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## Note

# Synthesis of some derivatives of 2-*O*-allyl-D-glucose*

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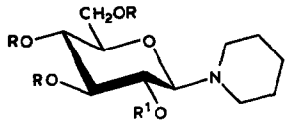
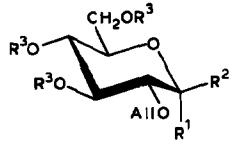
Allyl ethers are useful protecting groups in the chemical synthesis of oligosaccharides[1–3] since they can be removed in the presence of other protecting groups (for example, acyl, benzyl, or acetal) and can also act as a non-participating substituent to effect $\alpha$-glycosidation[4]. We now report the synthesis of some 2-*O*-allyl-D-glucose derivatives as part of a programme concerned with the synthesis of (1→2)-linked oligosaccharides.

The reaction of *N*-(3,4,6-tri-*O*-acetyl-$\beta$-D-glucosyl)piperidine (**1**), obtained[5] in good yield from $\beta$-D-glucose penta-acetate and piperidine, with allyl bromide–silver oxide–benzene for 24 h afforded 67% of the crystalline 2-*O*-allyl derivative **2**. Saponification of **2** with methanolic sodium methoxide afforded the triol **3** which was not characterised but treated with sodium hydride–benzyl bromide-*N*,*N*-dimethylformamide to give 77% of the tri-*O*-benzyl derivative **4**. Hydrolysis[6] of **4** with aqueous acetic acid in refluxing acetone gave 92% of **5**, previously prepared[7] from D-glucose in twelve steps. Treatment of **5** with acetic anhydride–pyridine gave 1-*O*-acetyl-2-*O*-allyl-3,4,6-tri-*O*-benzyl-$\alpha$-D-glucose (**6**), the $^1$H-n.m.r. spectrum of which contained signals at $\delta$ 2.06 (s, OAc) and 6.25 (d, $J$ 4 Hz, H-1).

Hydrolysis of **2** with dilute acetic acid (→**7**) and then acetylation gave 1,3,4,6-tetra-*O*-acetyl-2-*O*-allyl-D-glucose (**8**).




**1** R = Ac, $R^1$ = H
**2** R = Ac, $R^1$ = allyl
**3** R = H, $R^1$ = allyl
**4** R = Bn, $R^1$ = allyl

**5** $R^1$, $R^2$ = H, OH, $R^3$ = Bn
**6** $R^1$ = Ac, $R^2$ = H, $R^3$ = Bn
**7** $R^1$, $R^2$ = H, OH, $R^3$ = Ac
**8** $R^1$ = Ac, $R^2$ = H, $R^3$ = Ac

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EXPERIMENTAL

*N-(3,4,6-Tri-O-acetyl-2-O-allyl-β-D-glucosyl)piperidine* (**2**). — To a vigorously stirred solution of **1** (10 g, 26.8 mmol) in dry benzene (100 mL) containing freshly prepared silver oxide (40 g) was added allyl bromide (5 g, 41 mmol) in the dark. After 24 h, the mixture was filtered through Celite, the insoluble material was washed with benzene, and the combined filtrate and washings were concentrated. The residue was crystallised from ether–light petroleum to afford **2** (7.5 g, 67%), m.p. 103°, $[\alpha]_D$ +19° (*c* 1, chloroform). $^1$H-N.m.r. data ($CDCl_3$): δ 1.5 (bs, 6 H, piperidine $CH_2$-3,4,5), 2.00, 2.03, 2.06 (3 s, 9 H, 3 OAc), 2.8 (m, 4 H, piperidine $CH_2$-2,6), 3.5 (m, 2 H, $OCH_2$), 3.8–4.5 (m, 5 H, H-1,2,5,6,6'), 4.7–5.4 (m, 4 H, H-3,4, $CH_2$=), 5.5–6.1 (m, 1 H, CH=).

*Anal.* Calc. for $C_{20}H_{31}NO_8$: C, 58.1; H, 7.5. Found: C, 58.3; H, 7.8.

*2-O-Allyl-3,4,6-tri-O-benzyl-α,β-D-glucose* (**5**). — To a solution of **2** (5 g, 12.1 mmol) in methanol (25 mL) was added sodium (25 mg). After 24 h, the mixture was neutralised with IR-120 ($H^+$) resin, filtered, and concentrated, and dry toluene was distilled from the residue to afford the triol **3** (3.47 g, 100%).

To a stirred solution of **3** (3.47 g, 12.0 mmol) in dry *N,N*-dimethylformamide (25 mL) under nitrogen was added sodium hydride (2 g, 50% oil dispersion, 83.3 mmol) during 0.5 h, and stirring was continued for 1.5 h. To the cooled mixture was added benzyl bromide (7.0 g, 40.9 mmol) and, after 5 h at room temperature, the excess of sodium hydride was decomposed with methanol. The usual work-up afforded a product, column chromatography (ethyl acetate–light petroleum, 1:10) of which on silica gel gave **4** (5.2 g, 77%).

A mixture of **4** (5.2 g, 9.3 mmol), acetone (25 mL), water (5 mL), and acetic acid (1 mL) was heated under reflux for 2 h and then concentrated, and toluene was distilled from the residue which was crystallised from ether–light petroleum to afford **5** (3.1 g). Column chromatography (ethyl acetate–light petroleum, 1:4) of the material in the mother liquor gave more **5** (1.1 g; total yield, 92%), m.p. 138°, $[\alpha]_D$ +23° (*c* 1, chloroform); lit.[7] m.p. 137–139°, $[\alpha]_D$ +25.7° chloroform. $^1$H-N.m.r. data ($CDCl_3$): δ 5.5–6.1 (m, 1 H, CH=), 7.0–8.0 (m, 15 H, 3 Ph).

*1,3,4,6-Tetra-O-acetyl-2-O-allyl-α-D-glucose* (**8**). — A mixture of **2** (0.5 g, 1.21 mmol), acetone (5 mL), water (1 mL), and acetic acid (0.2 mL) was heated under reflux for 2 h and then concentrated. Toluene was distilled from the residue (**7**) which was then treated with acetic anhydride (2 mL) and pyridine (3 mL). The usual work-up, with elution of the crude product from a short column of silica gel with ethyl acetate–light petroleum (1:1), gave **8** (0.35 g, 74%), $[\alpha]_D$ +65° (*c* 0.9, chloroform). $^1$H-n.m.r. data ($CDCl_3$): δ 2.0 (m, 12 H, 4 OAc), 5.4–6.0 (m, 1 H, CH=), 6.30 (d, 1 H, *J* 4 Hz, H-1).

*Anal.* Calc. for $C_{17}H_{24}O_{10}$: C, 52.6; H, 6.2. Found: C, 52.2; H, 6.0.

*1-O-Acetyl-2-O-allyl-3,4,6-tri-O-benzyl-α-D-glucose* (**6**). — A solution of **5** (0.5 g, 1.02 mmol) in pyridine (3 mL) and acetic anhydride (2 mL) was stored overnight and then worked-up in the usual manner to afford **6** (0.5 g, 93%), $[\alpha]_D$

+30° (*c* 0.9, chloroform). $^1$H-N.m.r. data ($CDCl_3$): $\delta$ 2.06 (s, 3 H, OAc), 5.3–6.0 (m, 3 H, CH=, $CH_2$=), 6.25 (d, 1 H, *J* 4 Hz, H-1).

*Anal.* Calc. for $C_{32}H_{36}O_7$: C, 72.2; H, 6.8. Found: C, 72.2; H, 6.2.

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