*Carbohydrate Research*, 49 (1976) 325–333


# SYNTHESIS OF BENZYL AND ALLYL ETHERS OF D-GLUCOPYRANOSE*†

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(Received November 6th, 1975; accepted for publication, November 20th, 1975)

ABSTRACT

Starting from allyl 3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside as a key intermediate, the following crystalline compounds were prepared: 2-*O*-allyl-3,4,6-tri-*O*-benzyl-D-glucopyranose (**11**) and its *p*-nitrobenzoate; 2,3,5-tri-*O*-benzyl-D-arabinofuranose (**12**) and the corresponding arabinitol; allyl 3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (**7**); 3,4,6-tri-*O*-benzyl-D-glucopyranose (**8**); 2-*O*-allyl-3,4-di-*O*-benzyl-D-glucopyranose (**17**) and its bis(*p*-nitrobenzoate); and 3,4-di-*O*-benzyl-D-glucopyranose (**19**). The *p*-nitrobenzoates of compounds **11** and **17** are potential intermediates for the synthesis of the glycolipids of the cytoplasmic membranes of *Streptococci*.

## INTRODUCTION

The cytoplasmic membranes of *Streptococci* contain[1,2] neutral and phosphorylated glycolipids derived from 1,2-di-*O*-acyl-3-*O*-α-D-glucopyranosyl-L-glycerol. Mono- and di-glucosyl derivatives of this glycolipid (and phosphorylated derivatives thereof) occur; in the oligoglucosyl diglycerides, the glucose residues are joined by α linkages to position 2 of adjacent glucose residues and the phosphate groups are located at position 6. The serological activity of the glycolipids isolated from *Streptococci* has been demonstrated[3], and one of the phosphorylated lipids is covalently linked with a glycerol phosphate polymer to form the lipoteichoic acid of *Streptococcus faecalis*[2].

For synthetic studies in this series of glycolipids, some suitably protected derivatives of D-glucopyranose were required, and we describe here the preparation of some allyl and benzyl ethers of D-glucopyranose which should be suitable inter-

*Dedicated to the memory of Professor Edward J. Bourne.

†The Allyl Ether as a Protecting Group in Carbohydrate Chemistry: Part VIII. For Part VII, see Ref. 5.

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mediates for the synthesis of the α-linked D-glucose derivatives by the methods which we have described previously[4,5].

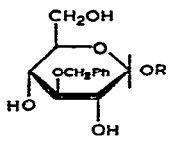
## DISCUSSION

3-*O*-Benzyl-D-glucopyranose[6] (**1**) was treated with allyl alcohol containing hydrogen chloride to give the anomeric mixture of allyl 3-*O*-benzyl-D-glucopyranosides (**2**), and these were converted into the corresponding 4,6-*O*-benzylidene derivatives by the action of zinc chloride in benzaldehyde. Allyl 3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (**3**) was readily crystallised from the mixture, and a pure sample of the corresponding β-anomer was obtained (for comparative purposes) by chromatography of the mixture of anomers. The allyl glycoside (**3**) was converted into the but-2-enyl ether **4** by the action of "crotyl bromide" and sodium hydride[7], and the benzylidene group was hydrolysed to give allyl 3-*O*-benzyl-2-*O*-(but-2-enyl)-α-D-glucopyranoside (**5**). Benzylation of **5** gave allyl 3,4,6-tri-*O*-benzyl-2-*O*-(but-2-enyl)-α-D-glucopyranoside (**6**).

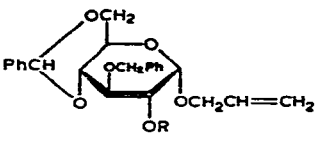
We have shown previously[7] that the but-2-enyl group is cleaved at a rate higher than that at which the allyl group is isomerised by the action of potassium *tert*-butoxide in methyl sulphoxide, and that it is possible to achieve cleavage of the but-2-enyl group with only partial isomerisation of the allyl group when both groupings are present in the same molecule. When compound **6** was treated with potassium *tert*-butoxide in methyl sulphoxide at 20°, it was possible to isolate allyl 3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (**7**) in ~40% yield. Compound **7** was readily separated from the isomerised product, prop-1-enyl 3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (**9**), which was also present, by hydrolysis of **9** to 3,4,6-tri-*O*-benzyl-D-glucopyranose (**8**) with dilute acid followed by column chromatography. Compound **7** is a suitable intermediate for joining D-glucose residues together in α-linkage at position 2.

When allyl 3,4,6-tri-*O*-benzyl-2-*O*-(but-2-enyl)-α-D-glucopyranoside (**6**) was treated with potassium *tert*-butoxide in methyl sulphoxide at 50°, cleavage of the but-2-enyl group and complete isomerisation of the allyl group occurred to give the prop-1-enyl glycoside **9** as the sole product. Acidic hydrolysis of **9** gave, as before, 3,4,6-tri-*O*-benzyl-D-glucopyranose (**8**), with properties similar to those reported previously[8] for this material prepared by a different method, thus confirming the structure of **7**. Compound **8** has been used[8] for the preparation of β-linked mannosides.

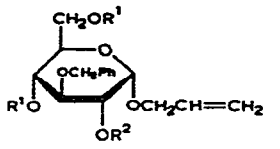
Prop-1-enyl 3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (**9**) was converted into the allyl ether **10**, from which the prop-1-enyl group was hydrolysed with dilute acid to give crystalline 2-*O*-allyl-3,4,6-tri-*O*-benzyl-D-glucopyranose (**11**). We have shown[5] that the 2-*O*-allyl group is a suitable non-participant in 1,2-*cis*-glycoside synthesis, and therefore compound **11** should be a suitable intermediate for the preparation of the neutral D-glucosyl diglycerides of *Streptococci* and for this purpose it was converted into a crystalline *p*-nitrobenzoate. For characterisation, **11** was reduced with sodium borohydride to give 2-*O*-allyl-3,4,6-tri-*O*-benzyl-D-glucitol, from which the allyl group was removed to give 3,4,6-tri-*O*-benzyl-D-glucitol. This compound was



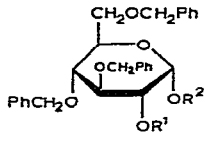
1 R = H
2 R = $CH_2CH{=}CH_2$



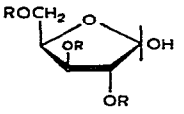
3 R = H
4 R = $CH_2CH{=}CHMe$



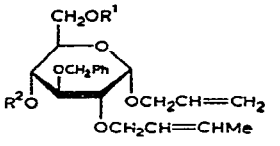
5 $R^1$ = H; $R^2$ = $CH_2CH{=}CHMe$
6 $R^1$ = $CH_2Ph$; $R^2$ = $CH_2CH{=}CHM$
7 $R^1$ = $CH_2Ph$; $R^2$ = H



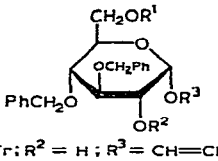
8 $R^1$ = $R^2$ = H
9 $R^1$ = H; $R^2$ = $CH{=}CHMe$
10 $R^1$ = $CH_2CH{=}CH_2$; $R^2$ = $CH{=}CHMe$
11 $R^1$ = $CH_2CH{=}CH_2$; $R^2$ = H



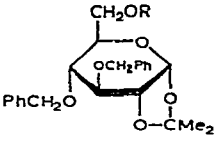
12 R = $CH_2Ph$



13 $R^1$ = Tr; $R^2$ = H
14 $R^1$ = Tr; $R^2$ = $CH_2Ph$



15 $R^1$ = Tr; $R^2$ = H; $R^3$ = $CH{=}CHMe$
16 $R^1$ = Tr; $R^2$ = $CH_2CH{=}CH_2$; $R^3$ = $CH{=}CHMe$
17 $R^1$ = $R^3$ = H; $R^2$ = $CH_2CH{=}CH_2$
18 $R^1$ = $R^3$ = H; $R^2$ = $CH{=}CHMe$
19 $R^1$ = $R^2$ = $R^3$ = H



20 R = H
21 R = $CH_2Ph$

oxidised with sodium metaperiodate to give crystalline 2,3,5-tri-*O*-benzyl-D-arabino-furanose (**12**) having properties consistent with those reported previously[9] for the enantiomer. Sodium borohydride reduction of **12** gave crystalline 2,3,5-tri-*O*-benzyl-D-arabinitol with properties similar to those reported previously[10].

Allyl 3-*O*-benzyl-2-*O*-(but-2-enyl)-α-D-glucopyranoside (**5**) was converted into the trityl ether **13**, and this was benzylated to give allyl 3,4-di-*O*-benzyl-2-*O*-(but-2-enyl)-6-*O*-trityl-α-D-glucopyranoside (**14**). Compound **14** was treated with potassium *tert*-butoxide in methyl sulphoxide, which caused cleavage of the but-2-enyl group and isomerisation of the allyl group to give prop-1-enyl 3,4-di-*O*-benzyl-6-*O*-trityl-α-D-glucopyranoside (**15**). Allylation of **15** gave prop-1-enyl 2-*O*-allyl-3,4-di-*O*-benzyl-6-*O*-trityl-α-D-glucopyranoside (**16**), which gave crystalline 2-*O*-allyl-3,4-di-*O*-benzyl-D-glucopyranose (**17**) on acidic hydrolysis. Compound **17** gave a crystalline bis(*p*-nitrobenzoate) which should be a suitable intermediate for the projected syntheses of the phosphorylated D-glucosyl diglycerides of *Streptococci*, as it will allow the introduction of a phosphate residue at position 6. For characterisation, **17** was treated with tris(triphenylphosphine)rhodium(I) chloride to isomerise[11] the allyl group, and subsequently the prop-1-enyl group was removed to give 3,4-di-*O*-benzyl-D-glucopyranose (**19**) identical with the material prepared and characterised as described below.

Prop-1-enyl 3,4-di-*O*-benzyl-6-*O*-trityl-α-D-glucopyranoside (**15**) was hydrolysed with dilute acid to give crystalline 3,4-di-*O*-benzyl-D-glucopyranose (**19**). For characterisation, **19** was converted into 3,4-di-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucopyranose (**20**), which was benzylated to give the tribenzyl ether (**21**). Acidic hydrolysis of **21** gave 3,4,6-tri-*O*-benzyl-D-glucopyranose (**8**) identical with the material prepared and characterised as described above.

## EXPERIMENTAL

*General methods.* — Solvents were evaporated under reduced pressure. Optical rotations were measured at 22–25° with a Bendix Automatic Polarimeter. T.l.c. was carried out on microscope slides coated with Silica Gel G. Light petroleum had b.p. 40–60°, unless otherwise stated.

*Allyl 3-O-benzyl-4,6-O-benzylidene-α-D-glucopyranoside* (**3**). — Hydrogen chloride (20 g) was added to a solution of 3-*O*-benzyl-D-glucose[6] (39.8 g) in allyl alcohol (250 ml), and the solution was heated under reflux for 1 h. T.l.c. (4:1, chloroform–methanol) then indicated a major product ($R_F$ 0.7), together with a minor product ($R_F$ 0.9) and a small proportion of starting material ($R_F$ 0.3). An excess of sodium hydrogen carbonate was added, and the inorganic material was filtered off. The solvent was evaporated, and the crude product was treated with benzaldehyde (300 ml) and powdered zinc chloride (50 g) at room temperature for 4 h. T.l.c. (1:1 ether–light petroleum) then showed two major products ($R_F$ 0.4 and 0.55). The mixture was poured into ice–water, and the product (and benzaldehyde) was extracted with chloroform. The solution was dried (potassium carbonate), and the solvents were evaporated in the presence of a small portion of potassium carbonate. The crude product was triturated with ether, and the insoluble material ($R_F$ 0.4) was recrystallised from methanol and then from isopropyl ether–methanol to give **3** (13.9 g, 24%), m.p. 143–145°, $[\alpha]_D$ +86.2° (*c* 1, chloroform).

*Anal.* Calc. for $C_{23}H_{26}O_6$: C, 69.33; H, 6.58. Found: C, 69.61; H, 6.52.

The ether extract of the crude product was chromatographed on alumina to give a component ($R_F$ 0.55) which was recrystallised from isopropyl ether to give allyl 3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside, m.p. 140–141°, $[\alpha]_D$ −39.9° (*c* 1, chloroform).

*Anal.* Found: C, 69.32; H, 6.53.

*2-O-Allyl-3,4,6-tri-O-benzyl-D-glucopyranose* (**11**). — Compound **3** (10 g) was treated with an excess of "crotyl bromide" and sodium hydride in benzene under reflux for 2 h; t.l.c. (1:1 ether–light petroleum) then showed complete conversion of **3** ($R_F$ 0.4) into allyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-(but-2-enyl)-α-D-glucopyranoside (**4**, $R_F$ 0.8). Methanol was added to destroy the excess of sodium hydride, the benzene solution was washed with water and dried (potassium carbonate), and the solvent evaporated off. The syrupy residue (**4**, 12 g) was added to methanol (180 ml) and M hydrochloric acid (20 ml), and the mixture was heated under reflux for 15 min. T.l.c. (as above) then showed complete hydrolysis of **4** to allyl 3-*O*-benzyl-

2-*O*-(but-2-enyl)-α-D-glucopyranoside (**5**) ($R_F$ 0.2). An excess of sodium hydrogen carbonate was added and the solvents were evaporated. The residue was extracted with chloroform, the dried (potassium carbonate) extract was evaporated, and the crude product (**5**; syrup, 10.7 g) was treated with an excess of benzyl chloride and sodium hydride in *N*,*N*-dimethylformamide at 50° for 4 h. T.l.c. (as above) then showed complete conversion of the diol **5** into allyl 3,4,6-tri-*O*-benzyl-2-*O*-(but-2-enyl)-α-D-glucopyranoside (**6**, $R_F$ 0.9). Methanol was added to the cooled solution, to destroy the excess of sodium hydride, and it was then diluted with water. The product was extracted with ether, the extract was washed with water and dried (potassium carbonate), and the ether and benzyl chloride were evaporated. The crude product (**6**; syrup, 14 g) was treated with potassium *tert*-butoxide (10 g) in dry methyl sulphoxide (100 ml) at 50° for 16 h. T.l.c. (as above) then showed complete conversion of **6** into prop-1-enyl 3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (**9**, $R_F$ 0.45). Water was added to the cooled solution and the product was extracted with ether. The extract was dried (potassium carbonate), the solvent was evaporated, and the crude product (**9**; syrup, 13.2 g) was treated with an excess of allyl bromide and sodium hydride in dry benzene under reflux for 2 h. T.l.c. (as above) then showed complete conversion of **9** into prop-1-enyl 2-*O*-allyl-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (**10**, $R_F$ 0.7). Compound **10** (syrup, 15.6 g) was isolated in the usual way, and treated with M hydrochloric acid (10 ml) and *p*-dioxane (90 ml) at 100° for 15 min; t.l.c. (as above) then showed complete conversion of **10** into a product having $R_F$ 0.2. Water (100 ml) was added, and the mixture was concentrated to a small volume and extracted with ether. The extract was dried (magnesium sulphate) and the solvent evaporated. The crude product (14.6 g) was chromatographed on neutral alumina (400 g). Elution with ether–methanol (99:1) removed some non-polar contaminants, and elution with ether–methanol (9:1) gave **11** (8.6 g, 70%), m.p. 137–139° [from ethyl acetate–light petroleum (b.p. 60–80°)], $[\alpha]_D$ +25.7° (*c* 0.9, chloroform).

*Anal.* Calc. for $C_{30}H_{34}O_6$: C, 73.44; H, 6.99. Found: C, 73.15; H, 6.92.

*2-O-Allyl-3,4,6-tri-O-benzyl-1-O-p-nitrobenzoyl-D-glucopyranose.* — *p*-Nitrobenzoyl chloride (4 g) was added to a solution of compound **11** (4.4 g) in dry dichloromethane (50 ml) and dry pyridine (2 ml), and the solution was kept at room temperature for 14 h. T.l.c. (1:1 ether–light petroleum) then showed complete conversion of **11** ($R_F$ 0.2) into the product ($R_F$ 0.6). Water (1 ml) was added, and the solution was stirred for 30 min and then washed successively with water, M hydrochloric acid, and saturated, aqueous sodium hydrogen carbonate, and dried (magnesium sulphate). The solvent was evaporated, and the *p*-nitrobenzoate (3.9 g, 68%) was recrystallised from ethanol; m.p. 86–88°, $[\alpha]_D$ −12.4° (*c* 1, chloroform).

*Anal.* Calc. for $C_{37}H_{37}NO_9$: C, 69.47; H, 5.83; N, 2.19. Found: C, 69.34; H, 5.92; N, 2.32.

*2,3,5-Tri-O-benzyl-D-arabinofuranose* (**12**). — Sodium borohydride (100 mg) was added to a solution of 2-*O*-allyl-3,4,6-tri-*O*-benzyl-D-glucopyranose (**11**, 0.5 g) in ethanol (20 ml) and methyl sulphoxide (2.5 ml), and kept at room temperature for

15 h. T.l.c. (4:1 toluene–acetone) then showed complete conversion of **11** ($R_F$ 0.7) into 2-*O*-allyl-3,4,6-tri-*O*-benzyl-D-glucitol ($R_F$ 0.65). The solution was diluted with water, the ethanol evaporated, and the aqueous layer extracted with chloroform. The extract was dried (potassium carbonate) and the solvent evaporated, and the product (0.52 g) was added to a solution of potassium *tert*-butoxide (2 g) in methyl sulphoxide (10 ml) and kept at 60° for 3 h. T.l.c. (1:1 toluene–ethyl acetate) then showed complete conversion of the glucitol allyl ether ($R_F$ 0.6) into the corresponding prop-1-enyl ether ($R_F$ 0.7). The product was isolated in the usual way and treated with methanol (17 ml) and M hydrochloric acid (3 ml) at reflux for 30 min, allowing the solvents to distil slowly from the reaction flask. T.l.c. (as above) then showed complete conversion of the glucitol prop-1-enyl ether into 3,4,6-tri-*O*-benzyl-D-glucitol ($R_F$ 0.3). An excess of sodium hydrogen carbonate was added, the solvents were evaporated, and the product was extracted with chloroform. The extract was dried (potassium carbonate), the solvent was evaporated, and the crude product was added to a solution of sodium metaperiodate (250 mg) in acetone (10 ml) and water (7.6 ml) and kept at room temperature for 1 h. T.l.c. (2:1 toluene–acetone) then showed complete conversion of the glucitol derivative ($R_F$ 0.5) into a product having $R_F$ 0.75. The mixture was diluted with water, the acetone was evaporated, and the aqueous layer was extracted with chloroform. The extract was dried (magnesium sulphate) and evaporated, and the crude product (0.36 g) was crystallised from cyclohexane and recrystallised from ethyl acetate–light petroleum (b.p. 60–80°) to give **12**, m.p. 74–76°, $[\alpha]_D$ −25.8 → +9.9° (15 h; *c* 1, 9:1 *p*-dioxane–water) [lit.[9] m.p. 88–89, $[\alpha]_D^{20}$ +27.1 → −11.6° (20 h, *c* 2, 9:1 *p*-dioxane–water) for 2,3,5-tri-*O*-benzyl-β-L-arabinofuranose; m.p. 78–80°, $[\alpha]_D^{20}$ −4.52° (*c* 3.49, dichloromethane) for 2,3,5-tri-*O*-benzyl-α-L-arabinofuranose].

*Anal.* Calc. for $C_{26}H_{28}O_5$: C, 74.26; H, 6.71. Found: C, 74.14; H, 6.82.

*2,3,5-Tri-O-benzyl-D-arabinitol.* — 2,3,5-Tri-*O*-benzyl-D-arabinofuranose was reduced with sodium borohydride, and the product was isolated as described above for 2-*O*-allyl-3,4,6-tri-*O*-benzyl-D-glucopyranose. T.l.c. (4:1 toluene–acetone) showed conversion of the reducing sugar ($R_F$ 0.6) into a product ($R_F$ 0.5) which was crystallised from ether–light petroleum to give the title arabinitol, m.p. 50.5–52.5°, $[\alpha]_D$ +1.0° (*c* 1, chloroform); lit.[10] m.p. 54–55°, $[\alpha]_D^{22}$ +1.3° (*c* 4.2, chloroform).

*Allyl 3,4,6-tri-O-benzyl-α-D-glucopyranoside* (**7**). — A solution of allyl 3,4,6-tri-*O*-benzyl-2-*O*-(but-2-enyl)-α-D-glucopyranoside (**6**, 8 g) and potassium *tert*-butoxide (5 g) in dry methyl sulphoxide (100 ml) was kept at room temperature and monitored by t.l.c. (10:1 toluene–acetone). After 6 h, **6** was completely converted into a mixture of the allyl and prop-1-enyl glycosides (**7** and **9**; $R_F$ 0.25) which were isolated in the usual way. The product was treated with M hydrochloric acid (5 ml) and *p*-dioxane (45 ml) at reflux for 15 min, allowing the solvents to distil slowly from the solution. T.l.c. (4:1 toluene–acetone) then showed the presence of the allyl glycoside (**7**, $R_F$ 0.6) and 3,4,6-tri-*O*-benzyl-D-glucopyranose (**8**, $R_F$ 0.2). An excess of sodium hydrogen carbonate was added and the solvents were evaporated. The residue was extracted with chloroform, the extract dried (magnesium sulphate), and the crude product chromatographed on alumina. Elution with 24:1 ether–methanol gave

**7** (2.8 g, 39%), m.p. 71.5–73.5° [from light petroleum (b.p. 60–80°)], $[\alpha]_D$ +93.3° (*c* 1, chloroform).

*Anal.* Calc. for $C_{30}H_{34}O_6$: C, 73.44; H, 6.99. Found: C, 73.41; H, 6.93.

*3,4,6-Tri-O-benzyl-α-D-glucopyranose* (**8**). — Allyl 3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (**7**, 0.5 g) was treated with potassium *tert*-butoxide (1 g) in dry methyl sulphoxide (10 ml) at 50° for 3 h; t.l.c. (2:1 ether–light petroleum) then showed complete conversion of the allyl glycoside **7** ($R_F$ 0.55) into the prop-1-enyl glycoside **9** ($R_F$ 0.6). The product was isolated in the usual way, and treated with M hydrochloric acid (2 ml) and *p*-dioxane (18 ml) at reflux for 15 min, allowing the solvents to distil slowly from the solution; t.l.c. (as above) then showed complete conversion of **9** into a product having $R_F$ 0.1. Water (20 ml) was added, the solution was evaporated to a small volume, and the product was extracted with chloroform. The extract was dried (magnesium sulphate) and the solvent was evaporated. Recrystallisation of the product from ethanol gave **8**, m.p. 85–86°, $[\alpha]_D$ +57.1° (*c* 0.9, chloroform); lit.[8] m.p. 85–87°, $[\alpha]_{578}^{22}$ +71 (2 min) → +65° (24 h; *c* 1.1, 0.1% 2-pyridone in chloroform).

*2-O-Allyl-3,4-di-O-benzyl-D-glucopyranose* (**17**). — Allyl 3-*O*-benzyl-2-*O*-(but-2-enyl)-α-D-glucopyranoside (**5**, 17 g) and triphenylmethyl chloride (20 g) in dry pyridine (100 ml) were kept at 80° for 17 h; t.l.c. (4:1 toluene–acetone) then showed complete conversion of **5** ($R_F$ 0.3) into the trityl ether **13** ($R_F$ 0.9). The product was isolated in the usual way, and treated with an excess of benzyl chloride and sodium hydride in *N,N*-dimethylformamide at room temperature for 17 h. T.l.c. (1:5 ether–light petroleum) then showed complete conversion of **13** ($R_F$ 0.2) into the dibenzyl ether **14** ($R_F$ 0.4). The product was isolated in the usual way, and the excess of benzyl chloride was removed at 100°/1 mmHg on a rotary evaporator. The crude product was treated with potassium *tert*-butoxide (20 g) in dry methyl sulphoxide (200 ml) at 50° for 17 h. T.l.c. (1:1 ether–light petroleum) then showed complete conversion of **14** ($R_F$ 0.8) into the prop-1-enyl glycoside **15** ($R_F$ 0.5). The product was isolated in the usual way, and treated with an excess of allyl bromide and sodium hydride in benzene under reflux for 14 h; t.l.c. (as above) then showed complete conversion of **15** into the allyl ether **16** ($R_F$ 0.9). The product was isolated in the usual way, and treated with M hydrochloric acid (20 ml) and *p*-dioxane (180 ml) at reflux for 15 min; t.l.c. (as above) then indicated complete conversion of **16** into a product having $R_F$ 0.2. Water (200 ml) was added, the solution was concentrated to a small volume, and the product was extracted with chloroform. The extract was dried (magnesium sulphate), the solvent evaporated, and the crude product chromatographed on neutral alumina. Elution with 45:1 ether–methanol removed the triphenylmethanol, and elution with 1:1 ether–methanol gave **17** (8.3 g, 44%), m.p. 108–110° [from ethyl acetate–light petroleum (b.p. 60–80°)], $[\alpha]_D$ +32 → +27.6° (36 h; *c* 1, chloroform).

*Anal.* Calc. for $C_{23}H_{28}O_6$: C, 68.98; H, 7.05. Found: C, 69.13; H, 7.05.

A portion of this compound was treated with *p*-nitrobenzoyl chloride, and the product was isolated, as described for compound **11**, to give 2-*O*-allyl-3,4-di-*O*-

benzyl-1,6-di-*O*-*p*-nitrobenzoyl-D-glucopyranose, m.p. 159.5–161° (from ethyl acetate–ethanol), $[\alpha]_D$ +9.8° (*c* 0.5, chloroform).

*Anal.* Calc. for $C_{37}H_{34}N_2O_{12}$: C, 63.60; H, 4.91; N, 4.01. Found: C, 63.54; H, 5.13; N, 4.03.

*3,4-Di-O-benzyl-D-glucopyranose* (**19**). — (*a*) A solution of prop-1-enyl 3,4-di-*O*-benzyl-6-*O*-trityl-α-D-glucopyranoside (**15**, 2.1 g) in M hydrochloric acid (5 ml) and *p*-dioxane (45 ml) was treated under reflux for 15 min, allowing the solvents to distil slowly from the reaction mixture. T.l.c. (ether) then showed complete conversion of **15** into a major product ($R_F$ 0.1). Water (50 ml) was added, the solution was concentrated to a small volume, and the product was extracted with chloroform. The extract was dried (magnesium sulphate) and evaporated, and the product was chromatographed on silica gel (B.D.H., 60–120 mesh). Triphenylmethanol and other non-polar contaminants were eluted with 4:1 toluene–acetone. Compound **19** was then eluted with 2:1 toluene–acetone and obtained as a gelatinous solid which was crystallised from aqueous methanol to give **19** as a hydrate (0.5 g), m.p. 120.5–122°, $[\alpha]_D$ +50.9° (*c* 1, chloroform).

*Anal.* Calc. for $C_{20}H_{24}O_6 \cdot H_2O$: C, 63.48; H, 6.93. Found: C, 63.81; H, 6.84.

(*b*) Tris(triphenylphosphine)rhodium(I) chloride (100 mg) and 2-*O*-allyl-3,4-di-*O*-benzyl-D-glucopyranose (**17**) (500 mg) in ethanol (14 ml), benzene (6 ml), and water (2 ml) were heated under reflux for 19 h. T.l.c. (ether) then showed the presence of the allyl ether **17** ($R_F$ 0.5), some of the prop-1-enyl ether **18** ($R_F$ 0.7), and 3,4-di-*O*-benzyl-D-glucopyranose (**19**, $R_F$ 0.2). More of the rhodium catalyst (100 mg) was added and refluxing was continued for 24 h; t.l.c. then showed the absence of the allyl ether **17**. The mixture was filtered, the filtrate was evaporated, and the residue was treated with M hydrochloric acid (2 ml) and *p*-dioxane (18 ml) at reflux for 15 min, allowing the solvents to distil slowly from the reaction mixture. T.l.c. then showed the presence of **19** only. Water (20 ml) was added, the solution was concentrated to a small volume, and the product was extracted with chloroform and chromatographed on silica gel, as described above, to give **19** (409 mg), m.p. and mixture m.p. 120.5–123°.

A solution of the dibenzyl ether **19** (400 mg) in dry acetone (25 ml) containing toluene-*p*-sulphonic acid (20 mg) was kept at room temperature for 24 h. T.l.c. (ether) then indicated partial conversion of the starting material ($R_F$ 0.2) into 3,4-di-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucopyranose (**20**, $R_F$ 0.85). An excess of sodium hydrogen carbonate was added, the solvent was evaporated, and the crude product was extracted with chloroform and chromatographed on alumina. Elution with 19:1 ether–methanol gave compound **20** (syrup, 300 mg) which was treated with an excess of benzyl chloride and sodium hydride in *N*,*N*-dimethylformamide at 20° for 2 h. T.l.c. (2:1 ether–light petroleum) then showed complete conversion of **20** ($R_F$ 0.4) into 3,4,6-tri-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucopyranose (**21**) ($R_F$ 0.8). The product was isolated in the usual way, and treated with M hydrochloric acid (1 ml) and *p*-dioxane (9 ml) at reflux for 15 min; t.l.c. (as above) then showed complete conversion of **21** into a product having $R_F$ 0.1. The product was isolated in the usual

way, and chromatographed on neutral alumina. Non-polar contaminants were eluted with 49:1 ether–methanol, and 3,4,6-tri-*O*-benzyl-D-glucopyranose (**8**, 200 mg) was eluted with 4:1 ether–methanol. Recrystallised from ethanol, **8** had m.p. 85.5–86.5°, mixture m.p. (with material prepared as described above) 87–88°.

ACKNOWLEDGMENT

We thank Mr. R. Conant for skilled technical assistance.

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