concentrated under reduced pressure, the concentrate redissolved in ethyl acetate (100 mL), and the solution washed with water (1 x 40 mL) and brine (3 x 30 mL). The organic phase was dried over sodium sulfate, and concentrated to give crude product (6.16 g), which was subjected to column chromatography on silica gel with 9:1 petroleum ether-acetone (1000 mL) to give **2** as a syrup (4.63 g, 89%), $[\alpha]_D^{25}$ +11.3° (*c* 1.06, $CHCl_3$); $^1H$ NMR ($CDCl_3$) δ 7.29-7.36 (m, 15 H, 3 Ph), 4.60-5.00 (m, 6 H, 3 PhC*H*$_2$), 4.61 (d, 1 H, *J* 3.5 Hz, H-1), 3.99 (dd, 1 H, *J* 9.5, 9.5 Hz, H-3), 3.52-3.80 (m, 6 H, H-2, H-4, H-5, H-6a, H-6b and H-1a', 3.36 (s, 3 H, OC*H*$_3$), 3.27-3.43 (m, 1 H, H-1b'), 3.11 (m, 1 H, H-2'), 2.73 (m, 1 H, H-3a') and 2.54 (m, 1 H, H-3b'); $^{13}C$ NMR ($CDCl_3$) δ 127.5-138.7 (3 Ph), 98.1 (C-1), 81.9 (C-3), 79.7 (C-2), 77.4 (C-4), 75.6, 74.9, and 73.3 (3 Ph*C*H$_2$), 72.5 (C-5), 71.9 (C-6), 69.8, and 69.6 (C-1'), 55.1 (O*C*H$_3$), 50.6, and 50.5 (C-2'), and 44.1, and 44.0 (C-3'). Syrupy **2** was used without further purification to prepare compound **3**.

**Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-(2'-hydroxypropyl)-α-D-glucopyranoside (3).** A solution of **2** (1.05 g) in ethyl ether (30 mL) was added dropwise to a suspension of lithium aluminium hydride (152 mg) in ethyl ether (12 mL) in 20 min. After stirring 30 min, 10 mL ethyl ether saturated with water was added and the mixture stirred for 30 min. The suspension was filtered and the filtrate concentrated to give a syrup (0.83 g), which was subjected to a silica gel column chromatography with 4:1:10 chloroform-acetone-petroleum ether (900 mL) to yield **3** (0.78 g, 74%) as a syrup, $[\alpha]_D^{25}$ +24.5° (*c* 1.0, $CHCl_3$); $^1H$ NMR ($CDCl_3$) δ 7.25-7.36 (m, 15 H, Ar-H), 4.61 (d, 1 H, *J* 3.5 Hz, H-1), 4.58-4.99 (m, 6 H, 3 PhC*H*$_2$), 3.99 (dd, 1 H, *J* 9.5, 9.5 Hz, H-3), 3.95 (m, 1 H, H-2'), 3.51-3.75 (m, 5 H, H-2, H-4, H-5, H-6a, and H-6b), 3.38-3.50 (m, 1 H, H-1a'), 3.37 (s, 3 H, OC*H*$_3$), 3.18-3.29 (m, 1 H, H-1b'), 2.50, and 2.46 (2 s, 1 H, O*H*), and 1.10 (d, 3 H, *J* 6.5 Hz, C*H*$_3$); $^{13}C$ NMR ($CDCl_3$) δ 127.6-138.7 (3 Ph), 98.1 (C-1), 82.0 (C-3), 80.0 (C-2), 77.7 (C-4), 77.2, 75.7 and 75.0 (3 PhC*H*$_2$), 73.4 (C-5), 70.1 (C-6), 70.1 (C-1'), 66.4 (C-2'), 55.2 (OC*H*$_3$), and 18.54 (C*H*$_3$). This product was used without further purification for the preparation of **4**.

**Methyl 6-*O*-(2'-Hydroxypropyl)-α-D-glucopyranoside (4). Method A.** A mixture of **3** (210 mg), ammonium formate (360 mg) and 10% palladium on carbon (480 mg) in methanol (24 mL) was refluxed until TLC indicated that the reaction was complete (1 h). The reaction mixture was filtered through celite, and the filter cake washed with methanol. The filtrate was concentrated to give the crude product (110 mg) as a syrup, which was subjected to silica gel column chromatography with 7:2:1 chloroform-acetone-methanol to give **4** (100 mg, 99%) as a syrup, $[\alpha]_D^{25}$ +114.1° (*c* 1.0, MeOH); $^1H$ NMR ($D_2O$) δ 4.81 (d, 1 H, *J* 3.5 Hz, H-1), 4.03 (m, 1 H, H-2'), 3.40-3.81 (m, 8 H, H-2, H-3, H-4, H-5, H-6a, H-6b, H-1a', and H-1b'), 3.43 (s, 3 H, OC*H*$_3$), and 1.16 (d, 3 H, *J* 6.5 Hz, C*H*$_3$); $^1H$ NMR (acetone-$d_6$) δ 4.65 (d, 1 H, *J* 3.5 Hz, H-1), 3.87 (m, 1 H, H-5), 3.60-3.73, and 3.32-3.42 (m, 8 H, H-2, H-3, H-4, H-6a, H-6b, H-1a', H-1b', and H-2'), 3.35 (s, 3 H, OC*H*$_3$), and 1.080, and 1.075 (2 d, 3 H, *J* 6.5 Hz, C*H*$_3$); $^{13}C$ NMR ($D_2O$) δ 102.3 (C-1), 79.2 (C-3), 76.0 (C-2), 74.2 (C-4), 73.4 (C-5), 72.6 (C-1'), 72.6 (C-6), 69.1 (C-2'), 58.2 (OC*H*$_3$), 21.1 (C-3'); $^{13}C$ NMR (acetone-$d_6$) δ 100.7 (C-1), 77.9 (C-3), 75.0 (C-2), 73.2 (C-4), 72.0 (C-5), 71.5 (C-1'), 71.4 (C-6), 66.6 (C-2'), 55.3 (OC*H*$_3$), and 19.8 (C-3'); HPLC-MS (PCI): 253 ($M^+$+1).

**Method B.** A mixture of **2** (1.57 g), ammonium formate (3.6 g) and 10% palladium on carbon (4.8 g) in methanol (200 mL) was refluxed 1 h and then filtered through celite. The filter cake was washed with methanol and the filtrate concentrated to give crude product (0.82 g), which was subjected to silica gel column chromatography with 7:2:1 chloroform-acetone-methanol (700 mL) to give **4** (0.75 g, 99%) as a syrup, $[\alpha]_D^{25}$ +110.4° (*c* 1.0, MeOH).

Anal. Calcd for $C_{10}H_{20}O_7 \cdot H_2O$ (270.3): C, 44.4; H, 8.20. Found: C, 44.2; H, 8.15.

**Methyl 4,6-*O*-Benzylidene-3-*O*-(2',3'-epoxypropyl)-α-D-glucopyranoside (6).** The procedure used was adopted from Lee and Perlin[4] and Kondo[9] with modifications. Compound **5** (5 g, mp 166-167°C), which was prepared according to Van Cleve,[10] was dissolved in DMF (50 mL) containing 6.25 g barium oxide and 2.5 g barium hydroxide octahydrate. Epibromohydrin (1.2 equiv) was added and the mixture was stirred at room temperature for 12 h. Chloroform was added and the mixture filtered through celite. The chloroform solution was washed with water and the water then extracted with ethyl acetate. The combined organic phases were concentrated, and the residue was fractionated on a silica gel column with 4:1:5 chloroform-acetone-petroleum ether to give syrupy **6** (0.63 g, yield 11%), $[\alpha]_D^{25}$ +100.2°(*c* 0.56,$CHCl_3$); $^1$H NMR ($CDCl_3$) δ 7.33-7.48 (m, 5 H, Ar-H), 5.55 (s, 1 H, PhC*H*), 4.80 (d, 1 H, *J* 3.7 Hz, H-1), 4.28 (dd, 1 H, *J* 4.5, 9.8 Hz, H-4), 4.14 (dd, 1 H, *J* 11.8, 3.0 Hz, H-1a'), 3.80 (dddd, 1 H, *J* 4.5, 9.2, 10.0 Hz, H-5), 3.74 (dd, 1 H, *J* 10.0, 9.5 Hz, H-6a), 3.73 (dd, 1 H, *J* 9.2, 9.5 Hz, H-3), 3.69 (dddd, 1 H, *J* 3.7, 7.3, 9.2 Hz, H-2), 3.62 (dd, 1 H, *J* 11.8, 6.5 Hz, H-1b'), 3.56 (dd, 1 H, *J* 9.2, 9.5 Hz, H-6b), 3.45 (s, 3 H, OC*H*$_3$), 3.23 (dddd, 1 H, *J* 6.5, 5.0, 3.0 Hz, H-2'), 2.77 (dd, 1 H, *J* 5.0, 5.0 Hz, H-3a'), 2.69 (d, 1 H, *J* 7.3 Hz, 2-O*H*), and 2.60 (dd, 1 H, *J* 5.0, 3.0 Hz, H-3b'); $^{13}$C NMR ($CDCl_3$) δ 137.3, 129.0, 128.2, and 126.0 (6 Ar-C), 101.4 (Ph*C*H), 99.9 (C-1), 81.5 (C-3), 80.0 (C-2), 73.7 (C-4), 72.3 (C-5), 69.0 (C-1'), 62.6 (C-6), 55.4 (O*C*H$_3$), 51.2 (C-2'), and 44.7 (C-3'). Syrupy **6** was used without further purification to produce **7**, although **6** eventually crystallized to form needles with mp 155-157 °C.

**Methyl 4,6-*O*-Benzylidene-3-*O*-(2'-hydroxypropyl)-α-D-glucopyranoside (7).** Compound **6** (0.63 g) in 40 mL ethyl ether was added dropwise to a suspension of 90 mg lithium aluminium hydride in ethyl ether, and TLC (4:1 chloroform-acetone) showed the reaction complete in 4 h. After adding water (1 mL), the mixture was filtered through celite and filter paper, and the filtrate was concentrated and fractionated on silica gel using 4:1:3

chloroform-acetone-petroleum ether as eluent. Compound **7** was obtained as colorless needles (acetone-petroleum ether, 0.52 g, 82%), mp 158-160 °C; $[\alpha]_D^{25}$ +81.5°(*c* 0.88, $CHCl_3$); $^1H$ NMR ($CDCl_3$) δ 7.34-7.47 (m, 5 H, Ar-H), 5.51 (s, 1 H, PhC*H*), 4.77 (d, 1 H, *J* 3.5 Hz, H-1), 4.27 (dd, 1 H, *J* 4.3, 9.7 hz, H-4), 3.40-3.97 (m, 8 H, H-2, H-3, H-5, H-6a, H-6b, H-1a', H-1b', and H-2'), 3.43 (s, 3 H, OC$H_3$), and 1.05 (d, 3 H, *J* 6.5 Hz, C$H_3$); $^{13}C$ NMR ($CDCl_3$) δ 137.1, 129.0, 128.2, and 126.0 (6 Ar-C), 101.4 (Ph*C*H), 100.0 (C-1), 81.3 (C-3), 80.7 (C-2), 79.1 (C-4), 72.6 (C-5), 68.9 (C-1'), 66.9 (C-2'), 62.6 (C-6), 55.4 (O*C*$H_3$), and 18.1 (C-3').

Anal. Calcd for $C_{17}H_{24}O_7$ (340.4): C, 60.0; H, 7.11. Found: C, 60.1; H, 7.02.

**Methyl 3-*O*-(2'-Hydroxypropyl)-α-D-glucopyranoside (8).** Compound 7 (0.20 g) was dissolved in methanol (50 mL) and stirred at 25 °C with Amberlite IR-120 $H^+$ ion exchange resin (20 g), which has been previously rinsed with methanol. After 5 h the mixture was filtered, concentrated and fractionated on silica gel using 17:3 chloroform-methanol as the eluent. Product **8** was obtained as a syrup (0.10 g, 67.3%), $[\alpha]_D^{25}$ +112.3°(*c* 0.80, MeOH); $^1H$ NMR ($D_2O$) δ 4.85 (d, 1 H, *J* 3.6 Hz, H-1), 4.03 (m, 1 H, H-2'), 3.46-3.88 (m, 8 H, H-2, H-3, H-4, H-5, H-6a, H-6b, H-1a', and H-1b'), 3.43 (s, 3 H, OC$H_3$), and 1.15 (d, 3 H, *J* 6.5 Hz, C$H_3$); $^{13}C$ NMR ($D_2O$) δ 100.1 (C-1), 83.3 (C-3), 78.7 (C-2), 72.5 (C-4), 71.9 (C-5), 70.1 (C-1'), 67.6 (C-2'), 61.3 (C-6), 55.8 (O*C*$H_3$) and 18.8 (C-3'); HPLC-MS (PCI): 253 ($M^+$+1).

Anal. Calcd for $C_{10}H_{20}O_7 \cdot H_2O$ (270.3): C, 44.4; H, 8.20. Found: C, 44.6; H, 8.18.

**Methyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-*O*-(2',3'-epoxypropyl)-α- and β-D-glucopyranosides (10a and 10b).** 3-*O*-Benzyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose[11] (8.99g) in 5% hydrogen chloride-methanol (140 mL) was heated to reflux for 1 h. After cooling, sodium bicarbonate (16.2 g) was added, and the mixture filtered and concentrated. The product was purified on silica gel with 95:5 chloroform-methanol to give 7.05 g of a semisolid. The semisolid (7.05 g, 24.8 mmol), freshly fused and powdered zinc chloride (4.0 g), and benzaldehyde (13 mL) was shaken in a glass bottle, and then kept at 25 °C for 1 h. Petroleum ether (100 mL) was added and the mixture stirred for 4 h. The precipitate was collected by filtration with suction, washed with petroleum ether (50 mL) and then cold water (3 x 50 mL), and dried in air to give crude product (7.49 g), which was crystallized from 95% ethanol to give a mixture of α- and

β-pyranosides (about 3:2) of **9** as colorless needles (6.82 g, 74%), mp 172-173 °C; $[\alpha]_D^{25}$ +40.0° (*c* 1.0, $CHCl_3$); Lit.[11,12] α-anomer: mp 187-188 °C, $[\alpha]_D$ +78°; 188-189 °C, $[\alpha]_D$ +59.3° (*c* 1.0, $CHCl_3$); β-anomer: mp 184-185 °C, $[\alpha]_D$ -48°.

To a mixture of **9** (2.23 g, 6 mmol), powdered Drierite (4.0 g) and powdered potassium hydroxide (1.12 g, 20 mmol) in DMF (30 mL) was added epibromohydrin (1.28 g, 9.3 mmol) and the mixture was stirred at 25 °C for 1.5 h. After filtration by suction, the filtrate was concentrated to give a syrup, which was dissolved in ethyl acetate and washed with water (50 mL) and brine (2 x 30 mL), dried over magnesium sulfate, and concentrated to give a mixture of **10a** and **10b** ($R_F$ 0.19 and 0.39, 1:9 acetone-petroleum ether). The crude product was fractionated on silica gel with 2:5:93 chloroform-acetone-petroleum ether (2000 mL) to give **10b** (0.63 g, 24.5%) and **10a** (0.95 g, 37.0%). Compound **10a** was crystallized from 95% ethanol to give colorless crystals, mp 103-104 °C; $[\alpha]_D^{25}$ +19.0° (*c* 1.0, $CHCl_3$); $^1$H NMR ($CDCl_3$) δ 7.27-7.58 (m, 10 H, Ar-H), 5.56 (s, 1 H, PhC*H*), 4.84 (d, 1 H, *J* 3.6 Hz, H-1), 4.76-4.92 (m, 2 H, PhC$H_2$), 4.29 (m, 1 H, H-4), 4.10 (dd, 1 H, *J* 2.9, 12.0 Hz, H-1a'), 3.47-4.02 (m, 6 H, H-2, H-3, H-5, H-6a, H-6b, and H-1b'), 3.46, and 3.44 (2 s, 3 H, OC$H_3$), 3.12-3.19 (m, 1 H, H-2'), 2.76-2.79 (m, 1 H, H-3a'), and 2.52-2.66 (m, 1 H, H-3b'); $^{13}$C NMR ($CDCl_3$) δ 126.0-138.7 (12 Ar-C), 101.2 (Ph*C*H), 99.8, and 98.2 (C-1), 82.2, and 82.1 (C-2), 80.8 (C-3), 78.5 (C-4), 75.1 (Ph*C*H), 74.0 (C-5), 69.0 (C-1'), 62.3 (C-6), 55.3 (O*C*$H_3$), 51.2, and 50.6 (C-2'), 44.3, and 44.0 (C-3').

Anal. Calcd for $C_{24}H_{28}O_7$ (428.2): C, 67.2; H, 6.59. Found: C, 66.9; H, 6.49.

Compound **10b** was crystallized from 95% ethanol to give colorless crystals, mp 134-135 °C; $[\alpha]_D^{25}$ -67.0° (*c* 1.0, $CHCl_3$); $^1$H NMR ($CDCl_3$) δ 7.26-7.50 (m, 10 H, Ar-H), 4.90, and 4.81 (2 d, 2 H, AB, *J* 11.4 Hz, PhC$H_2$), 4.37 (m, 1 H, H-4), 4.36 (d, 1 H, *J* 6.5 Hz, H-1), 3.62-4.03 (m, 5H, H-2, H-3, H-5, H-6a, and H-6b), 3.56, and 3.55 (2 s, 3 H, OC$H_3$), 3.40 (m, 1 H, H-1a'), 3.30 (m, 1 H, H-1b'), 3.15 (m, 1 H, H-2'), 2.77 (m, 1 H, H-3a'), and 2.59 (m, 1 H, H-3b'); $^{13}$C NMR ($CDCl_3$) δ 136.0-138.4 (12 Ar-C), 104.8 (C-1), 101.1 (Ph*C*H), 83.0, and 82.9 (C-2), 81.3 (C-3), 80.5 (C-4), 75.0 (Ph*C*H), 74.0 (C-5), 68.7 (C-1'), 65.9 (C-6), 50.7 (C-2'), and 44.4 (C-3').

Anal. Calcd for $C_{24}H_{28}O_7$ (428.2): C, 67.2; H, 6.59. Found: C, 67.1; H, 6.49.

**Methyl 4,6-*O*-Benzylidene-2-*O*-(2'-hydroxypropyl)- and 2-*O*-(2'-Hydroxypropyl)-α-D-glucopyranosides (11 and 12).** A mixture of **10a** (0.872 g, 2.04

mmol), ammonium formate (2.4 g) and 10% palladium on carbon (3.2 g) in methanol (240 mL) was refluxed on a water bath for 2 h with stirring. The mixture was then filtered and the filtrate concentrated to give a syrup (0.52 g), which was fractionated on silica gel with 17:3 chloroform-methanol (500 mL) to give mainly **12** (0.485 g, 94%) and a small amount (24 mg) of **11**. After standing at 25 °C for a week, compound **12** deposited colorless needles, mp 53-54 °C; $[\alpha]_D^{25}$ +108.8° (*c* 1.0, MeOH); $^1$H NMR ($D_2O$) δ 4.95, and 4.90 (d, 1 H, *J* 3.3 Hz, H-1), 4.00 (m, 1 H, H-2'), 3.87 (dd, 1 H, *J* 2.2, 12.3, H-1a'), 3.35-3.78 (m, 7 H, H-2, H-3, H-4, H-5, H-6a, H-6b, and H-1b'), 3.43 (s, 3 H, $OCH_3$), and 1.16, and 1.15 (2 d, 3 H, *J* 6.4 Hz, $CH_3$); $^{13}$C NMR ($D_2O$) δ 99.9, and 99.8 (C-1), 82.7, and 82.4 (C-2), 78.4 (C-3), 75.2 (C-4), 74.3 (C-5), 72.4, and 72.3 (C-1'), 69.6, 69.2 (C-2'), 63.4 (C-6), 57.6 ($OCH_3$), and 20.8 (C-3'); HPLC-MS (PCI): 253 ($M^+$+1).

Anal. Calcd for $C_{10}H_{20}O_7$ (252.3): C, 47.6; H, 7.99. Found: C, 47.7; H, 7.83.

Compound **11** was crystallized from acetone to give needles, mp 137-138 °C; $[\alpha]_D^{25}$ +86°(*c* 1.0, $CHCl_3$).

Anal. Calcd for $C_{17}H_{24}O_7$ (340.2): C, 60.0; H, 7.11. Found: C, 59.7; H, 7.02.

## REFERENCES AND NOTES


1. This is Contribution No. 96-387-J from the Kansas Agricultural Experiment Station.
2. A. Xu and P. A. Seib, *J. Cereal Sci.* In press.
3. T. Bieg, and W. Szeja, *Synthesis*,76 (1985).
4. D. L. Lee and A. S. Perlin, *Carbohydr. Res.*, **106**, 1 (1982).
5. G. W. J. Fleet, M. J. Gough, and T. K. M. Shing, *Tetrahedron Lett.*, **25**, 4029 (1984).
6. C. G. Casinovi, M. Framondino, G. Randazzo, and F. Siani, *Carbohydr. Res.*, **36**, 67(1974).
7. K. Tatsuta, K. Fujimoto, and M. Kinoshita, *Carbohydr. Res.*, **54**, 85 (1977).
8. P. Kovac, J. Alfoldi, and M. Kosik, *Chem. Zvesti*, **28**, 820 (1974).
9. Y. Kondo, *Agr. Biol. Chem.*, **39**, 1879 (1975).
10. J. W. Van Cleve, *Carbohydr. Res.*, **17**, 461 (1971).
11. S. Czernecki, C. Georgoulis, and C. Provelenghiou, *Tetrahedron Lett.*, 3535 (1976).
12. P. J. Garegg, T. Iversen, and S. Oscarson, *Carbohydr. Res.*, **50**, c12 (1976).
13. T. Ogawa and T. Kaburagi, *Carbohydr. Res.*, **103**, 53 (1982).