Phenyloxazoline Derivatives of Amino-sugars. Part 3.† Preparation of Intermediates for the Synthesis of Sphingoglycolipids

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1,2-Dideoxy-5,6-*O*-isopropylidene-2'-phenyl-α-D-glucofuranoso[2,1-*d*]-Δ²'-oxazoline (1) was readily converted into allyl 2-benzamido-2-deoxy-5,6-*O*-isopropylidene-β-D-glucofuranoside (4) by the action of the pyridine salt of toluene-*p*-sulphonic acid in allyl alcohol–pyridine at reflux. This method is superior to acid alcoholysis for the conversion. The mesylate of the alcohol (4) was converted into allyl 2,3-dideoxy-5,6-*O*-isopropylidene-2'-phenyl-β-D-allofuranosido[2,3-*d*]-Δ²' -oxazoline (9) by hot aqueous triethylamine. The isopropylidene group of compound (9) was hydrolysed preferentially in anhydrous methanol and the *allo*-diol (12) produced was converted into the *talo*-anhydride (17), which was hydrolysed to give the *talo*-diol (18). The *allo*-diol and the *talo*-anhydride are potential intermediates for the synthesis of sphingosine. The isomerisation of the allyl group of compound (9) to a prop-1-enyl group, without affecting the phenyloxazoline group, was accomplished by the action of commercial potassium t-butoxide in dimethyl sulphoxide containing t-butyl alcohol or preferably by the action of chloro(tristriphenylphosphine)rhodium(I).

The action of acidic benzyl alcohol, containing benzaldehyde, on 3-*O*-benzyl-1,2-dideoxy-5,6-*O*-isopropylidene-2'-phenyl-α-D-glucofuranoso[2,1-*d*]-Δ²'-oxazoline (2) at 20 °C led to the separation of the highly crystalline (m.p. 300°) benzyl 2-benzamido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (30) in high yield from the reaction mixture. This compound was converted, by two routes involving allyl ethers, into benzyl 2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (40), an intermediate required for the synthesis of the immunological determinant of the P'-antigen. The conversion of benzamido- into acetamido-groups was accomplished with acetic anhydride–acetic acid containing sodium acetate at reflux. It was shown that allyl ethers and *O*-benzylidene groups were stable to the conditions of this conversion. Benzyl 2-acetamido-6-*O*-allyl-3-*O*-benzyl-2-deoxy-β-D-glucopyranoside (48) was also prepared.

ZERVAS and his co-workers [1] showed that preferential opening of the phenyloxazoline ring of 1,2-dideoxy-5,6-*O*-isopropylidene-2'-phenyl-α-D-glucofuranoso-[2,1-*d*]-Δ²'-oxazoline (1) [1-6] occurred at 20 °C with 0.000 5N-hydrogen chloride in methanol to give the methyl β-furanoside (3); we [6-12] and others [3,13-15] have applied similar alcoholysis conditions to compound (1) and its derivatives in order to prepare various β-furanoside derivatives of 2-amino-2-deoxy-D-glucose including the allyl (4) [10] and benzyl (5) [10] glycosides. Since the isopropylidene group in these products is also readily hydrolysed, it is advantageous to follow the reaction carefully by t.l.c. to prevent further hydrolysis although in the preparation of the allyl furanoside (4) [10] it was sometimes found difficult to control this reaction satisfactorily.

We have shown [11] that the phenyloxazoline group in compound (8) is hydrolysed by the pyridinium salts of sulphonic acids in hot aqueous pyridine, to give the benzamido-alcohol (24), without affecting the isopropylidene group. This occurs because the phenyloxazoline is a stronger base than pyridine and is thus protonated, allowing attack by hydroxide anion and formation of the phenyloxazolidine (23), which collapses in basic media to the benzamido-alcohol (24). We have therefore investigated the reaction of the phenyloxazoline group of compound (1) with the pyridinium salt of toluene-*p*-sulphonic acid in alcoholic pyridine.

When compound (1) was heated under reflux for 2.5 h with toluene-*p*-sulphonic acid in allyl alcohol containing pyridine, complete conversion of (1) into the allyl glycoside (4) occurred without further decomposition. Similarly, the benzyl ether (2) was converted into the benzyl glucofuranoside (7) and the oxazoline (1) gave the methyl glucofuranoside (3) by using the appropriate alcohol under these conditions, although longer reaction times were required than with allyl alcohol.

The crude allyl glycoside (4), prepared in this way, was converted directly into the mesylate (6) by the action of an excess of methanesulphonyl chloride in pyridine. Water was added to the solution to convert the excess of chloride into acid and triethylamine was then added before heating the solution at 100 °C in order to convert the mesylate (6) into the phenyloxazoline (9).[10] Although methanesulphonic acid in aqueous pyridine causes [11] rupture of the phenyloxazoline ring under these conditions, it is stable in the presence of aqueous triethylamine since this is a stronger base than the phenyloxazoline and the latter is, therefore, not protonated. The pure phenyloxazoline (9) was obtained in about 60% yield from the phenyloxazoline (1), by this procedure, without isolating the intermediates.

The oxazoline (11) has been useful in the synthesis of

† Part 2, ref. 11.

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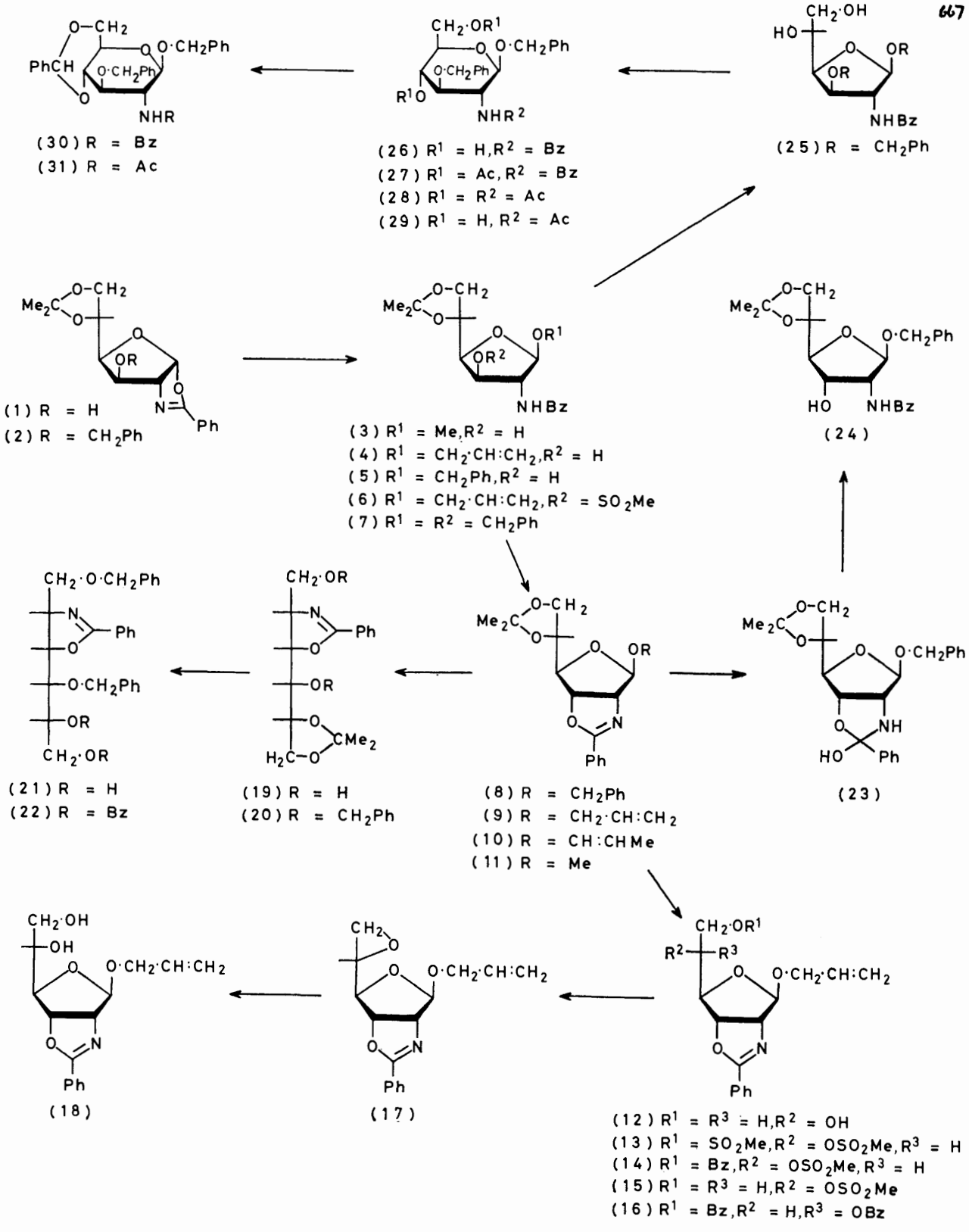
(30) R = Bz
(31) R = Ac
(26) R¹ = H, R² = Bz
(27) R¹ = Ac, R² = Bz
(28) R¹ = R² = Ac
(29) R¹ = H, R² = Ac
(25) R = CH₂Ph
(1) R = H
(2) R = CH₂Ph
(3) R¹ = Me, R² = H
(4) R¹ = CH₂·CH:CH₂, R² = H
(5) R¹ = CH₂Ph, R² = H
(6) R¹ = CH₂·CH:CH₂, R² = SO₂Me
(7) R¹ = R² = CH₂Ph
(24)
(21) R = H
(22) R = Bz
(19) R = H
(20) R = CH₂Ph
(8) R = CH₂Ph
(9) R = CH₂·CH:CH₂
(10) R = CH:CHMe
(11) R = Me
(23)
(18)
(17)
(12) R¹ = R³ = H, R² = OH
(13) R¹ = SO₂Me, R² = OSO₂Me, R³ = H
(14) R¹ = Bz, R² = OSO₂Me, R³ = H
(15) R¹ = R³ = H, R² = OSO₂Me
(16) R¹ = Bz, R² = H, R³ = OBz

phytosphingosines,[7] and compound (9) was required for the preparation of the diol (12) which would serve as an intermediate for a proposed synthesis [10] of spingosine. In contrast to the ready acidic alcoholysis of the phenyloxazoline group in compound (1),[1-15] the phenyloxazoline group has been shown to be reasonably stable to acidic methanol if the oxygen atom is not attached to the anomeric centre,[10,16] and we found [10] that the isopropylidenedioxy-group of compound (8) could be hydrolysed preferentially to give the corresponding diol. However, at times this reaction has proved capricious: we found,[10] for example, that it was difficult to hydrolyse preferentially the isopropylidene dioxy-group of compound (20). This has now been shown to be due to the presence of water. In anhydrous acidic methanol the phenyloxazoline groups in compounds (9) and (20) are stable at 20° and under reflux and the corresponding diols can be readily prepared from the isopropylidene derivatives. 2,2-Dimethoxypropane was used as a water scavenger.

For the proposed synthesis [10] of sphingosine one route involved an oxiran [*e.g.* (17)]. For the conversion of the diol (12) into the oxiran (17), the sulphonate (15) was required. The diol (12) was therefore converted into the dimesylate (13), which was treated with sodium benzoate in dimethyl sulphoxide to cause replacement of the primary mesyl group preferentially, to give the benzoate (14) in high yield with only a trace of the dibenzoate (16). Compound (14) was readily converted into the oxiran (17) with sodium methoxide in chloroform–methanol.[17] The oxiran (17) was cleanly hydrolysed by 0.1N-tetrabutylammonium hydroxide in aqueous dioxan to give the 2-amino-2-deoxy-L-talose derivative (18).

We have previously described [10] the isomerisation of the allyl group in compound (9) to give the prop-1-enyl glycoside (10) by the action of potassium t-butoxide in dimethyl sulphoxide at 20 °C, and also [11] the instability of the phenyloxazoline ring with this reagent at higher temperatures. The successful isomerisations of the allyl group in compound (9) were carried out using laboratory-prepared potassium t-butoxide. Subsequently we used commercially available potassium t-butoxide and even at 20 °C this material caused cleavage of the phenyloxazoline ring in the manner described previously.[11] However, the activity of the commercial material is reduced considerably by the addition of t-butyl alcohol to the dimethyl sulphoxide, and the isomerisation of compound (9) to the prop-1-enyl glycoside (10) was then successful. We have also shown, in a preliminary communication,[18] that the allyl group in compound (9) is isomerised to the prop-1-enyl group by chloro(tristriphenylphosphine)rhodium(I) without affecting the phenyloxazoline group, and this is a more satisfactory way for the isomerisation of the allyl group in these compounds.

The immunological determinant of the P′-antigen, which is a sphingosine-containing glycolipid (' glycosphingolipid '), has been shown [19] to be the trisaccharide α-D-galactopyranose (1 ⟶ 4)-β-D-galactopyranose (1 ⟶ 4)-*N*-acetyl-D-glucosamine. We have recently [20] prepared the fully acetylated derivative of α-D-galactopyranose (1 ⟶ 4)-D-galactopyranose, which should be a suitable intermediate for joining in β-linkage to an *N*-acetyl-D-glucosamine derivative for the synthesis of the trisaccharide portion of the P′-antigen.

The protected *N*-acetyl-D-glucosamine derivative (40) appeared suitable for this condensation and a route to it from the phenyloxazoline (1) was investigated. It was expected that when the benzyl ether (2) [8,21] was treated with benzyl alcohol in the presence of toluene-*p*-sulphonic acid at 20 °C, it would be converted by way of the intermediates (7) and (25) into the β-benzyl pyranoside (26) as described previously [1-3,22] for similar reactions of the oxazoline (1) and its derivatives. It has been reported,[21] however, that this reaction gives a mixture of the α- and β-benzyl 2-benzamido-3-*O*-benzyl-2-deoxy-D-glucopyranosides in varying proportions depending on the reaction time, and that even after 3 h 25% of the α-anomer was present. This is in contrast with previous experience [3,12,22] in this field: the oxazoline (1) and its derivatives have been used successfully for the preparation of several β-glucopyranosides in high yield, although the presence of small amounts of the α-anomer has been reported.[15,23]

In our experiments, when the benzyl ether (2) was treated with benzyl alcohol and toluene-*p*-sulphonic acid at 20 °C, a highly crystalline product separated from the reaction mixture during 24 h and analysis showed that this was the benzylidene derivative (30), presumably formed from the benzaldehyde present as a contaminant of the benzyl alcohol (B.D.H., ' containing 0.2% benzaldehyde '). The stable crystalline structure (m.p. 300°) of this benzylidene derivative (30) and hence its very low solubility in benzyl alcohol (and other organic solvents) presumably favoured its formation in this unfavourable medium and this indicated a convenient method for the isolation of the required product. The reaction was repeated using benzyl alcohol containing sufficient benzaldehyde to convert all the required product (26) into the benzylidene derivative (30), and after 36 h at 20 °C the benzylidene derivative (30) was filtered off (*ca.* 90% yield). Hydrolysis of compound (30) in hot aqueous acetic acid or in acidic aqueous dimethyl

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sulphoxide gave the crystalline diol (26), which was converted into the crystalline acetate (27), with properties similar to those reported previously.[21]

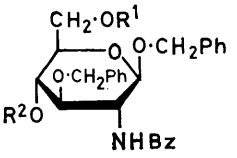
We have shown previously [12] that it is possible to convert a benzamido-group into an acetamido-group by treatment with acetic anhydride and acetic acid at reflux; the benzamido-derivative (27) was converted in this way into the acetamido-derivative (28) in high yield. Since the solvents used for this conversion are similar to those required for acetolysis [24] (which occurs at a much lower temperature), the presence of a trace of contaminating mineral acid could lead to acetolysis of the benzyl groups in this reaction; we therefore now add a small quantity of sodium acetate to the reaction mixture to guard against this possibility. Alkaline hydrolysis of the acetate (28) gave the diol (29). Compound (29) has been prepared previously [25] but our constants were different from those reported. Gross and Jeanloz [26] had also prepared several derivatives of benzyl 2-acetamido-2-deoxy-β-D-glucopyranoside and reported that their constants were different from those recorded by the Japanese workers.[25] After this work was complete a further preparation of compound (29) was reported by Shaban and Jeanloz; [27] our constants are similar to those recorded by these authors.

For the preparation of the required intermediate (40), two routes were available: (a) *via* the benzamido-diol (26), and (b) *via* the acetamido-diol (29). The α-anomer of compound (29) has been partially benzylated [28] on the primary hydroxy-group using benzyl bromide, barium oxide, and barium hydroxide in *NN*-dimethylformamide (but a separation from some dibenzylated product was still required) and the benzyl 2-acetamido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranoside has also been prepared by a longer route, by the same workers [29] (see also ref. 27). Initially, we carried out benzylation studies on the benzamido-derivative (26), since the benzamido-derivatives are frequently highly crystalline and the benzamido-group is less readily benzylated than is the acetamido-group,[12] and we decided, after initial attempts at partial benzylation, to adopt a longer route.

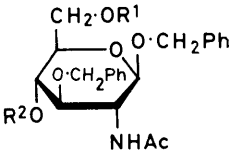
Compound (26) was converted into the crystalline trityl ether (32) and this gave the crystalline allyl derivative (33), which was hydrolysed to give the alcohol (34). Benzylation of the allyl ether (34) gave crystalline benzyl 4-*O*-allyl-2-benzamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (35). The allyl group was removed in the usual way [8,30] to give the alcohol (37) and this was converted into the acetamido-derivative (39) by the action of acetic anhydride–acetic acid. Compound (39) was hydrolysed by base to give the required alcohol (40), with properties similar to those reported by Shaban and Jeanloz.[27]

Using a similar route, the acetamido-diol (29) was converted *via* the trityl ether (41) and the allyl ether (42) into the highly crystalline alcohol (43). Benzylation of compound (43) and removal of the allyl group in the usual way gave the required benzyl 2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (40), identical with that described above. When this work had been completed, a similar route to compound (40) was reported by Shaban and Jeanloz [27] from benzyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside.

As an extension of the method we had developed for the conversion of benzamido-groups into acetamido-groups with acetic anhydride–acetic acid, we investigated the stability of other groups to these conditions. When the benzylidene derivative (30) was treated under these conditions it was converted into the acetamido-derivative



(32) $R^1 = CPh_3, R^2 = H$
(33) $R^1 = CPh_3, R^2 = CH_2{\cdot}CH{:}CH_2$
(34) $R^1 = H, R^2 = CH_2{\cdot}CH{:}CH_2$
(35) $R^1 = CH_2Ph, R^2 = CH_2{\cdot}CH{:}CH_2$
(36) $R^1 = CH_2Ph, R^2 = CH{:}CHMe$
(37) $R^1 = CH_2Ph, R^2 = H$
(38) $R^1 = R^2 = CH_2Ph$



(39) $R^1 = CH_2Ph, R^2 = Ac$
(40) $R^1 = CH_2Ph, R^2 = H$
(41) $R^1 = CPh_3, R^2 = H$
(42) $R^1 = CPh_3, R^2 = CH_2{\cdot}CH{:}CH_2$
(43) $R^1 = H, R^2 = CH_2{\cdot}CH{:}CH_2$
(44) $R^1 = CH_2Ph, R^2 = CH_2{\cdot}CH{:}CH_2$
(45) $R^1 = CH_2Ph, R^2 = CH{:}CHMe$
(46) $R^1 = H, R^2 = CH{:}CHMe$
(47) $R^1 = CH_2{\cdot}CH{:}CH_2, R^2 = CH{:}CHMe$
(48) $R^1 = CH_2{\cdot}CH{:}CH_2, R^2 = H$
(49) $R^1 = Ac, R^2 = CH_2{\cdot}CH{:}CH_2$

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(31), which was isolated in *ca.* 50% yield. The acetamido-derivative (31) was also prepared from the diol (29) by the action of benzaldehyde and zinc chloride for comparative purposes since there was some doubt about the m.p. reported previously.[25] Our m.p. was different from that reported [25] but similar to that recorded by Shaban and Jeanloz [27] after this work was completed. The stability of the allyl group to these conditions was also studied and as a model compound we chose benzyl 6-*O*-allyl-2,3,4-tri-*O*-benzyl-α-D-galactopyranoside.[31] This compound was recovered in 95% yield after treatment under the standard conditions. Benzyl 4-*O*-allyl-2-benzamido-3-*O*-benzyl-2-deoxy-β-D-glucopyranoside (34) was also treated under these conditions to give the acetamido-derivative (49). Alkaline hydrolysis of compound (49) gave the highly crystalline allyl ether (43) in good yield.

The allyl ether (43) was also converted into the prop-1-enyl ether (46) by the action of potassium t-butoxide in dimethyl sulphoxide, and this was converted into the allyl ether (47). Removal of the prop-1-enyl group in compound (47) by acidic hydrolysis gave the alcohol (48). Compound (48) is a suitable intermediate for a substitution of *N*-acetyl-D-glucosamine at the 4-position with subsequent liberation of a free 6-hydroxy-group; this would then be available for further substitution along the lines proposed for our general oligosaccharide synthesis [32] using benzyl ethers for ' persistent ' protection and allyl ethers for ' temporary ' protection.

EXPERIMENTAL

Solvents were evaporated off under reduced pressure. Optical rotations were measured at 22—24 °C with a Bendix automatic polarimeter. T.l.c. was carried out on microscope slides coated with silica gel G unless otherwise stated.

Allyl 2,3-Dideoxy-5,6-O-isopropylidene-2′-phenyl-β-D-allofuranosido[2,3-d]-*Δ²′-oxazoline* (9).[10]—The oxazoline (1) (20 g), allyl alcohol (100 ml), dry pyridine (20 ml), and toluene-*p*-sulphonic acid monohydrate (500 mg) were heated under reflux for 2.5 h; t.l.c. (ether, on Merck No. 5721 silica gel 60 plates) then showed complete conversion of the oxazoline (1) (R_F 0.5) into a major product (4) (R_F 0.6) and traces of other products. Sodium hydrogen carbonate (500 mg) was added, the solvents were evaporated off, and toluene (25 ml) was then added to and evaporated from the residue to remove the last traces of allyl alcohol. Dry pyridine (100 ml) was added to the residue and the solution was cooled to 0 °C. Methanesulphonyl chloride (10 ml) was added with stirring and the solution was kept at 20 °C for 2 h. The solution was cooled to 0 °C and water (5 ml) was added to decompose the excess of methanesulphonyl chloride. Triethylamine (40 ml) was added to the solution of the mesylate (6), which was then heated at 100 °C for 3 h. The solvents were evaporated off, and the residue was extracted with ether, and the extract was evaporated. Toluene (25 ml) was added to and evaporated from the residue, which was then taken up in ether and passed through a column of alumina (500 g). The ethereal eluate was evaporated to give the oxazoline (9) (13.5 g, 60%) [R_F 0.8 in ether–light petroleum (1 : 1)] as an oil which crystallised. Recrystallisation from ether–light petroleum gave the oxazoline (9), m.p. 59—61°, identical with the material described previously.[10]

Benzyl 2-Benzamido-3-O-benzyl-2-deoxy-5,6-O-isopropylidene-β-D-glucofuranoside (7).—A solution of 3-*O*-benzyl-1,2-dideoxy-5,6-*O*-isopropylidene-2′-phenyl-α-D-glucofuranoso[2,1-*d*]-*Δ²′*-oxazoline (2) [8,21] (20 g) and toluene-*p*-sulphonic acid monohydrate (500 mg) in benzyl alcohol (100 ml) and dry pyridine (20 ml) was kept at 100 °C for 12 h. T.l.c. (ether–light petroleum, 1 : 1) then showed conversion of the oxazoline (2) (R_F 0.5) into a major product (R_F 0.25) and traces of other products. Triethylamine (2 ml) and sodium hydrogen carbonate (1 g) were added and the solvents were evaporated off. The product was extracted with chloroform and the extract was passed through a column of alumina (400 g). Elution with chloroform gave a syrup (15 g, 59%), which crystallised from ether–light petroleum (1 : 1) to give the *furanoside* (7) as needles, m.p. 136—138°, $[\alpha]_D$ −85.1° (*c* 1 in $CHCl_3$), $\nu_{max.}$ 3 300 (NH) and 1 640 and 1 535 cm^{-1} (NHCOPh) (Found: C, 71.75; H, 6.55; N, 2.8. $C_{30}H_{33}NO_6$ requires C, 71.55; H, 6.6; N, 2.8%).

Methyl 2-Benzamido-2-deoxy-5,6-O-isopropylidene-β-D-glucofuranoside (3).[1,5]—A solution of the oxazoline (1) (1 g) and toluene-*p*-sulphonic acid monohydrate (50 mg) in dry methanol (20 ml) and dry pyridine (2 ml) was heated under reflux for 24 h. T.l.c. (ether) then showed complete conversion of the oxazoline (1) (R_F 0.5) into a major product (R_F 0.3). Triethylamine (1 ml) and sodium hydrogen carbonate (100 mg) were added and the solvents were evaporated off. The product was extracted with chloroform and the solution was passed through a column of silica gel (2 × 20 cm). The product was eluted with chloroform–acetone (9 : 1), free from a trace of more polar material, and was recrystallised from ethyl acetate–ether (1 : 10) to give compound (3), m.p. and mixed m.p. 136—138°, identical with the material prepared previously.[5]

Allyl 2,3-Dideoxy-2′-phenyl-β-D-allofuranosido[2,3-d]-*Δ²′-oxazoline* (12).—(*a*) The oxazoline (9) (12.4 g, 35.8 mmol) was added to a mixture of dry methanol (500 ml), N-hydrogen chloride in methanol (50 ml) and 2,2-dimethoxypropane (10 ml), and the solution was kept at 20 °C for 24 h. Triethylamine (10 ml) and sodium hydrogen carbonate (10 g) were added and the solvents were evaporated off. The product was extracted with chloroform and the extract was washed with water, dried (K_2CO_3), and evaporated. Ether was added to the residue and the solid product (8 g, 73%) was filtered off and recrystallised from ethyl acetate to give the *diol* (12), m.p. 176—178°, $[\alpha]_D$ −67.2° (*c* 0.87 in $CHCl_3$) (Found: C, 63.0; H, 6.45; N, 4.6. $C_{16}H_{19}NO_5$ requires C, 62.9; H, 6.3; N, 4.6%).

(*b*) A solution of the oxazoline (9) (17.5 g, 50.5 mmol) and toluene-*p*-sulphonic acid monohydrate (10.5 g, 55 mmol) in dry methanol (800 ml) and 2,2-dimethoxypropane (80 ml) was kept at 50 °C for 35 min. Triethylamine (10 ml) was added, the solvents were evaporated off, and the product (7 g, 45%), m.p. 176—178°, was obtained as in (*a*). The ether-soluble starting material (9) was further treated as above to give more (3 g) of the diol (12).

1,4-Di-O-benzyl-2,3-dideoxy-2′-phenyl-D-allitolo[2,3-d]-*Δ²′-oxazoline* (21).—2,3-Dideoxy-5,6-*O*-isopropylidene-2′-phenyl-D-allitolo[2,3-*d*]-*Δ²′*-oxazoline (19) [10] was converted into the benzyl derivative (20) with an excess of sodium

[31] P. A. Gent and R. Gigg, *J.C.S. Perkin I*, 1974, 1446.
[32] R. Gigg in A.C.S. Symposium Series No. 39, 1977, p. 253.

hydride and benzyl chloride in *NN*-dimethyl formamide at 20 °C. A solution of the isopropylidene derivative (20) (1 g, 2 mmol) and toluene-*p*-sulphonic acid monohydrate (650 mg, 3.4 mmol) in dry methanol (150 ml) and 2,2-dimethoxypropane (5 ml) was kept at 20 °C for 24 h; t.l.c. (toluene–acetone, 3 : 2) showed partial conversion of compound (20) (R_F 0.85) into the diol (21) (R_F 0.5). Triethylamine (5 ml) was added, the solvents were evaporated off, and the residue was extracted with chloroform. The extract was evaporated and the residue was chromatographed on alumina. Elution with ether removed the remaining starting material (20), and elution with methanol gave the crude product, which crystallised from aqueous methanol to give the *diol* (21) (450 mg, 50%), m.p. 106—108°, $[\alpha]_D$ −61.4° (*c* 1 in $CHCl_3$) (Found: C, 72.4; H, 6.5; N, 3.2. $C_{27}H_{29}NO_5$ requires C, 72.5; H, 6.5; N, 3.1%). This gave a crystalline *benzoate* (22), m.p. 125—127°, $[\alpha]_D$ +0.25° (*c* 1 in $CHCl_3$) (Found: C, 74.7; H, 5.85; N, 2.2. $C_{41}H_{37}NO_7$ requires C, 75.1; H, 5.7; N, 2.1%).

Allyl 5,6-Anhydro-2,3-dideoxy-2′-phenyl-β-L-talofurano-sido[2,3-d]-$\Delta^{2'}$-*oxazoline* (17).—Methanesulphonyl chloride (15 ml) was added to a solution of the diol (12) (8.26 g, 27 mmol) in dry pyridine (50 ml) at 0 °C; the solution was kept at 20 °C for 2 h and then poured into ice–water. The product was extracted with ether and the extract was washed with ice-cold N-hydrochloric acid (to remove the pyridine) and then with saturated sodium hydrogen carbonate solution, dried ($MgSO_4$), and evaporated. A solution of the crude mesylate (13) and sodium benzoate (12 g, 83 mmol) in dimethyl sulphoxide (130 ml) was heated at 100 °C for 2 h; t.l.c. (toluene–acetone, 5 : 1) then showed complete conversion of the mesylate (13) (R_F 0.35) into the monobenzoate (14) (R_F 0.5) with only a trace of the dibenzoate (16) (R_F 0.6). The solution was cooled and poured into water and the product (14) was extracted with ether. The extract was dried ($MgSO_4$) and evaporated. A solution of the crude product (14) in chloroform (100 ml) was cooled to −15 °C and a solution of sodium methoxide in methanol [from sodium hydride–oil (50%; 3 g) and dry methanol (35 ml)] was added. After 15 min, t.l.c. (as above) showed complete conversion of the benzoate (14) (R_F 0.5) into the alcohol (15) (R_F 0.3). The solution was then kept at 0 °C for 2.5 h; t.l.c. then showed a major product (R_F 0.5). Water (100 ml) was added to the solution and the chloroform layer was separated, dried ($MgSO_4$), and evaporated. The crude product was dissolved in ether–light petroleum (1 : 4) and passed through a column of neutral alumina (300 g) to remove the oil (from the sodium hydride–oil) and methyl benzoate. The major product (4.9 g, 63%) was eluted with ether–light petroleum (1 : 2) as an oil which crystallised from light petroleum to give the *oxiran* (17), m.p. 90—91°, $[\alpha]_D$ −64.0° (*c* 1 in $CHCl_3$) (Found: C, 66.6; H, 5.95; N, 4.9. $C_{16}H_{17}NO_4$ requires C, 66.9; H, 6.0; N, 4.9%).

Allyl 2,3-*Dideoxy-2′-phenyl-β-L-talofuranosido*[2,3-d]-$\Delta^{2'}$-*oxazoline* (18).—A solution of the oxiran (17) (1 g) in dioxan (40 ml), aqueous 40% tetrabutylammonium hydroxide (3.25 ml), and water (6.75 ml) was kept at 60 °C for 6 h. T.l.c. (toluene–acetone, 2 : 1) then showed conversion of the oxiran (17) (R_F 0.85) into a major product (R_F 0.45). The solution was diluted with water and the product was extracted with chloroform. The extract was washed with water, dried (K_2CO_3), and evaporated. The crude product was crystallised from ether–light petroleum to give the *diol* (18) (400 mg), m.p. 98—100°, $[\alpha]_D$ −50.8° (*c* 1 in $CHCl_3$) (Found: C, 63.2; H, 6.3; N, 4.7. $C_{16}H_{19}NO_5$ requires C, 62.9; H, 6.3; N, 4.6%).

Isomerisation of the Allyl Glycoside (9) *to the Prop-1-enyl Glycoside* (10).—(*a*) The allyl glycoside (9) (4.37 g) was added to a solution of potassium t-butoxide (Courtorch Chemicals Ltd.) (2 g) in dry dimethyl sulphoxide (50 ml) containing t-butyl alcohol (6 ml) and the solution was kept at 20 °C for 26 h. T.l.c. (toluene–acetone, 9 : 1) then showed complete conversion of compound (9) (R_F 0.5) into the prop-1-enyl glycoside (10) (R_F 0.6) together with smaller amounts of more polar by-products. The solution was diluted with water, the product was extracted with ether, and the extract was dried (K_2CO_3) and evaporated. The crude product was chromatographed on alumina; elution with ether–light petroleum (1 : 3) gave the pure product (10) (3.4 g, 77%), m.p. 58—60°, identical with the material prepared previously.[10]

(*b*) The allyl glycoside (9) (1 g), chloro(tristriphenylphosphine)rhodium(I) (150 mg), and 1,4-diazabicyclo[2.2.2]-octane (65 mg) in ethanol–water (9 : 1; 50 ml) were heated under reflux for 1 h. T.l.c. (as above) showed *ca.* 95% conversion of the allyl glycoside (9) (R_F 0.5) into the prop-1-enyl glycoside (10) (R_F 0.6). After refluxing for a further 1 h the small amount of starting material (9) was still present. The solution was evaporated to dryness, the residue was extracted with ether, and the extract washed with water, dried (K_2CO_3), and passed through an alumina column. Elution with ether gave the prop-1-enyl ether (10) (900 mg), still contaminated with a small amount of starting material (9). Hydrolysis of the glycoside (10) with mercury(II) chloride and reduction of the product with sodium borohydride as described previously [10] gave the oxazoline (19), identical with the material described before.[10]

Benzyl 2-*Benzamido*-3-O-*benzyl*-4,6-O-*benzylidene*-2-*deoxy*-β-D-*glucopyranoside* (30).—3-*O*-Benzyl-1,2-dideoxy-5,6-*O*-isopropylidene-2′-phenyl-α-D-glucofuranoso[2,1-*d*]-$\Delta^{2'}$-oxazoline (2) [8,21] (R_F 0.6 in ether–light petroleum, 1 : 1) was prepared from the alcohol (1) (30 g) (R_F 0.1, system as above) with an excess of benzyl chloride and sodium hydride in *NN*-dimethylformamide at 20 °C for 3 h, and isolated in the usual way. The crude product, containing the excess of benzyl chloride, was added to a solution of toluene-*p*-sulphonic acid monohydrate (18.4 g) in benzyl alcohol (1 000 ml) and benzaldehyde (45 ml) and the solution was kept at 20 °C. The crystalline product, which started to separate after 1 h, was filtered off after 36 h and washed with acetone (250 ml). It was suspended in acetone (1 000 ml) and the mixture was stirred for 15 min to remove the last traces of benzyl alcohol, filtered again, washed with acetone (250 ml), and dried to give the product (30) (50 g, 90%). A portion recrystallised from *NN*-dimethyl formamide (30 ml per g at 100 °C) gave the *benzylidene derivative* (30), m.p. 299—301°, $[\alpha]_D$ −40.7° (*c* 0.25 in Me_2NCHO) (Found: C, 74.0; H, 6.1; N, 2.6. $C_{34}H_{33}NO_6$ requires C, 74.0; H, 6.0; N, 2.5%).

Benzyl 2-*Benzamido*-3-O-*benzyl*-2-*deoxy*-β-D-*glucopyranoside* (26).[21]—(*a*) The benzylidene derivative (30) (500 mg) was added to a refluxing mixture of acetic acid (8.5 ml) and water (1.5 ml). After 9 min a clear solution had resulted and after 10 min the solution was cooled in ice. Water (30 ml) was added and the precipitate was filtered off, washed with water, and dried to give the benzyl glycoside (26) (300 mg, 71%) [R_F 0.75 in chloroform–methanol (4 : 1)]. The mother liquors were evaporated to give by-products (110 mg), R_F 0.85 and 0.65.

(*b*) The benzylidene derivative (30) (10 g) was added to a mixture of dimethyl sulphoxide (360 ml) and N-hydrochloric acid (40 ml) at 95 °C. The mixture was stirred at 95 °C for 20 min (a clear solution resulted), and after 35 min the solution was cooled in ice and poured into water (1.5 l). The product was filtered off, washed with water, and dried (yield 7.5 g, 90%). A portion recrystallised from acetone gave the benzyl glycoside (26), m.p. 228—230°, $[\alpha]_D$ +6.3° (*c* 0.6 in methanol) (Found: C, 69.5; H, 6.4; N, 3.1. Calc. for $C_{27}H_{29}NO_6$: C, 70.0; H, 6.3; N, 3.0%) {lit.,[21] m.p. 219—221°, $[\alpha]_D^{23}$ +7° (*c* 0.7 in methanol)}.

Benzyl 4,6-*Di*-O-*acetyl*-2-*benzamido*-3-O-*benzyl*-2-*deoxy*-β-D-*glucopyranoside* (27).[21]—The diol (26) was acetylated with acetic anhydride–pyridine and the product crystallised from acetone (60 ml per g) or methanol (200 ml per g) to give the acetate (27), m.p. 224—226°, $[\alpha]_D$ −10° (*c* 1 in $CHCl_3$) (Found: C, 68.1; H, 6.0; N, 2.6. Calc. for $C_{31}H_{33}NO_8$: C, 68.0; H, 6.1; N, 2.6%) {lit.,[21] m.p. 212—214°, $[\alpha]_D$ −9° (*c* 0.8 in $CHCl_3$)}.

Benzyl 2-*Acetamido*-4,6-*di*-O-*acetyl*-3-O-*benzyl*-2-*deoxy*-β-D-*glucopyranoside* (28).—A mixture of the benzamido-derivative (27) (10 g), anhydrous sodium acetate (1 g), acetic anhydride (200 ml), and acetic acid (50 ml) was heated under reflux for 24 h. Water (38 ml) was added dropwise to the refluxing solution and refluxing was continued for 1 h. T.l.c. (chloroform–acetone, 10 : 1) then showed complete conversion of the benzamido-derivative (27) (R_F 0.75) into the acetamido-derivative (28) (R_F 0.55) with only traces of faster running by-products. The solution was evaporated to dryness and water (50 ml) was added to the residue. An excess of sodium hydrogen carbonate was added to neutralise the residual acetic and benzoic acids and the product (8.3 g, 93%) was filtered off, washed with water, and dried. Recrystallisation from methanol (75 ml) gave the *acetamido-derivative* (28), m.p. 185—187°, $[\alpha]_D$ −28.4° (*c* 1 in $CHCl_3$) (Found: C, 64.6; H, 6.2; N, 2.9. $C_{26}H_{31}NO_8$ requires C, 64.3; H, 6.4; N, 2.9%).

Benzyl 2-*Acetamido*-3-O-*benzyl*-2-*deoxy*-β-D-*glucopyranoside* (29).[25,27]—A mixture of the acetate (28) (5.4 g) and sodium hydroxide (1.5 g) in methanol (100 ml) was stirred at 20 °C for 45 min. Water (750 ml) was added and the solution was kept at 20 °C for 18 h. The crystalline diol (29) (3.57 g, 80%) was filtered off, washed with water, and dried; m.p. 187—189°, $[\alpha]_D$ −18.8° (*c* 0.86 in ethanol) (Found: C, 65.9, H, 6.7; N, 3.5. Calc. for $C_{22}H_{27}NO_6$: C, 65.8; H, 6.8; N, 3.5%) {lit.,[25] m.p. 169—170°, $[\alpha]_{578}^{15}$ −20° (*c* 0.5 in ethanol); lit.,[27] m.p. 183—184°, $[\alpha]_D^{25}$ −19° (*c* 0.84 in methanol)}.

Benzyl 4-O-*Allyl*-2-*benzamido*-3-O-*benzyl*-2-*deoxy*-6-O-*trityl*-β-D-*glucopyranoside* (33).—(*a*) A solution of benzyl 2-benzamido-3-*O*-benzyl-2-deoxy-β-D-glucopyranoside (26) (3.6 g, 7.8 mmol) and triphenylmethyl chloride (3.6 g, 12.9 mmol) in dry pyridine (50 ml) was kept at 80 °C for 4 h. Methanol (5 ml) and sodium hydrogen carbonate (5 g) were added and the mixture was evaporated to dryness. Toluene (20 ml) was added to and evaporated from the residue, to remove the last traces of pyridine, and the product was extracted with chloroform. The extract was evaporated and ether (100 ml) and light petroleum (b.p. 40—60°; 100 ml) were added to the residue. The mixture was stirred at 20 °C for 15 min and filtered to give the trityl ether (32) (4.2 g, 76%) [t.l.c. (chloroform–acetone, 24 : 1) R_F 0.55]. The trityl ether (32) (3.6 g), barium oxide (10 g), barium hydroxide octahydrate (3.5 g), allyl bromide (3 ml), and *NN*-dimethylformamide (40 ml) were stirred at 20 °C for 40 h; t.l.c. (as above) then showed complete conversion into the allyl ether (33) (R_F 0.8). Water (500 ml) was added, the mixture was filtered through Celite, and the crystalline product was washed with water and sucked dry. Chloroform was then passed through the filter to extract the product and the chloroform filtrate was dried ($MgSO_4$) and evaporated to give the crude trityl derivative (33) (3.8 g, 100%). Recrystallisation from methanol gave the pure *allyl ether* (33) as needles, m.p. 214—216°, $[\alpha]_D$ +23.1° (*c* 1 in $CHCl_3$) (Found: C, 78.9; H, 6.3; N, 1.9. $C_{49}H_{47}NO_6$ requires C, 78.9; H, 6.35; N, 1.9%).

(*b*) A mixture of the crude trityl ether (32) [2 g; prepared as described in (*a*)], sodium hydride (250 mg), and allyl bromide (0.5 ml) in dry tetrahydrofuran was heated under reflux for 2 h. T.l.c. [as in (*a*)] then showed complete conversion of the alcohol (32) (R_F 0.55) into the allyl ether (33) (R_F 0.8). Continued refluxing led to the slow formation of a further product (R_F 0.85), presumably the *N*-allyl benzamido-derivative. Methanol was added, to react with excess of sodium hydride, and then solid carbon dioxide was added and the solution was evaporated to dryness. The product was extracted from the residue with chloroform and purified as described in (*a*).

Benzyl 2-*Acetamido*-4-O-*acetyl*-3,6-*di*-O-*benzyl*-2-*deoxy*-β-D-*glucopyranoside* (39).—Benzyl 4-*O*-allyl-2-benzamido-3-*O*-benzyl-2-deoxy-6-*O*-trityl-β-D-glucopyranoside (33) (3.8 g) in N-hydrochloric acid–acetone (1 : 9; 100 ml) was heated under reflux for 70 min. T.l.c. (chloroform–acetone, 24 : 1) then showed complete conversion of compound (33) (R_F 0.8) into the alcohol (34) (R_F 0.25). Sodium hydrogen carbonate (5 g) was added, the solution was evaporated to dryness, and the product was extracted from the residue with chloroform. The extract was evaporated, the residue was triturated with ether (to dissolve the triphenylmethanol), and the crude alcohol (34) (2.3 g, 89%) was filtered off. The crude alcohol (34), barium oxide (10 g), barium hydroxide octahydrate (3.5 g), benzyl bromide (6 g, 4.2 ml), and *NN*-dimethylformamide (40 ml) were stirred at 20 °C for 8 h. T.l.c. (as above) then showed complete conversion of the alcohol (34) (R_F 0.25) into the ether (35) (R_F 0.6). Water (300 ml) was added, the mixture was filtered through Celite, and the solid was washed with water and sucked dry. The solid was then washed on the filter funnel with light petroleum (b.p. 40—60 °C) to remove benzyl bromide. Chloroform was then passed through the filter to dissolve the product, and the filtrate was dried ($MgSO_4$) and evaporated to give the crude ether (35) (2.2 g, 81%). The crude allyl ether (35) and potassium t-butoxide (1 g) in dry dimethyl sulphoxide (40 ml) were kept at 50 °C for 3 h. T.l.c. (as above) then showed complete conversion of the allyl ether (35) (R_F 0.6) into the prop-1-enyl ether (36) (R_F 0.65). The solution was poured into water (250 ml), the mixture was filtered through Celite, and the solid was washed with water and sucked dry. The product was extracted from the funnel with chloroform and the filtrate was dried ($MgSO_4$) and evaporated. The crude prop-1-enyl ether (36) was taken up in acetone (45 ml) and N-hydrochloric acid (5 ml) and the solution was heated under reflux for 15 min. T.l.c. (as above) then showed complete conversion of the prop-1-enyl ether (36) (R_F 0.65) into the alcohol (37) (R_F 0.35). An excess of sodium hydrogen carbonate was added and the solvents were evaporated off. The product was extracted from the residue with chloroform and the extract was dried ($MgSO_4$) and evaporated to give the

crude alcohol (37) (1.8 g, 89%). A solution of the crude alcohol (37) and anhydrous sodium acetate (300 mg) in acetic anhydride (25 ml) and acetic acid (6 ml) was heated under reflux for 24 h. Water (4.5 ml) was added to the refluxing solution and the refluxing was continued for 1 h. The solvents were then evaporated off, the residue was taken up in chloroform, and the solution was washed with sodium hydrogen carbonate solution, dried ($MgSO_4$), and evaporated to give the crude acetamido-derivative (39) (R_F 0.3, system as above) (1.5 g, 87%). Recrystallisation from ethyl acetate–light petroleum (b.p. 60—80 °C) gave the pure *glucopyranoside* (39), m.p. 181—183°, $[\alpha]_D$ −16.2° (*c* 1 in $CHCl_3$) (Found: C, 70.1; H, 6.5; N, 2.7. $C_{31}H_{35}NO_7$ requires C, 69.8; H, 6.6; N, 2.6%).

Benzyl 2-Acetamido-4-O-allyl-3-O-benzyl-2-deoxy-β-D-glucopyranoside (43).[27]—(*a*) Benzyl 2-acetamido-3-*O*-benzyl-2-deoxy-β-D-glucopyranoside (29) (3.2 g) and triphenylmethyl chloride (5 g) in dry pyridine (30 ml) were kept at 70 °C for 5 h and then dry methanol (5 ml) was added. After 15 min, the solution was poured into water and the product was extracted with ether. The extract was washed with ice-cold N-hydrochloric acid and then with saturated potassium chloride solution, dried (K_2CO_3), and evaporated. The crude trityl ether (41) was taken up in dry *NN*-dimethylformamide (40 ml); barium oxide (10 g), barium hydroxide octahydrate (3.6 g), and allyl bromide (4 g) were added and the mixture was stirred at 20 °C for 12 h, and t.l.c. (chloroform–acetone, 10 : 1) then showed *ca.* 75% conversion of the alcohol (41) (R_F 0.5) into the allyl ether (42) (R_F 0.75). The same quantities of the reagents were added to the mixture and stirring was continued for a further 12 h; t.l.c. then showed complete conversion into the allyl ether (42). The mixture was diluted with water and extracted with ether; the extract was washed with water, dried (K_2CO_3), and evaporated. The crude product was triturated with ether–light petroleum to remove the triphenylmethyl methyl ether, and the crude allyl ether (42) was filtered off. A solution of the crude product in N-hydrochloric acid (10 ml) and acetone (90 ml) was heated under reflux for 1 h; t.l.c. (as above) then showed complete conversion of the trityl derivative (42) (R_F 0.75) into the alcohol (43) (R_F 0.2). An excess of sodium hydrogen carbonate was added, the solvents were evaporated off, and the product was extracted from the residue with chloroform. The extract was dried and evaporated and ether (75 ml) was added to the residue. The crude alcohol (43) (2.3 g, 66%) was filtered off and washed with ether. Recrystallisation from acetone gave the pure alcohol (43), m.p. 210—212°, $[\alpha]_D$ −20° (*c* 0.4 in ethanol) (Found: C, 68.05; H, 7.1; N, 3.2. Calc. for $C_{25}H_{31}NO_6$: C, 68.0; H, 7.1; N, 3.2%) {lit.,[27] m.p. 209°, $[\alpha]_D^{22}$ −17° (*c* 2.2 in $CHCl_3$)}.

(*b*) A solution of the crude alcohol (34) (220 mg) (described above) and sodium acetate (200 mg) in acetic anhydride (20 ml) and acetic acid (5 ml) was heated under reflux for 23 h. Water (3.6 ml) was added dropwise to the refluxing solution and refluxing was continued for 1 h. The solvent was evaporated off and saturated sodium hydrogen carbonate solution was added to the residue. The product was extracted with chloroform and treated with sodium hydroxide (100 mg) in methanol (15 ml) at 20 °C for 30 min; the alcohol (43) then began to crystallise from the solution. Water (100 ml) was added and the product (150 mg, 77%) was filtered off, washed with water, and dried. Recrystallisation from acetone gave the pure alcohol (43), identical with the material described in (*a*).

Benzyl 2-Acetamido-3,6-di-O-benzyl-2-deoxy-β-D-glucopyranoside (40).—(*a*) The acetate (39) (600 mg) was treated with sodium hydroxide (1 g) in methanol (100 ml) at 20 °C for 1 h. Solid carbon dioxide was added and the solution was evaporated to dryness. The product was extracted from the residue with chloroform and recrystallised from ethyl acetate–light petroleum (b.p. 60—80 °C) to give the pure alcohol (40), m.p. 182—184°, $[\alpha]_D$ −35° (*c* 1 in $CHCl_3$) (Found: C, 70.6; H, 6.8; N, 2.9. Calc. for $C_{29}H_{33}NO_6$: C, 70.85; H, 6.8; N, 2.85%) {lit.,[27] m.p. 181°, $[\alpha]_D^{22}$ −37° (*c* 1.7 in $CHCl_3$)}.

(*b*) The alcohol (43) (1 g) was added to a mixture of *NN*-dimethylformamide (30 ml), barium oxide (10 g), barium hydroxide octahydrate (3 g), and benzyl bromide (2.5 g) and the mixture was stirred at 20 °C for 21 h. T.l.c. (chloroform–acetone, 10 : 1) then showed complete conversion of compound (43) (R_F 0.25) into the benzyl ether (44) (R_F 0.6). Water (200 ml) was added and the mixture was filtered through Celite. The residue was washed with water and light petroleum and sucked dry. The product in the funnel was extracted with chloroform and the extract was dried (K_2CO_3) and evaporated. The crude allyl ether (44) was treated with potassium t-butoxide (2 g) in dry dimethyl sulphoxide (25 ml) at 50 °C for 3 h; t.l.c. (as above, on Merck No. 5721 silica gel plates) then showed complete conversion of the allyl ether (44) (R_F 0.6) into the prop-1-enyl ether (45) (R_F 0.65). The solution was diluted with water and the product was filtered off through Celite and washed with water. The prop-1-enyl ether (45) was extracted from the funnel with chloroform and the extract was dried (K_2CO_3) and evaporated. The crude product was taken up in acetone (45 ml) and N-hydrochloric acid (5 ml) and the solution was heated under reflux for 15 min. An excess of sodium hydrogen carbonate was added and the solvents were evaporated off. The product was extracted with chloroform and recrystallised from ethyl acetate–light petroleum to give the alcohol (40), identical with the material described in (*a*).

Benzyl 2-Acetamido-3-O-benzyl-4,6-O-benzylidene-2-deoxy-β-D-glucopyranoside (31).[25,27]—(*a*) Benzyl 2-benzamido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (30) (1 g) and sodium acetate (50 mg) in acetic anhydride (20 ml) and acetic acid (5 ml) were heated under reflux. After 6.5 h compound (30) had completely dissolved and the solution was heated under reflux for a further 20 h and then cooled to 20 °C. Water (3.5 ml) was added, and the solution was kept at 20 °C for 1 h and then heated under reflux for 1 h. The solution was cooled and poured into ice–water (250 ml) and the product (500 mg) was filtered off, washed with water, and dried. T.l.c. (chloroform–acetone, 10 : 1) showed a major product (R_F 0.75) with traces of other products. Recrystallisation from *NN*-dimethylformamide gave the pure benzylidene derivative (31), m.p. 284—286°, $[\alpha]_D$ −65° (*c* 0.2 in Me_2NCHO) (Found: C, 71.0; H, 6.4; N, 2.9. Calc. for $C_{29}H_{31}NO_6$: C, 71.15; H, 6.4; N, 2.9%) {lit.,[25] m.p. 266—267°, $[\alpha]_{578}$ −75° (*c* 0.2 in Me_2NCHO); lit.,[27] m.p. 279—281°, $[\alpha]_D$ −72° (*c* 0.9 in pyridine)}.

(*b*) Benzyl 2-acetamido-3-*O*-benzyl-2-deoxy-β-D-glucopyranoside (29) (150 mg) and anhydrous zinc chloride (1 g) were stirred with benzaldehyde (5 ml) at 25 °C for 24 h. The resulting clear solution was diluted with ice–water (100 ml) and light petroleum (50 ml) and the product (155 mg) was filtered off and washed with water and light petroleum. Recrystallisation from *NN*-dimethylformamide (5 ml) gave the benzylidene derivative (31) (100 mg),

m.p. and mixed m.p. [with the material described in (*a*)] 284—286°.

Benzyl 2-*Acetamido*-6-O-*allyl*-3-O-*benzyl*-2-*deoxy*-β-D-*glucopyranoside* (48).—The alcohol (43) (580 mg) was treated with potassium t-butoxide (2 g) in dimethyl sulphoxide (20 ml) at 50 °C for 3 h. T.l.c. [chloroform–acetone (2 : 1), on Merck No. 5721 silica gel plates] then showed complete conversion of the allyl ether (43) (R_F 0.6) into the prop-1-enyl ether (46) (R_F 0.65). Water (200 ml) was added and the mixture was stirred at 20 °C for 15 min; then the solid product (520 mg) was filtered off, washed with water, and dried. The product (46) was added to a mixture of barium oxide (3.5 g), barium hydroxide octahydrate (1 g), *NN*-dimethylformamide (10 ml), and allyl bromide (1 g) and the mixture was stirred at 20 °C for 12 h. T.l.c. (as above) then showed complete conversion into the allyl ether (47) (R_F 0.85). Water (200 ml) was added and the mixture was filtered through Celite to collect the product. The solid was washed with water and sucked dry and then extracted from the funnel with chloroform. The chloroform extract was dried (K_2CO_3) and evaporated, and the crude compound (47) was added to acetone (45 ml) and N-hydrochloric acid (5 ml). The solution was heated under reflux for 15 min; t.l.c. (as above) then showed complete conversion of the prop-1-enyl ether (47) into the alcohol (48) (R_F 0.7). An excess of sodium hydrogen carbonate was added to the solution and the solvents were evaporated off. The product was extracted with chloroform and the extract was dried (K_2CO_3) and evaporated; the product (350 mg) was recrystallised from ethyl acetate–light petroleum (b.p. 60—80 °C) to give the *allyl ether* (48), m.p. 163—165°, $[\alpha]_D$ −39.4° (*c* 1 in $CHCl_3$) (Found: C, 68.0; H, 7.1; N, 3.1. $C_{25}H_{31}NO_6$ requires C, 68.0; H, 7.1; N, 3.2%).

[7/505 *Received*, 22*nd March*, 1977]