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The Allyl Group for Protection in Carbohydrate Chemistry. XXXI* Conversion of Allyl 2,6-Di-*O*-benzyl-α-D-galactopyranoside into Allyl 2,6-Di-*O*-benzyl-α-D-glucopyranoside and 2,6-Di-*O*-benzyl-D-glucopyranose†

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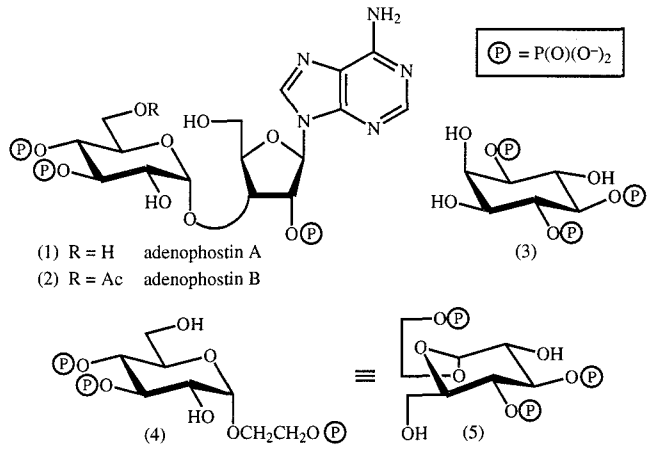
Allyl 2,6-di-*O*-benzyl-α-D-galactopyranoside was converted by tin-mediated alkylation into the 3-*O*-*p*-methoxybenzyl ether which gave the 4-*O*-mesyl derivative. Sodium benzoate in refluxing *N,N*-dimethylformamide converted the last compound into allyl 4-*O*-benzoyl-2,6-di-*O*-benzyl-3-*O*-*p*-methoxybenzyl-α-D-glucopyranoside in high yield. This was saponified and the product was treated with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone to give the required allyl 2,6-di-*O*-benzyl-α-D-glucopyranoside whose structure was confirmed by conversion into the known 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose. Removal of the allyl group from allyl 2,6-di-*O*-benzyl-α-D-glucopyranoside by a standard procedure gave 2,6-di-*O*-benzyl-D-glucopyranose. Both of the title compounds are required as intermediates for the synthesis of analogues of the 'adenophostins'.

Introduction

Japanese scientists reported recently[1–5] that compounds (1) and (2) ('adenophostins A and B') isolated from the culture medium of *Penicillium brevicompactum* were *c.* 100-fold more potent than D-*myo*-inositol 1,4,5-trisphosphate (3) (IP_3) at the IP_3-receptor (IP_3R). We decided therefore to synthesize[6] a simple analogue of (1), i.e. 2′-hydroxyethyl α-D-glucopyranoside 2′,3,4-trisphosphate (4) (which we have called 'glucositol trisphosphate') which appears to be a minimal structure with respect to the three phosphate esters of the 'adenophostins', and (4) was shown by our colleagues[7] to be *c.* 10-fold less active than IP_3 at the IP_3R. Nevertheless, because 'glucositol trisphosphate' (4), like the 'adenophostins' (1) and (2), is resistant[7] to the enzymes (3-kinase and 5-phosphatase) which normally inactivate IP_3, and because it can be readily labelled radiochemically, it should be useful for biological studies at the IP_3R. If 'glucositol trisphosphate' (4) is represented as in (5), then the relationship with IP_3 (3) is more apparent and the molecule is shown to fit the criteria for activity in the inositol phosphate series as described[8] by Kozikowski *et al.*



Results and Discussion

Allyl 2,6-di-*O*-benzyl-α-D-glucopyranoside (15) was required as an intermediate for the synthesis of 'glucositol trisphosphate' (4) and as an intermediate for the preparation of the previously undescribed 2,6-di-*O*-benzyl-D-glucopyranose (21) and its derivatives which are required for the synthesis of 'adenophostin A' and other simpler analogues.

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† Dedicated to Professor Stephen Angyal on reaching his 80th birthday and for his pioneering contributions to inositol chemistry which have helped us considerably in the last 10 years.

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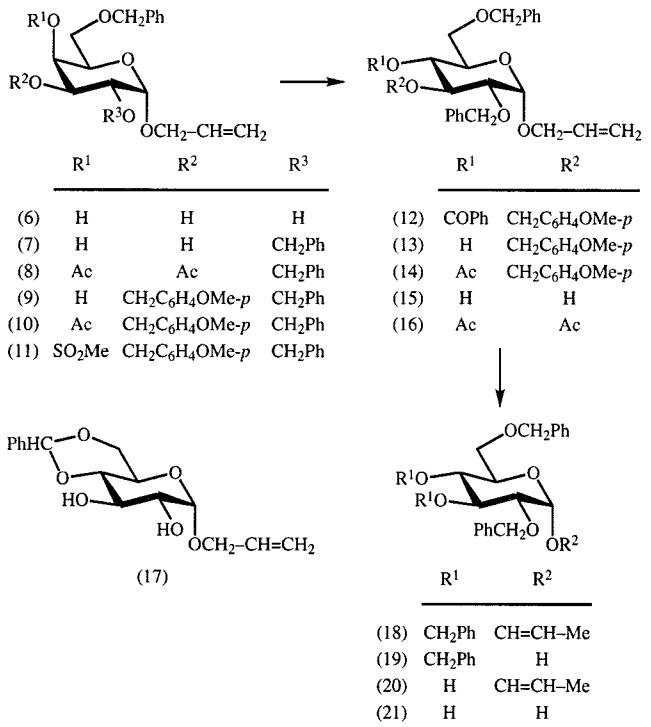
A conventional route to (15) would be the tin-mediated[9] benzylation of the known[9–11] allyl 4,6-*O*-benzylidene-α-D-glucopyranoside (17) followed by reductive opening[12] of the benzylidene acetal with sodium cyanoborohydride–HCl to give a 6-*O*-benzyl derivative. On consideration of this route some potential problems are apparent: (i) the separation of the mixture of 2-*O*- and 3-*O*-benzyl ethers obtained after the tin-mediated benzylation of (17) (see ref. 9 and refs 13 and 14 for related experiments with the methyl glycoside) and (ii) the possible production of some 4-*O*-benzyl ether as well as 6-*O*-benzyl ether on reductive opening of the 4,6-*O*-benzylidene acetal (see ref. 12).



	R^1	R^2	R^3
(6)	H	H	H
(7)	H	H	CH_2Ph
(8)	Ac	Ac	CH_2Ph
(9)	H	$CH_2C_6H_4OMe$-*p*	CH_2Ph
(10)	Ac	$CH_2C_6H_4OMe$-*p*	CH_2Ph
(11)	SO_2Me	$CH_2C_6H_4OMe$-*p*	CH_2Ph

	R^1	R^2
(12)	COPh	$CH_2C_6H_4OMe$-*p*
(13)	H	$CH_2C_6H_4OMe$-*p*
(14)	Ac	$CH_2C_6H_4OMe$-*p*
(15)	H	H
(16)	Ac	Ac

	R^1	R^2
(18)	CH_2Ph	CH=CH–Me
(19)	CH_2Ph	H
(20)	H	CH=CH–Me
(21)	H	H

After this work was completed Qin and Grindley[15] described the conversion of methyl α-D-glucopyranoside into the 2,6-di-*O*-benzyl ether by tin-mediated benzylation in benzyl bromide. An adaptation of this method using allyl α-D-glucopyranoside (which has been isolated from the mixture of anomers obtained on Fischer glycosidation of D-glucose with allyl alcohol[10,16,17]) could be an alternative route for the preparation of (15)* if the separation of the mixture of products obtained by the direct tin-mediated benzylation presents no problems.

We however considered an alternative route by the conversion of a suitably substituted allyl α-D-galactopyranoside into (15). We[18] have described a general route[19] for the preparation of the highly crystalline alkyl 6-*O*-alkyl-α-D-galactopyranosides from 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose, and a considerable quantity of allyl 6-*O*-benzyl-α-D-galactopyranoside (6) prepared[20] by this general method was in stock. The ready conversion of (6) into allyl 2,6-di-*O*-benzyl-α-D-galactopyranoside (7) has been described,[21,22] and other routes to compound (7) are also available.[23,24]

In the galactose series the vicinal *cis*-diol system on C 3 and C 4 allows[23,25] the ready preparation of 3-*O*-alkyl derivatives by using the tin-mediated alkylation reaction. Thus (7) was converted into the 3-*O*-*p*-methoxybenzyl ether (9) in near quantitative yield by this method and the latter was converted into the 4-methanesulfonate (11).

The inversion of the 4-sulfonate group in galactose derivatives by sodium benzoate in *N,N*-dimethylformamide was first described[26,27] in 1959. However, the reaction has not been exploited for the preparation of glucose derivatives from the corresponding galactose derivatives, possibly because the outcome of the reaction depends to some extent on the type of protecting group on the other hydroxy groups (for reviews see refs 28 and 29), despite the fact that conversion of an axial sulfonate into an equatorial ester should be favourable. The replacement of the sulfonate group by stronger nucleophiles, e.g. azide or halide, has however been documented,[29–31] and the reverse reaction, i.e. the conversion of a glucose derivative into a galactose derivative, has been widely used for preparation of rare 2-amino-2-deoxy-D-galactose derivatives from readily available 2-amino-2-deoxy-D-glucose derivatives.[32–34]

After various unsuccessful experiments with more modern reagents for replacing sulfonate groups (e.g. caesium acetate[35] and crown ethers) we returned to the conventional sodium benzoate procedure, and when the methanesulfonate (11) was treated with sodium benzoate in *N,N*-dimethylformamide at reflux for 5 h the benzoate (12) was obtained in high yield (85%) with only minor contamination from the expected unsaturated elimination products. Saponification of the benzoate (12) gave the alcohol (13) which was readily separated from the elimination products at this stage by chromatography. The *p*-methoxybenzyl group was removed[36] by the action of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone to give the required allyl 2,6-di-*O*-benzyl-α-D-glucopyranoside (15) as a crystalline compound.

For proof of structure, compound (15) was isomerized[20] with potassium t-butoxide in dimethyl sulfoxide to give the prop-1′-enyl glycoside (20), and this was converted into the tetra-*O*-benzyl derivative (18). Mild acidic hydrolysis of (18) gave the well known 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (19) which was identical with material prepared previously[20] from D-glucose. For the preparation of 2,6-di-*O*-benzyl-D-glucopyranose (21) the prop-1′-enyl glycoside (20) was hydrolysed to give (21) as a crystalline compound.

* *Note added in proof.* After the submission of this manuscript a synthesis of (15) by this procedure was described (Jenkins, D. J., and Potter, B. V. L., *J. Chem. Soc., Chem. Commun.*, 1995, 1169).

The alkyl 6-*O*-alkyl-α-D-galactopyranosides are readily prepared by the general procedure,[18,19] and the 2-, 3- and 4-hydroxy groups in these compounds are readily differentiated, allowing the introduction of any combination of protecting groups at all of the hydroxy groups of D-galactose. This, combined with the facile inversion of the 4-mesylate described here, should allow the ready preparation of many differently protected alkyl α-D-glucopyranosides by this procedure.

Experimental

General

General conditions were as described previously.[37,38]

Allyl 2,6-Di-O-benzyl-3-O-p-methoxybenzyl-α-D-galactopyranoside (9)

The diol (7)[21–24] (5·6 g, 13·98 mmol), dibutyltin oxide (4 g, 16·07 mmol), tetrabutylammonium bromide (4·5 g, 13·96 mmol) and acetonitrile (100 ml) were heated under reflux with a Soxhlet apparatus containing molecular sieve 3A (10 g) for 3 h. *p*-Methoxybenzyl chloride (2·5 ml, 2·9 g, 18·4 mmol) was then added and refluxing was continued for 12 h. The solvent was evaporated and toluene was evaporated from the residue which was then distributed between ether (100 ml) and water (100 ml). The ether layer was separated and stirred with an excess of sat. aq. $NaHCO_3$ for 2 h and then the mixture was filtered through Celite. The ether layer was separated, dried (K_2CO_3) and concentrated to give a syrup. T.l.c. (ether/light petroleum, 1:1) showed conversion of (7) (R_F 0) into a major product (R_F 0·35) with trace products at R_F 0·6 and 0·8. Column chromatography (same solvent) gave the pure *alcohol* (9) (7 g, 96%) as a syrup, $[\alpha]_D$ +43° (*c*, 3 in $CHCl_3$) (Found: C, 71·2; H, 6·8. $C_{31}H_{36}O_7$ requires C, 71·5; H, 7·0%). ^{1}H n.m.r. δ 2·58, s, 1H, OH; 3·64–4·15, m, 8H, ring protons, OCH_2CH= and 2×H6; 3·80, s, 3H, OMe; 4·56, 4·59, 2s, each 2H, CH_2Ph; 4·70, AB q, 2H, $CH_2C_6H_4$; 4·87, d, *J* 1·5 Hz, 1H, H1; 5·12–5·37, m, 2H, $=CH_2$; 5·74–6·17, m, 1H, =CH; 6·82–7·32, m, 14H, aromatic.

This gave a syrupy acetate (10). ^{1}H n.m.r. δ 2·02, s, 3H, $COCH_3$; 3·48, d, *J* 6·1 Hz, 2H, 2×H6; 3·73, s, 3H, OMe; 3·79–4·15, m, 5H, OCH_2CH= and 3 ring protons with major peaks at 3·79, 3·83, 3·90, 3·94, 4·04, 4·11; 4·47–4·75, m, 6H, 3×CH_2Ph with major peaks at 4·48, 4·52, 4·65, 4·67, 4·76; 4·88, d, *J* 3·6 Hz, 1H, H1; 5·03–5·38, m, 2H, $=CH_2$; 5·60, d, *J* 1·8 Hz, 1H, H4; 5·74–6·16, m, 1H, =CH; 6·78–7·30, m, 14H, aromatic.

Allyl 2,6-Di-O-benzyl-3-O-p-methoxybenzyl-4-O-methylsulfonyl-α-D-galactopyranoside (11)

Methanesulfonyl chloride (0·5 ml, 0·74 g, 6·4 mmol) was added to a solution of the alcohol (9) (2 g, 3·84 mmol) in dry pyridine (10 ml) at 0° and the solution was kept at 20° for 3 h. Ice-water (45 ml) was added and the product was extracted with ether. The extract was washed successively with 1 M HCl, sat. aq. KCl and sat. aq. $NaHCO_3$, dried ($MgSO_4$) and concentrated to give a syrup (2·2 g, 96%). T.l.c. (ether/light petroleum, 1:1) showed conversion of (9) (R_F 0·35) into a product (R_F 0·5). Column chromatography (ether/light petroleum, 2:1) gave the *methanesulfonate* (11) as a syrup, $[\alpha]_D$ +53° (*c*, 1·8 in $CHCl_3$) (Found: C, 63·6; H, 6·3; S, 5·2. $C_{32}H_{38}O_9S$ requires C, 64·2; H, 6·4; S, 5·4%). ^{1}H n.m.r. δ 2·94, s, 3H, SMe; 3·60–4·15, m, 7H, OCH_2CH=, 2×H6 and 3 ring protons with major peaks at 3·60, 3·67, 3·78, 3·92, 3·96, 4·04, 4·09, 4·11, 4·15; 3·81, s, 3H, OMe; 4·40–4·80, m, 6H, 2×CH_2Ph and $CH_2C_6H_4$, with major peaks at 4·53, 4·58, 4·67, 4·69, 4·71, 4·75; 4·89, d, *J* 3·0 Hz, 1H, H1; 5·14–5·38, m, 3H, $=CH_2$ and H4; 5·72–6·15, m, 1H, CH=; 6·81–7·41, m, 14H, aromatic.

Allyl 2,6-Di-O-benzyl-3-O-p-methoxybenzyl-α-D-glucopyranoside (13)

A solution of the methanesulfonate (11) (8 g, 13·36 mmol) in *N,N*-dimethylformamide (150 ml) and sodium benzoate (4·8 g, 33·3 mmol) was heated under reflux in the absence of moisture, with stirring for 6 h. T.l.c. (ether/light petroleum, 1:1) then showed complete conversion of (11) (R_F 0·5) into a major product (R_F 0·65) and trace products (R_F 0·7 and 0·4). The solution was cooled, diluted with water (300 ml), and the mixture was extracted with ether; the extract was dried ($MgSO_4$) and concentrated to give the crude product as a syrup (8·2 g). A solution of this in MeOH (150 ml) containing NaOH (1·5 g, 37·5 mmol) was heated under reflux for 1·5 h. Solid CO_2 was added to the cooled solution and the MeOH was removed by evaporation. Water was added to the residue and the product was extracted with ether, and the extract dried (K_2CO_3) and concentrated to give the crude product (6·7 g). T.l.c. (as above) now showed a major product (R_F 0·4) together with trace products (R_F 0·7 and 0·5). Column chromatography (same solvents) removed the trace product R_F 0·7 (280 mg), probably an unsaturated elimination product [^{1}H n.m.r. δ 3·75–3·95, m, 4H, with major peak at 3·91; 3·78, s, 3H, OMe; 4·20, m, 2H, OCH_2CH=; 4·53, 4·55, 4·76, 3s, 2×CH_2Ph and $CH_2C_6H_4$; 4·82–5·04, m, 2H, with major peaks at 4·82, 4·99, 5·02, 5·04; 5·13–5·42, m, 2H, $=CH_2$; 5·7–6·15, m, 1H, =CH; 6·80–7·31, m, 14H, aromatic], and the trace product R_F 0·5 (216 mg, the ^{1}H n.m.r. of which showed it to be a mesylate), and the major *product* (13) R_F 0·4 (6·04 g, 87%) as a syrup, $[\alpha]_D$ +22° (*c*, 2·9 in $CHCl_3$) (Found: C, 71·1; H, 7·0. $C_{31}H_{36}O_7$ requires C, 71·5; H, 7·0%). ^{1}H n.m.r. δ 2·31, d, *J* 1·2 Hz, 1H, OH; 3·44–3·83, m, 6H, ring protons and 2×H6; 3·79, s, 3H, OMe; 4·02–4·15, m, 2H, OCH_2CH=; 4·55–4·88, m, 7H, 2×CH_2Ph, $CH_2C_6H_4$ and H1, with major peaks at 4·55, 4·69, 4·71, 4·82, 4·85, 4·88; 5·01–5·39, m, 2H, $=CH_2$; 5·74–6·17, m, 1H, CH=; 6·82–7·33, m, 14H, aromatic.

This gave a syrupy acetate (14). ^{1}H n.m.r. δ 1·84, s, 3H, $COCH_3$; 3·43–3·64, m, 3H, 1 ring proton and 2×H6; 3·77, s, 3H, OMe; 3·83–4·16, m, 4H, OCH_2CH= and 2 ring protons; 4·49, s, 2H, $CH_2C_6H_4$; 4·53–4·85, m, 4H, 2×CH_2Ph, with major peaks at 4·63, 4·67, 4·72, 4·76, 4·79, 4·83; 4·90, d, *J* 3·1 Hz, 1H, H1; 5·02–5·39, m, 3H, $=CH_2$ and H4; 5·75–6·19, m, 1H, CH=; 6·79–7·31, m, 14H, aromatic.

Allyl 2,6-Di-O-benzyl-α-D-glucopyranoside (15)

A stirred solution of the *p*-methoxybenzyl ether (13) (6·0 g, 11·5 mmol) in CH_2Cl_2 (400 ml) with water (10 ml) was cooled to 0° and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (6 g, 26·4 mmol) was added portionwise during 5 min, and then the course of the reaction was followed by t.l.c. (ether/light petroleum, 1:1). After 45 min the ether (13) (R_F 0·4) was completely converted into a product (R_F 0) together with trace by-products (R_F 0·35 and 0·45). The mixture was shaken with an excess of saturated aqueous sodium metabisulfite, and the layers were separated and the CH_2Cl_2 layer was washed with sat. aq. $NaHCO_3$ and dried (K_2CO_3) and concentrated. T.l.c. (ether) showed the product (R_F 0·5) with the traces of the by-products (R_F 1·0). Column chromatography (ether) gave the pure *diol* (15) (4·0 g, 86%), m.p. 78–79° (from ether/light petroleum), $[\alpha]_D$ +79° (*c*, 2·6 in $CHCl_3$) (Found: C, 68·7; H, 6·9. $C_{23}H_{28}O_6$ requires C, 69·0; H, 7·1%). ^{1}H n.m.r. δ 2·75, s, 2H, 2 OH; 3·38, dd, *J* 3·66, 9·15 Hz, 1H; 3·54–4·12, m, 7H, OCH_2CH=, 2×H6 and 3 ring protons, with major peak at 3·70; 4·57, 4·65, 2s, each 2H, 2×CH_2Ph; 4·83, d, *J* 3·67 Hz, 1H, H1; 5·11–5·37, m, 2H, $=CH_2$; 5·70–6·11, m, =CH; 7·32, 7·33, 2s, 10H, aromatic.

Allyl 3,4-Di-O-acetyl-2,6-di-O-benzyl-α-D-glucopyranoside (16)

The diol (15) was treated with acetic anhydride in pyridine in the usual way to give the syrupy *diacetate* (16), $[\alpha]_D$ +103° (*c*, 2·4 in $CHCl_3$) (Found: C, 66·7; H, 6·5. $C_{27}H_{32}O_8$ requires C, 66·9; H, 6·7%). ^{1}H n.m.r. δ 1·88, 1·99, 2s, each 3H, 2×$COCH_3$; 3·47, d, *J* 3·67 Hz, 2H, 2×H6; 3·59, dd, *J* 3·7, 9·8 Hz, 1H, H2; 3·84–4·30, m, 3H, OCH_2CH= and H5; 4·51, AB q, 2H, CH_2Ph; 4·60, s, 2H, CH_2Ph; 4·85, d, *J* 3·7 Hz, 1H, H1; 5·05, t, *J* 9·5 Hz, 1H, H3 or H4; 5·14–5·39, m, 2H, $=CH_2$; 5·45, t, *J* 9·8 Hz, 1H, H3 or H4; 5·72–6·15, m, 1H, CH=; 7·30, s, 10H, aromatic.

For comparison the galactopyranoside diacetate (8) had ^{1}H n.m.r. δ 1·98, 2·01, 2s, each 3H, 2×$COCH_3$; 3·44, d, *J* 6·7 Hz, 2H, 2×H6; 3·83, dd, *J* 3·7, 10·4 Hz, 1H, H2; 4·01–4·32, m, 3H, OCH_2CH= and H5; 4·47, d, *J* 4·3 Hz, 2H, CH_2Ph; 4·64, d, *J* 1·8 Hz, 2H, CH_2Ph; 4·91, d, *J* 3·7 Hz, 1H, H1; 5·13–5·50, m, 4H, $=CH_2$ and H3 and H4; 5·72–6·15, m, 1H, CH=; 7·25–7·31, m, 10H, aromatic.

(Z)-*Prop-1′-enyl 2,6-Di-O-benzyl-α-D-glucopyranoside (20)*

The allyl glucoside (15) was treated with potassium t-butoxide in dimethyl sulfoxide, and the product isolated in the usual way[20] to give the prop-1′-enyl glucoside (20). T.l.c. (ether) showed conversion of (15) (R_F 0·6) into (20) (R_F 0·75). Column chromatography (ether) gave pure (20) as a *syrup*, $[\alpha]_D$ +49° (*c*, 2 in $CHCl_3$) (Found: C, 68·5; H, 6·9. $C_{23}H_{28}O_6$ requires C, 69·0; H, 7·1%). ^{1}H n.m.r. δ 1·63, dd, *J* 1·83, 6·71 Hz, 3H, $=CHCH_3$; 2·90, br s, 2H, 2×OH; 3·42, dd, *J* 3·3, 9·4 Hz, 1H; 3·67, s, 4H; 3·80–4·11, m, 1H; 4·40–4·74, m, 5H, 2×CH_2Ph and 1 ring proton, with major peaks at 4·54, 4·66; 4·96, d, *J* 3·66 Hz, 1H, H1; 6·0, dd, *J* 1·83, 6·11 Hz, 1H, OCH=; 7·30–7·32, m, 10H, aromatic.

(Z)-*Prop-1′-enyl 2,3,4,6-Tetra-O-benzyl-α-D-glucopyranoside (18)*

The prop-1′-enyl glucoside (20) was treated with an excess of sodium hydride and benzyl bromide in *N,N*-dimethylformamide, and the product isolated in the usual way to give the tetra-*O*-benzyl derivative (18). T.l.c. (ether/light petroleum, 3:1) showed conversion of (20) (R_F 0·25) into (18) (R_F 0·9). Column chromatography (ether/light petroleum, 1:2) gave pure (18) as a *syrup*, $[\alpha]_D$ +17° (*c*, 2 in $CHCl_3$) (Found: C, 76·7; H, 7·1. $C_{37}H_{40}O_6$ requires C, 76·5; H, 6·9%). ^{1}H n.m.r. δ 1·64, dd, *J* 1·83, 6·71 Hz, 3H, $=CHCH_3$; 3·53–4·17, m, 6H, H2–H6; 4·35–5·08, m, 10H, 4×CH_2Ph, H1 and CH_3CH=, with major peaks at 4·48, 4·55, 4·70, 4·75, 4·79, 4·89, 4·93, 4·97; 6·02, dd, *J* 1·83, 6·11 Hz, 1H, OCH=; 7·24–7·32, m, 20H, aromatic (cf. ref. 39).

2,3,4,6-Tetra-O-benzyl-D-glucopyranose (19)[20]

The prop-1′-enyl glucoside (18) (400 mg) was heated under reflux in acetone/MeOH/1 M HCl (3:7:1, 10 ml) for 30 min, whereupon t.l.c. (ether/light petroleum, 1:2) showed complete conversion of (18) (R_F 0·55) into a product (R_F 0). T.l.c. (ether/light petroleum, 2:1) showed cochromatography of the product with an authentic sample[20] of (19), R_F 0·5 (major) and R_F 0·55 for α- and β-anomers. Sodium acetate (100 mg) and water (10 ml) were added and the solution was concentrated to remove the organic solvents, and the crystalline product then separated. Column chromatography (ether/light petroleum, 2:1) removed trace impurities and gave pure (19) (350 mg, 94%), m.p. and mixed m.p. 153–155° (from ethyl acetate/light petroleum, b.p. 60–80°, 1:3), $[\alpha]_D$ +20° (*c*, 2·1 in $CHCl_3$) {lit.[20] m.p. 153–155°, $[\alpha]_D$ +21° (*c*, 3·5 in $CHCl_3$)}. ^{1}H n.m.r. (which was identical with that of the authentic sample) δ 2·96, d, *J* 2·44 Hz, 1H, OH; 3·25–4·60, m, 6H, H2–H6; 4·92–5·02, m, 8H, 4×CH_2Ph, with major peaks at 4·52, 4·55, 4·73, 4·77, 4·80, 4·84, 4·90; 5·23, d, *J* 2·4 Hz, 1H, H1; 7·18–7·31, m, 20H, aromatic.

2,6-Di-O-benzyl-D-glucopyranose (21)

The prop-1′-enyl glucoside (20) (220 mg) was heated under reflux in acetone/1 M HCl (9:1, 20 ml) for 1 h. T.l.c. (ether) showed conversion of (20) (R_F 0·75) into (21) (R_F 0·45 and 0·5 for the mixture of anomers). Sodium acetate (200 mg) and water (10 ml) were added and the solution was concentrated to remove the acetone. The *product* was extracted with ethyl acetate, and column chromatography (ethyl acetate) gave (20) (188 mg, 95%), m.p. 103–105° (from ether with a little ethyl acetate), $[\alpha]_D$ +35 → +31° (23 h) (*c*, 2·1 in $CHCl_3$) (Found: C, 66·7; H, 6·7. $C_{20}H_{24}O_6$ requires C, 66·7; H, 6·7%).

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