The Allyl Ether as a Protecting Group in Carbohydrate Chemistry. Part IV.[1] The 2-Methylallyl Ether Group

By **Patricia A. Gent, Roy Gigg,*** and **Roy Conant,** Laboratory of Lipid and General Chemistry, National Institute for Medical Research, Mill Hill, London NW7 1AA

The *O*-2-methylallyl group, which is isomerised more slowly than the allyl group, is most suitable for use (in protection of OH) in the presence of the *O*-but-2-enyl group, since the latter can be eliminated without concomitant rearrangement of the 2-methylallyl group. 2-Methylallyl 2-benzamido-4,6-*O*-benzylidene-2-deoxy-β-D-gluco- and -galacto-pyranosides were prepared from the corresponding 3-*O*-but-2-enyl derivatives and these benzamido-derivatives were converted into the acetamido-derivatives by alkaline hydrolysis followed by acetylation. A convenient method for the conversion of an *N*-benzoyl amino-sugar into the corresponding *N*-acetyl amino-sugar by refluxing in acetic anhydride–glacial acetic acid is described. The benzylation of *N*-acetyl amino-sugars with benzyl chloride and sodium hydride is less satisfactory than the benzylation of the corresponding *N*-benzoyl amino-sugars, owing to extensive formation of *N*-benzylacetamido-derivatives.

We have previously described the use of the but-2-enyl system for the protection of hydroxy-groups.[1] We showed that it was readily removed by potassium t-butoxide in dimethyl sulphoxide under much milder conditions than those required for the conversion of an allyl ether into a prop-1-enyl ether, and that only a small amount of isomerisation of the allyl group occurred during the removal of the but-2-enyl group when both groups were present in the same molecule.

We have shown previously that both the 1-methylallyl [1] and 2-methylallyl [2] groups are rearranged at considerably lower rates than the allyl group by potassium t-butoxide in dimethyl sulphoxide, and have taken advantage of the lower rate of isomerisation of the 2-methylallyl group for the present work in which the but-2-enyl system has been used for the temporary protection of a hydroxy-group in the presence of a 2-methylallyl group. Methylallyl alcohols and halides are subject to allylic rearrangements during reactions but since the 2-methylallyl cation is symmetrical the problem of geometrical isomerism in the products does not arise as it does in the case of the 1- and 3-methylallyl derivatives.[1]

Allyl ethers of carbohydrates are reactive sites which can be converted into epoxides and then condensed with amines and alcohols. This reactivity has been exploited recently [3] in the preparation of enzyme inhibitors. We have considered allyl groups as potential sites for linking sugars to polymeric supports to provide suitable substrates for affinity chromatography.

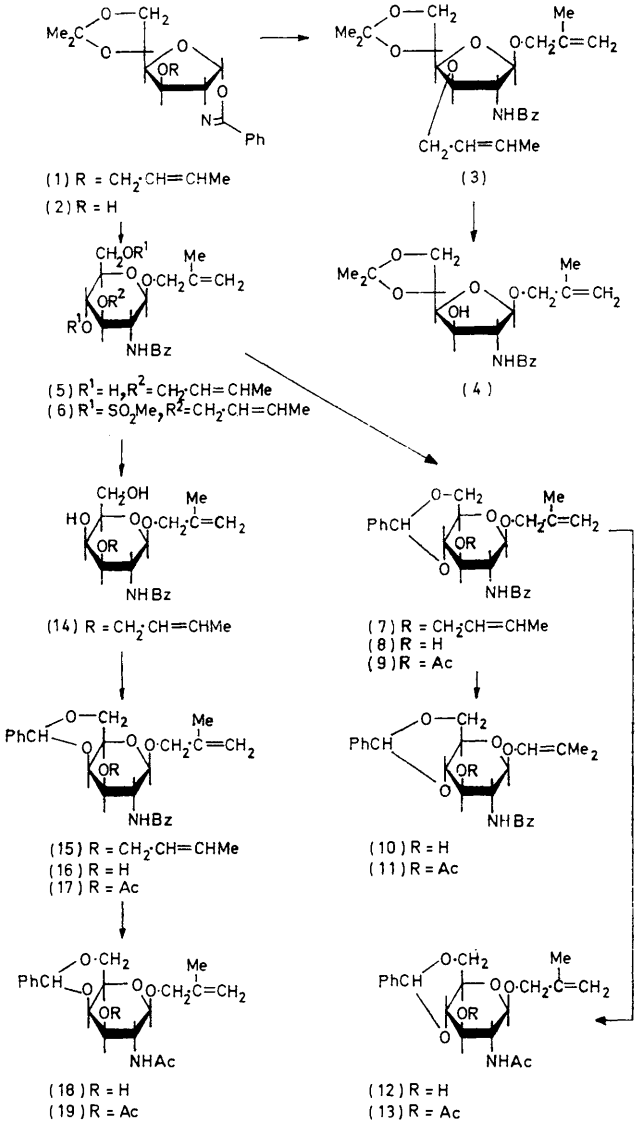
Our initial experiments in this direction required the preparation of a derivative of D-galactosamine, containing an allyl glycoside linkage (for attachment to a polymer), which was suitably protected in other parts of the molecule for the attachment of a further sugar

[1] Part III, P. A. Gent, R. Gigg, and R. Conant, *J.C.S. Perkin I*, 1972, 1535.

[2] R. Gigg and C. D. Warren, *J. Chem. Soc.* (*C*), 1968, 1903.

[3] E. M. Bessell and J. H. Westwood, *Carbohydrate Res.*, 1972, **25**, 11.

residue. Since we envisaged using the but-2-enyl group for temporary protection in the same molecule we initially investigated the preparation and stability of 2-methylallyl glycosides of glucosamine derivatives containing a but-2-enyl group and the effect of the conditions for the removal of the latter group on the 2-methylallyl group.



SCHEME 1

The phenyloxazoline (1) [1] was converted into the 2-methylallyl glucofuranoside (3) by the action of toluene-*p*-sulphonic acid in 2-methylallyl alcohol under the general conditions described previously [4] for the conversion of the phenyloxazoline (2) into furanoside derivatives. Treatment of the 2-methylallyl glycoside (3) with potassium t-butoxide in dimethyl sulphoxide at room temperature removed the but-2-enyl group to give the alcohol (4), identical with the material prepared by the action of 2-methylallyl alcohol containing toluene-*p*-sulphonic acid on the phenyloxazoline (2).

Previously [5] we have described the preparation of D-galactosamine derivatives from derivatives of D-glucosamine obtained from the phenyloxazoline (2). We now show that this procedure is also applicable *via* the 2-methylallyl glucopyranoside (5). The phenyloxazoline (1) was converted into the 2-methylallyl glucopyranoside (5) by the action of toluene-*p*-sulphonic acid in 2-methylallyl alcohol, and compound (5) was then converted into the 4,6-*O*-benzylidene derivative (7) by reaction with benzaldehyde dimethyl acetal.[6] The but-2-enyl group was removed to give 2-methylallyl 2-benzamido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (8), and isomerisation of this compound with potassium t-butoxide in dimethyl sulphoxide gave the 2-methylprop-1-enyl glycoside (10). In this case the course of the isomerisation could not be followed by t.l.c. on silica gel since the product had a mobility similar to that of the starting material. However the isomers were readily resolved by t.l.c. on silica gel impregnated with silver nitrate. N.m.r. spectroscopy has also been used to follow the course of isomerisations of this type.[7] The benzamido-group of compound (8) was readily hydrolysed with sodium hydroxide in aqueous 2-methoxyethanol [8] to give the corresponding amine, which was converted into the *N*-acetyl derivative (12) and the *NO*-diacetyl derivative (13).

For the preparation of the D-galactosamine derivatives, the diol (5) was converted into the bismethanesulphonate (6), which was treated with sodium benzoate in dimethylformamide; [5] the product was saponified to give 2-methylallyl 2-benzamido-3-*O*-(but-2-enyl)-2-deoxy-β-D-galactopyranoside (14).

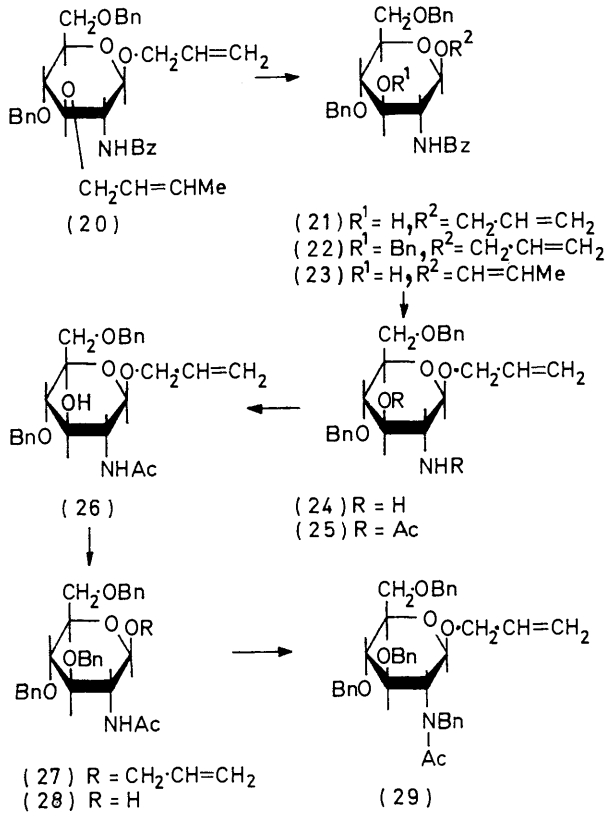
Similar treatments to those described for the D-glucosamine derivative gave the D-galactosamine derivatives (15), (16), and (18). Acidic hydrolysis of compound (18) gave D-galactosamine, which was identified by use of an amino-acid analyser.

We have reported previously [1] that the benzamido-group of allyl 2-benzamido-3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranoside (22) is very resistant to hydrolysis under basic conditions, but that the benzamido-group of compound (23) was readily hydrolysed with sodium hydroxide in aqueous 2-methoxyethanol.

The following route was therefore followed to synthesize allyl 2-acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranoside (27). The but-2-enyl ether (20) [1] was converted into the alcohol (21), which was hydrolysed with base to give the amino-alcohol (24) and this gave the acetate (26). Benzylation of the alcohol (26) under the conditions described previously [1] for the benzylation of the corresponding benzamido-derivative gave a low

[4] R. Gigg and C. D. Warren, *J. Chem. Soc.*, 1965, 1351; S. Konstas, I. Photaki, and L. Zervas, *Chem. Ber.*, 1959, **92**, 1288.
[5] P. A. Gent, R. Gigg, and R. Conant, *J.C.S. Perkin I*, 1972, 277.
[6] M. E. Evans, *Carbohydrate Res.*, 1972, **21**, 473.
[7] J.-C. Jacquinet, Thesis, Université de Paris-Sud, Orsay, 1972, p. 21.
[8] Y. Ali, A. C. Richardson, C. F. Gibbs, and L. Hough, *Carbohydrate Res.*, 1968, **7**, 255; M. W. Horner, L. Hough, and A. C. Richardson, *J. Chem. Soc.* (*C*), 1970, 1336.

yield of the required tri-*O*-benzyl-acetamido-derivative (27), which was characterised as the previously known free sugar (28). The major product isolated in this reaction was the *N*-benzylacetamido-derivative (29).



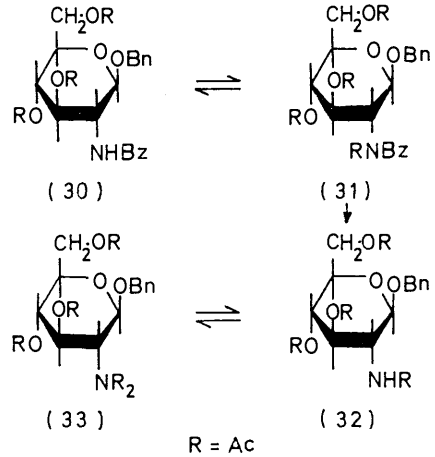
SCHEME 2

Thus the benzylation of *N*-acetyl derivatives of amino-sugars by this method is less suitable than the benzylation of *N*-benzoyl derivatives.

We have utilized the phenyloxazoline (2) in the synthesis of several compounds of biological interest, *e.g.* phytosphingosine, muramic acid, and galactosamine derivatives; the intermediate products are obtained as the *N*-benzoyl derivatives which are less interesting biologically than the *N*-acetyl derivatives. We and others [8,9] have observed difficulties in the basic hydrolysis of the benzamido-group as a preliminary to replacing it by the acetamido-group, particularly in fully substituted derivatives of *N*-benzoyl amino-sugars and we have therefore looked for an alternative method for the conversion of benzamido-derivatives into the corresponding acetamido-derivatives.

The preparation and hydrolysis of *NN*-diacyl derivatives of amino-sugars has been investigated in some detail by Inch and Fletcher,[10] who found that sodium methoxide preferentially removed the benzoyl group from *N*-acetylbenzamido-derivatives of amino-sugars to give products which were mixtures of acetamido- and benzamido-derivatives in ratios of *ca.* 5 : 1. In an earlier paper, Kornhauser *et al.*[11] showed that refluxing glacial acetic acid readily converted an *NN*-diacetyl compound into the corresponding acetamido-derivative and that with a mixture of acetic anhydride and acetic acid the amount of conversion of the *NN*-diacetyl compound into the acetamido-derivative was proportional to the amount of acetic acid in the acetic anhydride.

We therefore investigated the following procedure for the conversion of a benzamido-derivative into the acetamido-derivative. Benzyl 3,4,6-tri-*O*-acetyl-2-benzamido-2-deoxy-β-D-glucopyranoside (30) was readily converted into a less polar product (t.l.c.) on refluxing with acetic anhydride during 24 h. Addition of water to convert the acetic anhydride into acetic acid and continued refluxing for 1 h gave predominantly a product which was more polar than the benzamido-derivative and was assumed to be the acetamido-derivative (32). The reaction was repeated using 4 : 1 acetic anhydride–acetic acid in order that the *NN*-diacyl compound (31) would be degraded in the reaction mixture and that eventually the benzamido-derivative (30) would be converted entirely into an equilibrium mixture of the acetamido-derivative (32) and the *NN*-diacetyl derivative (33). After the benzamido-derivative (30) had been refluxed in this mixture for 22 h it was converted entirely into a mixture of the acetamido-derivative (32) (*ca.* 80%) and an *NN*-diacyl derivative. Water was then added to the reaction mixture, to convert all of the acetic anhydride into acetic acid, and



SCHEME 3

refluxing was continued for 1 h, after which the product was entirely in the form of the acetamido-derivative (32), which was isolated in high yield.

This method therefore appears to be satisfactory for

[9] R. D. Guthrie and G. P. B. Mutter, *J. Chem. Soc.*, 1964, 1614.

[10] T. Inch and H. G. Fletcher, *J. Org. Chem.*, 1966, **31**, 1815.

[11] A. Kornhauser, D. Keglevic, and O. Hadzija, *Croat. Chem. Acta*, 1962, **34**, 167.

the ready, quantitative replacement of a benzamido-group by an acetamido-group, and should make the intermediate (2) even more valuable for investigations in the amino-sugar series. The scope of the reaction will be investigated in more detail with other benzamido-derivatives of amino-sugars and with other naturally occurring amides, *e.g.* sphingolipids and peptides, and also with mixtures of other acids and their anhydrides.

EXPERIMENTAL

Solvents were evaporated off under reduced pressure. Optical rotations were measured at 22—24° with a Bendix Automatic Polarimeter. T.l.c. was carried out on microscope slides coated with silica gel G. The light petroleum used had b.p. 40—60° unless otherwise stated.

2-Methylprop-2-enyl 2-Benzamido-3-O-(but-2-enyl)-2-deoxy-5,6-O-isopropylidene-β-D-glucofuranoside (3).—3-*O*-But-2-enyl-1,2-dideoxy-5,6-*O*-isopropylidene-2′-phenyl-β-D-glucofuranoso[2,1-*d*]-$\Delta^{2'}$-oxazoline (1) [1] (1 g) in redistilled 2-methylallyl alcohol (45 ml) containing toluene-*p*-sulphonic acid (10 mg) was kept at 20° for 24 h; t.l.c. (ether–light petroleum, 1 : 1) then indicated complete conversion of the starting material (R_F 0·7) into a major product (R_F 0·4). An excess of sodium hydrogen carbonate was added and the alcohol was evaporated off. The residue was extracted with ether and the dried ethereal solution was passed through a column of alumina. Further elution with ether gave *compound* (3) as a syrup which solidified, $[\alpha]_D$ −61·7° (*c* 0·4 in $CHCl_3$) (Found: C, 66·7; H, 7·7; N, 3·2. $C_{24}H_{33}NO_6$ requires C, 66·8; H, 7·7; N, 3·2%).

2-Methylprop-2-enyl 2-Benzamido-2-deoxy-5,6-O-isopropylidene-β-D-glucofuranoside (4).—(*a*) A solution of compound (3) (0·5 g) and potassium t-butoxide (1 g) in dry dimethyl sulphoxide (10 ml) was stirred at 20° for 33 h; t.l.c. (toluene–acetone, 2 : 1) then indicated complete conversion of the starting material (R_F 0·8) into a major product (R_F 0·55). The solution was diluted with water and extracted with chloroform and the extract washed with water and dried (Na_2SO_4). The product was chromatographed on alumina; elution with ether–methanol (48 : 1) gave the *alcohol* (4) (330 mg), m.p. 100—104° [from ethyl acetate–light petroleum (b.p. 60—80°)], $[\alpha]_D$ −27·8° (*c* 1 in $CHCl_3$) (Found: C, 63·7; H, 7·1; N, 3·6. $C_{20}H_{27}NO_6$ requires C, 63·6; H, 7·2; N, 3·7%).

(*b*) A solution of the oxazoline (2) [4] (2 g) and toluene-*p*-sulphonic acid (15 mg) in redistilled 2-methylallyl alcohol (45 ml) was kept at 20° for 30 h; t.l.c. (toluene–acetone, 2 : 1) then indicated complete conversion of the starting material (R_F 0·6) into a major product (R_F 0·7) and traces of more polar products. An excess of sodium hydrogen carbonate was added and the alcohol was evaporated off. The residue was extracted with ethyl acetate and the extract was passed through a column of alumina. Further elution with ethyl acetate gave the alcohol (4) (1·3 g), m.p. 105—106°, $[\alpha]_D$ −32·1° (*c* 0·7 in $CHCl_3$) (Found: C, 63·6; H, 7·2; N, 3·8%). The i.r. spectra of the two samples were identical.

2-Methylprop-2-enyl 2-Benzamido-4,6-O-benzylidene-3-O-(but-2-enyl)-2-deoxy-β-D-glucopyranoside (7).—A solution of the phenyloxazoline (1) (10 g) and toluene-*p*-sulphonic acid (500 mg) in redistilled 2-methylallyl alcohol was kept at 20° for 40 h; t.l.c. (toluene–acetone, 2 : 1) then indicated complete conversion of the starting material (R_F 0·9) into a major product (R_F 0·4) together with traces of more polar materials. An excess of sodium hydrogen carbonate was added and the alcohol was evaporated off. The residue was triturated with water and the solid product was filtered off, washed with water and ether, and dried to give the crude diol (5) (7·8 g). The diol (5) (3·5 g), αα-dimethoxytoluene (3 ml), toluene-*p*-sulphonic acid (12 mg), and dry dimethylformamide (20 ml), in a round-bottomed flask attached to a Büchi evaporator, were heated at 55° so that the dimethylformamide refluxed in the vapour duct.[6] After 1 h a short-path evaporation adaptor [6] was attached to the flask and the dimethylformamide was evaporated off at a bath temperature of 90°. A solution of sodium hydrogen carbonate (0·5 g) in water (25 ml) was added to the cooled residue and the mixture was then heated on a steam-bath until the product was finely dispersed. The product was filtered off, washed with water and light petroleum, and recrystallised from ethyl acetate–methanol (19 : 1) to give the pure *benzylidene derivative* (7) (3·15 g), m.p. 244—248° (decomp.), $[\alpha]_D$ −36·7° (*c* 0·5 in Me_2SO) (Found: C, 69·9; H, 6·8; N, 3·2. $C_{28}H_{33}NO_6$ requires C, 70·1; H, 6·9; N, 2·9%).

2-Methylprop-2-enyl 2-Benzamido-4,6-O-benzylidene-2-deoxy-β-D-glucopyranoside (8).—A solution of the benzylidene derivative (7) (2 g) and potassium t-butoxide (1 g) in dry dimethyl sulphoxide (250 ml) was kept at 20° for 4 h; t.l.c. (chloroform–ethyl acetate, 2 : 1) then indicated complete conversion of the starting material (R_F 0·8) into a single product (R_F 0·5). The mixture was diluted with water and extracted with chloroform and the extract was washed with water and dried (Na_2SO_4). The product was recrystallised from ethyl acetate–methanol (19 : 1) to give the *alcohol* (8) (1·56 g) containing one mol. equiv. of methanol of crystallisation; m.p. 263—267° (decomp.), $[\alpha]_D$ −43·4° (*c* 0·5 in Me_2SO) (Found: C, 65·7; H, 6·7; N, 3·1. $C_{24}H_{27}NO_6,CH_3OH$ requires C, 65·6; H, 6·8; N, 3·1%). Compound (8) was acetylated with acetic anhydride in pyridine to give the *acetate* (9), m.p. 288·5—294° (decomp.) (from ethanol), $[\alpha]_D$ −30·8° (*c* 0·5 in $CHCl_3$) (Found: C, 67·1; H, 6·2; N, 3·0. $C_{26}H_{29}NO_7$ requires C, 66·8; H, 6·25; N, 3·0%).

2-Methylprop-1-enyl 2-Benzamido-4,6-O-benzylidene-2-deoxy-β-D-glucopyranoside (10).—A solution of the alcohol (8) (1 g) and an excess of potassium t-butoxide in dry dimethyl sulphoxide (50 ml) was kept at 80° for 22 h; t.l.c. (chloroform–methanol, 4 : 1, on silver nitrate-impregnated plates) then indicated complete conversion of the 2-methylprop-2-enyl glycoside (8) (R_F 0·55) into the 2-methylprop-1-enyl glycoside (10) (R_F 0·65). The product was isolated in the usual way and recrystallised from ethyl acetate–methanol (19 : 1) to give the *glycoside* (10) (0·64 g), containing one mol. equiv. of methanol of crystallisation; m.p. 256—259° (decomp.), $[\alpha]_D$ −46·7° (*c* 0·5 in Me_2SO) (Found: C, 65·2; H, 6·8; N, 3·0. $C_{24}H_{27}NO_6,CH_3OH$ requires C, 65·6; H, 6·8; N, 3·1%). Compound (10) was acetylated with acetic anhydride in pyridine to give the *acetate* (11), m.p. 288—290°, $[\alpha]_D$ −55·4° (*c* 0·5 in $CHCl_3$) (Found: C, 66·7; H, 6·3; N, 3·0. $C_{26}H_{29}NO_7$ requires C, 66·8; H, 6·25; N, 3·0%).

2-Methylprop-2-enyl 2-Acetamido-3-O-acetyl-4,6-O-benzylidene-2-deoxy-β-D-glucopyranoside (13).—A solution of compound (8) (0·5 g) and sodium hydroxide (0·8 g) in 2-methoxyethanol (9 ml) and water (1 ml) was refluxed for 5 h; t.l.c. (chloroform–ethyl acetate, 1 : 1) then indicated complete conversion of the starting material (R_F 0·6) into a single product (R_F 0·3). The mixture was diluted with water and extracted with chloroform. The extract was washed with

water, dried (Na_2SO_4), and evaporated and the residue was acetylated with acetic anhydride in pyridine to give the *diacetate* (13) (0·29 g), m.p. 273—276° (decomp.) (from ethanol), $[\alpha]_D$ −86·7° (*c* 0·7 in $CHCl_3$) (Found: C, 62·4; H, 6·75; N, 3·5. $C_{21}H_{27}NO_7$ requires C, 62·2; H, 6·7; N, 3·5%).

The diacetate was hydrolysed with N-sodium hydroxide in methanol at 20° to give the *acetamido-derivative* (12), m.p. 272—275° (decomp.) (from aqueous ethanol), $[\alpha]_D$ −85·2° (*c* 0·5 in MeOH) (Found: C, 62·9; H, 7·0; N, 4·4. $C_{19}H_{25}NO_6$ requires C, 62·8; H, 6·9; N, 3·85%).

2-*Methylprop*-2-*enyl* 2-*Benzamido*-3-O-(*but*-2-*enyl*)-2-*deoxy*-4,6-*di*-O-*methylsulphonyl*-β-D-*glucopyranoside* (6).—The crude diol (5) (21 g) was treated with methanesulphonyl chloride in pyridine and the product was recrystallised from aqueous ethanol to give the *bismethanesulphonate* (6) (20·3 g), m.p. 175—176° (decomp.), $[\alpha]_D$ +15·4° (*c* 1 in $CHCl_3$) (Found: C, 50·5; H, 6·0; N, 2·7; S, 11·6. $C_{23}H_{33}NO_{10}S_2$ requires C, 50·4; H, 6·1; N, 2·6; S, 11·7%).

2-*Methylprop*-2-*enyl* 2-*Benzamido*-3-O-(*but*-2-*enyl*)-2-*deoxy*-β-D-*galactopyranoside* (14).—A mixture of the bismethanesulphonate (6) (20 g), sodium benzoate (20 g), and dimethylformamide (500 ml) was stirred under reflux for 22 h, cooled, and diluted with chloroform (500 ml) and water (500 ml). The chloroform layer was separated, washed with water and aqueous sodium hydrogen carbonate solution, dried (Na_2SO_4), and evaporated. The residue was saponified with N-sodium hydroxide in methanol (100 ml) at 20° for 1 h. The solution was neutralised with Amberlite 1R 120 (H^+) resin, filtered, and treated with decolourising charcoal. The solvent was evaporated off and the residue was extracted with ether to remove impurities. The solid residue (7·1 g) was recrystallised from ethyl acetate–methanol (2 : 1) to give the *diol* (14) (5·6 g, 35%), m.p. 223—227° (decomp.), $[\alpha]_D$ +0·5° (*c* 0·25 in MeOH), $[\alpha]_D$ +0·3° (*c* 1 in $Me_2N{\cdot}CHO$) (Found: C, 65·0; H, 7·5; N, 3·4. $C_{21}H_{29}NO_6$ requires C, 64·4; H, 7·5; N, 3·6%).

2-*Methylprop*-2-*enyl* 3-O-*Acetyl*-2-*benzamido*-4,6-O-*benzylidene*-2-*deoxy*-β-D-*galactopyranoside* (17).—The diol (14) (4·9 g) was converted into the benzylidene derivative (15) as described for the corresponding *gluco*-derivative. The crude dry product was treated with an excess of potassium t-butoxide in dimethyl sulphoxide (120 ml) at 20° for 6 h; t.l.c. (chloroform–methanol, 15 : 1) then indicated complete conversion of the starting material (15) (R_F 0·6) into a single product (R_F 0·4). The mixture was diluted with water and extracted with chloroform. The extract was washed with water, dried (Na_2SO_4), and evaporated and the residue was acetylated with acetic anhydride in pyridine to give the *acetate* (17) (3·7 g) (from ethanol), m.p. 275—279° (decomp.), $[\alpha]_D$ +49·6° (*c* 0·5 in $CHCl_3$) (Found: C, 66·9; H, 6·1; N, 3·35. $C_{26}H_{29}NO_7$ requires C, 66·8; H, 6·25; N, 3·0%).

2-*Methylprop*-2-*enyl* 2-*Acetamido*-3-O-*acetyl*-4,6-O-*benzylidene*-2-*deoxy*-β-D-*galactopyranoside* (19).—A solution of the acetate (17) (3·2 g) and sodium hydroxide (4·8 g) in 2-methoxyethanol (54 ml) and water (6 ml) was refluxed for 5 h. The solution was diluted with water and extracted with chloroform and the extract washed with water and dried (Na_2SO_4). The residue was acetylated with acetic anhydride in pyridine to give the *acetate* (19) (2 g), m.p. 251—253° (from ethanol), $[\alpha]_D$ +37·8° (*c* 0·5 in $CHCl_3$) (Found: C, 62·1; H, 6·9; N, 3·5. $C_{21}H_{27}NO_7$ requires C, 62·2; H, 6·7; N, 3·5%).

The diacetate (19) was saponified with N-sodium hydroxide in methanol at 20° to give 2-*methylprop*-2-*enyl* 2-*acetamido*-4,6-O-*benzylidene*-2-*deoxy*-β-D-*galactopyranoside* (18), m.p. 236—237° (decomp.) (from aqueous ethanol), $[\alpha]_D$ −9·0° (*c* 0·5 in MeOH) (Found: C, 62·3; H, 6·9; N, 4·1. $C_{19}H_{25}NO_6$ requires C, 62·8; H, 6·9; N, 3·85%). A portion of this material was hydrolysed with 3N-hydrochloric acid at 100° for 4 h; the product was analysed as described previously [5] on an amino-acid analyser. It had the same retention time as an authentic sample of D-galactosamine.

Allyl 2-*Benzamido*-4,6-*di*-O-*benzyl*-2-*deoxy*-β-D-*glucopyranoside* (21).—A solution of allyl 2-benzamido-4,6-di-*O*-benzyl-3-*O*-(but-2-enyl)-2-deoxy-β-D-glucopyranoside (20) [1] (6·5 g) and potassium t-butoxide (1 g) in dry dimethyl sulphoxide (100 ml) was kept at 20° for 6·5 h; t.l.c. (toluene–acetone, 2 : 1) then indicated complete conversion of the starting material (R_F 0·6) into a product (R_F 0·5). The solution was diluted with water and extracted with chloroform and the extract washed with water and evaporated. The residue was dissolved in acetone–water (10 : 1; 25 ml). Mercuric chloride (3·2 g) was dissolved in the solution (to hydrolyse any prop-1-enyl glycoside), which was kept at 20° for 10 min and then diluted with water. The precipitate was filtered off, washed with water, dried, and chromatographed on alumina. Elution with chloroform–cyclohexane (2 : 1) gave the *allyl glycoside* (21) (3 g), m.p. 132—133·5° (from aqueous methanol), $[\alpha]_D$ −12·5° (*c* 1 in $CHCl_3$) (Found: C, 71·3; H, 6·7; N, 2·7. $C_{30}H_{33}NO_6$ requires C, 71·55; H, 6·6; N, 2·8%).

Allyl 2-*Acetamido*-3-O-*acetyl*-4,6-*di*-O-*benzyl*-2-*deoxy*-β-D-*glucopyranoside* (25).—The benzamido-derivative (21) was hydrolysed with N-sodium hydroxide in aqueous 2-methoxyethanol, as described for other compounds, to give the amino-alcohol (24), which was acetylated with acetic anhydride in pyridine to give the *diacetate* (25), m.p. 143·5—145·5° [from benzene–light petroleum (b.p. 60—80°)], $[\alpha]_D$ −42·7° (*c* 0·7 in $CHCl_3$) (Found: C, 66·9; H, 6·6; N, 2·8. $C_{27}H_{33}NO_7$ requires C, 67·1; H, 6·9; N, 2·9%).

The diacetate (25) was saponified with N-sodium hydroxide in methanol at 20° to give *allyl* 2-*acetamido*-4,6-*di*-O-*benzyl*-2-*deoxy*-β-D-*glucopyranoside* (26), m.p. 119·5—121·5° (from aqueous methanol), $[\alpha]_D$ −27·8° (*c* 0·7 in $CHCl_3$) (Found: C, 67·75; H, 7·0; N, 3·4. $C_{25}H_{31}NO_6$ requires C, 68·0; H, 7·1; N, 3·2%).

Allyl 2-*Acetamido*-3,4,6-*tri*-O-*benzyl*-2-*deoxy*-β-D-*glucopyranoside* (27).—A solution of compound (26) (0·9 g) in dry benzene (20 ml) was added slowly to a heated, stirred mixture of benzyl chloride (10 ml), dry benzene (20 ml), and sodium hydride (0·5 g), and the mixture was then stirred under reflux for 3·5 h; t.l.c. (toluene–acetone, 2 : 1) then indicated conversion of the starting material (R_F 0·18) into two products (R_F 0·5 and 0·73). Methanol was added to destroy the excess of sodium hydride and the benzene solution was washed with water, dried (Na_2SO_4) and evaporated. The syrupy residue was chromatographed on silica gel; elution with carbon tetrachloride–acetone (15 : 1) gave the less polar product (R_F 0·73) (0·5 g) as a syrup, $\nu_{max.}$ 1650 cm^{-1} (amide I), $[\alpha]_D$ −2·9° (*c* 0·6 in $CHCl_3$). The analysis indicated that it was *allyl* 2-(N-*benzylacetamido*)-3,4,6-tri-O-*benzyl*-2-*deoxy*-β-D-*glucopyranoside* (29) (Found: C, 75·1; H, 7·1; N, 2·1. $C_{39}H_{43}NO_6$ requires C, 75·3; H, 7·0; N, 2·25%). Elution with carbon tetrachloride–acetone (5 : 1) gave the *acetamido-derivative* (27), m.p. 133—135° (from aqueous methanol) (0·17 g), $[\alpha]_D$ +7° (*c* 0·4 in $CHCl_3$), $\nu_{max.}$ 1650 (amide I), 1560 (amide II), and 3280 cm^{-1}

(NH) (Found: C, 72·0; H, 6·9; N, 2·8. $C_{32}H_{37}NO_6$ requires C, 72·3; H, 7·0; N, 2·6%).

The allyl group of compound (27) was isomerised with potassium t-butoxide in dimethyl sulphoxide and the prop-1-enyl group was hydrolysed with dilute acid [12] to give 2-acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranoside (28), m.p. 207—209°, $[\alpha]_D$ +60·6° (*c* 0·6 in pyridine) (Found: C, 71·2; H, 6·9; N, 3·3. Calc. for $C_{29}H_{33}NO_6$: C, 70·9; H, 6·8; N, 2·85%) {lit.,[1] m.p. 208·5—210·5°, $[\alpha]_D$ +62·1° (*c* 0·43 in pyridine)}.

Conversion of Benzyl 3,4,6-*Tri*-O-*acetyl*-2-*benzamido*-2-*deoxy*-β-D-*glucopyranoside* (30) *into Benzyl* 2-*Acetamido*-3,4,6-*tri*-O-*acetyl*-2-*deoxy*-β-D-*glucopyranoside* (32).—Benzyl 3,4,6-tri-*O*-acetyl-2-benzamido-2-deoxy-β-D-glucopyranoside [13] (1 g) (prepared from the corresponding triol [14]) in acetic anhydride (40 ml) and glacial acetic acid (10 ml) was refluxed for 24 h. The course of the reaction was followed by t.l.c. (chloroform–acetone, 10 : 1) after evaporation of a portion of the solution, and after 24 h the starting material (R_F 0·55) was completely converted into two products (R_F 0·75 and 0·35), with the more polar product predominating (*ca.* 4 : 1). Water (7·5 ml) was added dropwise to the refluxing solution, to convert all the acetic anhydride into acetic acid, and the refluxing was continued for 1 h, after which time a single product (R_F 0·35) was present. The solvent was evaporated off, the residue was taken up in chloroform, and the solution was washed with saturated sodium hydrogen carbonate solution, dried (Na_2SO_4), and evaporated. The residue was crystallised from methanol–water (1 : 4) to give the acetate (32) (800 mg, 96%), m.p. 170—172°, $[\alpha]_D$ −42·7° (*c* 2 in MeOH) (Found: C, 57·75; H, 6·25; N, 3·0. Calc. for $C_{21}H_{27}NO_9$: C, 57·6; H, 6·2; N, 3·2%) {lit.,[15] m.p. 165—167°, $[\alpha]_D$ −43·4° (MeOH)}.

[3/624 *Received*, 26*th March*, 1973]

[12] J. Gigg and R. Gigg, *J. Chem. Soc.* (*C*), 1966, 82.
[13] P. H. Gross, K. Brendel, and H. K. Zimmerman, *Annalen*, 1965, **683**, 175.
[14] P. A. Gent, R. Gigg, and R. Conant, *J.C.S. Perkin I*, 1972, 248.
[15] R. Kuhn and W. Kirschenlohr, *Chem. Ber.*, 1953, **86**, 1331.