The Allyl Ether as a Protecting Group in Carbohydrate Chemistry. Part III.[1] The But-2-enyl Ether Group

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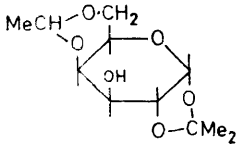
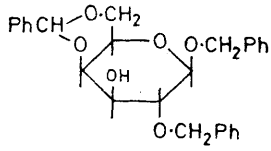
2,4,6-Tri-*O*-benzyl-D-galactopyranose was prepared from allyl 3-*O*-allyl-2,4,6-tri-*O*-benzyl-α-D-galactopyranoside for use in the synthesis of oligosaccharides containing a galactose residue substituted on the 3-position. The use of the but-2-enyl (crotyl) ether system for the protection of hydroxy-groups was investigated. The but-2-enyl ethers were stable to mild acid hydrolysis and to the basic conditions required for benzylation, and were readily cleaved by the action of potassium t-butoxide in dimethyl sulphoxide. Prop-1-enyl 2,4,6-tri-*O*-benzyl-α-D-galactopyranoside was prepared from allyl 2,4,6-tri-*O*-benzyl-3-*O*-but-2-enyl-α-D-galactopyranoside and prop-1-enyl 2-benzamido-4,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside was prepared from allyl 2-benzamido-4,6-di-*O*-benzyl-3-*O*-but-2-enyl-2-deoxy-β-D-glucopyranoside. 2-Benzamido-3,4,6-tri-*O*-benzyl-2-deoxy-D-gluco- and D-galacto-pyranoses were prepared from the corresponding β-allyl glycosides.

MANY glycolipids, *e.g.* the sulphatides,[2] the Forsmann antigen,[3] globosides,[4] and the gangliosides[5] contain galactopyranose residues substituted on the 3-position. For synthetic work in this series a suitably protected derivative of galactose with a free 3-hydroxy-group was required so that new methods of glycoside synthesis could be investigated.



(I)



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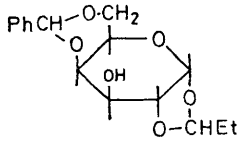


(III)

Several protected derivatives of galactose with a free 3-hydroxy-group are known but were not considered suitable for our purposes. Compound (I)[6] has been used previously[6a,7] for the synthesis of various 3-*O*-substituted galactose derivatives, and compound (II),[7c] has been used similarly. Compound (III), prepared recently,[1b] is also potentially useful for the synthesis of 3-*O*-substituted galactose derivatives. In this connection, Flowers[7a,8] also showed that protected galactose derivatives containing free 3- and 4-hydroxy-groups reacted preferentially at the 3-position in glycosidation reactions.

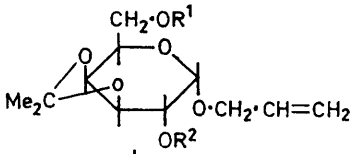
With the allyl group for protection we planned a route to 2,4,6-tri-*O*-benzylgalactopyranose (XXI), which should be a suitable intermediate for investigating new methods of glycoside synthesis in the glycolipid field. For this purpose allyl α-D-galactopyranoside[9] was converted into the 3,4-*O*-isopropylidene derivative (IV) which gave the crystalline triphenylmethyl ether (V). Compound (V) was converted into the benzyl ether (VI), which was hydrolysed by acid to give allyl 2-*O*-benzyl-α-D-galactopyranoside (IX). Compound (IX) was converted into the crystalline benzylidene derivative (XII) which gave the crystalline allyl 3-*O*-allyl-2-*O*-benzyl-4,6-*O*-benzylidene-α-D-galactopyranoside (XIII). Hydrolysis of the benzylidene group from compound (XIII) gave the diol (XVI), which was benzylated to give the tri-*O*-benzyl ether (XIX). Isomerisation[1] of the allyl groups with potassium t-butoxide in dimethyl sulphoxide gave the di-*O*-prop-1-enyl derivative (XX), which on acidic hydrolysis gave the crystalline 2,4,6-tri-*O*-benzyl-D-galactopyranose (XXI).

A shorter route to the tri-*O*-benzyl ether (XXI) was envisaged, involving preferential allylation of the equatorial 3-hydroxy-group of allyl 2,6-di-*O*-benzyl-α-D-galactopyranoside (X), by analogy with the work of Flowers[7a,8] on the preferential glycosidation of the 3-hydroxy-group in 3,4-unsubstituted galactose derivatives. Compound (X) was prepared from allyl 6-*O*-benzyl 3,4-*O*-isopropylidene-α-D-galactopyranoside (VII)[1a] by conversion into the dibenzyl ether (VIII) followed by acidic hydrolysis of the isopropylidene group. Allylation of compound (X) with allyl bromide and sodium hydroxide in benzene at room temperature gave a mixture of the monoallyl derivative(s) and the 3,4-di-*O*-allyl derivative in which the latter predominated; this route was therefore abandoned.

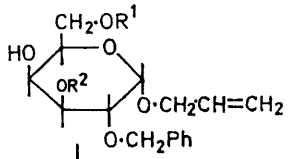
We have shown previously[1b,10] that γ-substituted allyl ethers are rapidly cleaved by the action of potassium t-butoxide in dimethyl sulphoxide and have suggested[1b]

[1] (*a*) Part I, J. Gigg and R. Gigg, *J. Chem. Soc.* (*C*), 1966, 82; (*b*) Part II, R. Gigg and C. D. Warren, *ibid.*, 1968, 1903.
[2] T. H. Haines, *Progr. Chem. Fats and Lipids*, 1971, **11**, 297.
[3] B. Siddiqui and S. Hakomori, *J. Biol. Chem.*, 1971, **246**, 5766.
[4] J. Kawanami and T. Tsuji, *Chem. and Phys. Lipids*, 1971, **7**, 49.
[5] H. Wiegandt, *Angew. Chem. Internat. Edn.*, 1968, **7**, 87.
[6] (*a*) D. H. Ball and J. K. N. Jones, *J. Chem. Soc.*, 1958, 905; (*b*) J. G. Buchanan and K. J. Miller, *Chem. and Ind.*, 1958, 625; D. H. Ball, *J. Org. Chem.*, 1966, **31**, 220; G. J. F. Chittenden, *Carbohydrate Res.*, 1970, **15**, 101.
[7] (*a*) H. M. Flowers, *Carbohydrate Res.*, 1967, **4**, 312; (*b*) S. Peat, D. M. Bowker, and J. R. Turvey, *ibid.*, 1968, **7**, 225; (*c*) A. Stoffyn and P. Stoffyn, *J. Org. Chem.*, 1967, **32**, 4001.
[8] D. Beith-Halahmi, H. M. Flowers, and D. Shapiro, *Carbohydrate Res.*, 1967, **5**, 25.
[9] E. A. Talley, M. D. Vale, and E. Yanovsky, *J. Amer. Chem. Soc.*, 1945, **67**, 2037.
[10] J. Cunningham and R. Gigg, *J. Chem. Soc.*, 1965, 2968.

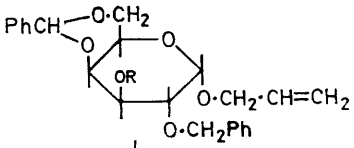
that the but-2-enyl (crotyl) ether should prove an effective protecting group in carbohydrate chemistry. Similar cleavages of γ-substituted allyl ethers have been observed with potassium t-butoxide at 120° [11a] and with



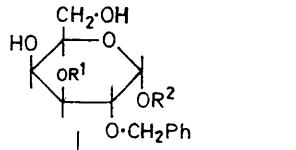
(IV) $R^1 = R^2 = H$
(V) $R^1 = CPh_3$, $R^2 = H$
(VI) $R^1 = CPh_3$, $R^2 = CH_2Ph$
(VII) $R^1 = CH_2Ph$, $R^2 = H$
(VIII) $R^1 = R^2 = CH_2Ph$



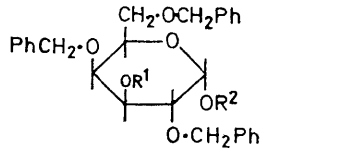
(IX) $R^1 = R^2 = H$
(X) $R^1 = CH_2Ph$, $R^2 = H$
(XI) $R^1 = CH_2Ph$, $R^2 = CH_2{\cdot}CH{=}CH_2$



(XII) R = H
(XIII) $R = CH_2{\cdot}CH{=}CH_2$
(XIV) $R = CH_2{\cdot}CH{=}CHMe$
(XV) R = Me



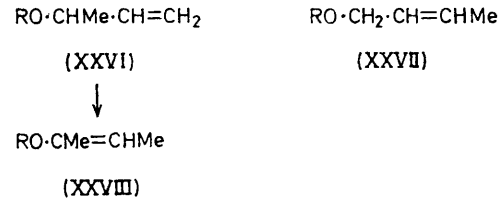
(XVI) $R^1 = R^2 = CH_2{\cdot}CH{=}CH_2$
(XVII) $R^1 = CH_2{\cdot}CH{=}CHMe$, $R^2 = CH_2{\cdot}CH{=}CH_2$
(XVIII) $R^1 = Me$, $R^2 = H$



(XIX) $R^1 = R^2 = CH_2{\cdot}CH{=}CH_2$
(XX) $R^1 = R^2 = CH{=}CHMe$
(XXI) $R^1 = R^2 = H$
(XXII) $R^1 = CH_2{\cdot}CH{=}CHMe$, $R^2 = CH_2{\cdot}CH{=}CH_2$
(XXIII) $R^1 = H$, $R^2 = CH_2{\cdot}CH{=}CH_2$
(XXIV) $R^1 = H$, $R^2 = CH{=}CHMe$
(XXV) $R^1 = Me$, $R^2 = CH{=}CHMe$

powdered potassium hydroxide at 160—200°,[11b] and the reaction has been shown [11c] to occur without a preliminary isomerisation to the alk-1-enyl ethers. We have shown [12a] that alk-1-enyl ethers are considerably more stable to the action of potassium t-butoxide in dimethyl sulphoxide than are alk-2-enyl ethers and this has been confirmed by Preobrazhenskii and his co-workers.[12b] However when but-2-enyl sulphides are treated with potassium t-butoxide in dimethyl sulphoxide, cleavage is accompanied by isomerisation to the but-1-enyl sulphides.[13]

To establish the but-2-enyl ether as an effective protecting group it was necessary to show that it could be readily prepared and that it was stable to some of the normal manipulative conditions of carbohydrate chemistry, *e.g.* acidic hydrolysis and the basic conditions of benzylation. Crotyl bromide in the presence of sodium hydroxide or (preferably) sodium hydride readily converts alcohols into ethers. However, crotyl bromide as normally prepared or obtained commercially is an equilibrium mixture [14] of *ca.* 86% but-2-enyl bromide and 14% 1-methylallyl bromide, and it should be possible for a mixture of the ethers (XXVI) and (XXVII) to be formed from these two bromides during the S_N2 alkylation reaction.



$RO{\cdot}CHMe{\cdot}CH{=}CH_2$ (XXVI) $RO{\cdot}CH_2{\cdot}CH{=}CHMe$ (XXVII)

$RO{\cdot}CMe{=}CHMe$ (XXVIII)

Compound (XXVI) would be expected to rearrange to the enol ether (XXVIII) on treatment with potassium t-butoxide in dimethyl sulphoxide, rather than undergo the cleavage reaction. All of the ethers which we have prepared from crotyl bromide have been converted entirely (as observed by t.l.c.) into the corresponding alcohols, by the action of potassium t-butoxide in dimethyl sulphoxide, indicating that the starting materials were entirely in the form of the but-2-enyl ethers (XXVII).

The mechanistic studies of England and Hughes [15] showed that the S_N2 replacement of bromine from but-2-enyl bromide was much faster than the replacement of bromine from 1-methylallyl bromide. This result, coupled with the rapid thermal equilibration [14] in favour of the but-2-enyl bromide, probably explains the exclusive formation of the but-2-enyl ethers (XXVII) from crotyl bromide. Similar mechanistic studies with the methylallyl chlorides [16] showed the same difference in reaction rates. However since the chlorides are much more thermally stable than the corresponding bromides

[11] (*a*) M. Julia and M. Baillargé, *Compt. rend.*, 1962, **254**, 4313. (*b*) G. M. Mkryan, N. A. Papazyan, and A. A. Pogosyan, *Zhur. org. Khim.*, 1967, **3**, 1160; G. M. Mkryan, A. A. Pogosyan, and E. A. Ovanesyan, *ibid.*, 1968, **4**, 978; G. M. Mkryan and A. A. Pogosyan, *ibid.*, 1969, **5**, 1746; G. M. Mkryan, A. A. Pogosyan, N. A. Papazyan, and R. M. Ispiryan, *ibid.*, 1971, **7**, 2056; G. M. Mkryan, E. A. Ovanesyan, A. A. Pogosyan, and N. A. Papazyan, *Armyan Khim. Zhur.*, 1968, **21**, 300; (*c*) G. Kesslin and C. M. Orlando, *J. Org. Chem.*, 1966, **31**, 2682.

[12] (*a*) J. Gigg and R. Gigg, *J. Chem. Soc.* (*C*), 1968, 2030; (*b*) I. B. Vtorov, G. A. Serebrennikova, and N. A. Preobrazhenskii, *Zhur. org. Khim.*, 1970, **6**, 669; V. I. Titov, G. A. Serebrennikova, and N. A. Preobrazhenskii, *ibid.*, p. 1154.

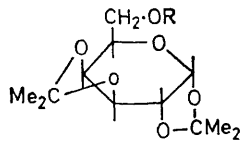
[13] D. E. O'Connor and W. I. Lyness, *J. Amer. Chem. Soc.*, 1964, **86**, 3840; A. L. Müller and A. I. Virtanen, *Acta Chem. Scand.*, 1966, **20**, 1163; J. F. Carson, L. E. Boggs, and R. Lundin, *J. Org. Chem.* 1968, **33**, 3739.

[14] S. Winstein and W. G. Young, *J. Amer. Chem. Soc.*, 1936, **58**, 104; B. D. England, *J. Chem. Soc.*, 1955, 1618; R. F. Nystrom and C. R. A. Berger, *Chem. and Ind.*, 1958, 559.

[15] B. D. England and E. D. Hughes, *Nature*, 1951, **168**, 1002.

[16] C. A. Vernon, *J. Chem. Soc.*, 1954, 4462; R. H. Dewolfe and W. G. Young, *Chem. Rev.*, 1956, **56**, 753.

it is possible to effect the S_N2 replacement of chlorine by alkoxide in both 1-methylallyl and but-2-enyl chlorides.[17]



(XXIX) R = $CH_2 \cdot CH{=}CHMe$
(XXX) R = $CHMe \cdot CH{=}CH_2$
(XXXI) R = $CMe{=}CHMe$

In order to study the behaviour of the two types of ether (XXVI) and (XXVII), the but-2-enyl ether (XXIX) and the 1-methylallyl ether (XXX) of 1,2:3,4-di-*O*-isopropylidene-D-galactopyranose were prepared by the action of crotyl bromide and 1-methylallyl chloride respectively on 1,2:3,4-di-*O*-isopropylidene-D-galactose in the presence of sodium hydride in benzene. T.l.c. did not distinguish between the isomers (XXIX) and (XXX). On treatment with potassium t-butoxide in dimethyl sulphoxide at 80°, the but-2-enyl ether (XXIX) was completely converted into di-*O*-isopropylidene-D-galactose (as observed by t.l.c.) in 1 h. On the other hand, the presumed 1-methylallyl ether (XXX) was partially (*ca.* 40%) converted into di-*O*-isopropylidene-D-galactose after this time. Further treatment under the same conditions did not result in the formation of more di-*O*-isopropylidene-D-galactose, but the residue of the starting material was slowly converted (during 24 h) into a product with a higher mobility on t.l.c.; this was transformed into di-*O*-isopropylidene-D-galactose by the action of mercury(II) chloride in the presence of mercury(II) oxide.[16] The results indicate either that the 1-methylallyl chloride was contaminated with but-2-enyl chloride or that it was isomerised under the reaction conditions, so that a mixture of compounds (XXIX) and (XXX) was formed during the alkylation reaction. A large excess of the chloride was used in the reaction; therefore if a small amount of the but-2-enyl chloride was present as a contaminant it would react preferentially to give the observed mixture of products. The very low rate of isomerisation of the 1-methylallyl ether (XXX) to the 1-methylprop-1-enyl ether (XXXI) indicated that the 1-methylallyl ether might be useful in conjunction with the but-2-enyl and allyl ether groups for selective protection and deprotection of specific hydroxy-groups in the carbohydrate series. It has been shown,[18] however, that the rate of isomerisation of allyl to prop-1-enyl ethers by potassium t-butoxide is considerably reduced by the presence of t-butyl alcohol, and the low rate of isomerisation of the ether (XXX) might therefore have been due to the presence of t-butyl alcohol produced by reaction of potassium t-butoxide with the di-*O*-isopropylidene-D-galactose produced in the mixture. Therefore a pure sample of the isomer (XXX) was obtained by treating the mixture of isomers with potassium t-butoxide in dimethyl sulphoxide to decompose the ether (XXIX). The pure ether (XXX) was isolated by column chromatography and distillation and was re-treated with potassium t-butoxide in dimethyl sulphoxide. Although the rate of isomerisation of the pure 1-methylallyl ether (XXX) to the 1-methylprop-1-enyl ether (XXXI) was higher than that observed with the mixed ethers it was still very much lower than the rate of isomerisation of allyl to prop-1-enyl ethers; this property may prove to be valuable in future work.

The but-2-enyl ether (XXIX) was treated with allyl alcohol and hydrogen chloride, as described previously [19] for the preparation of allyl 6-*O*-allyl-α-D-galactopyranoside, to give crystalline allyl 6-*O*-but-2-enyl-α-D-galactopyranoside.

To study the stability of the but-2-enyl ether under various reaction conditions, the benzylidene derivative (XII) was converted into the but-2-enyl ether (XIV) by the action of crotyl bromide and sodium hydride. Compound (XIV) was hydrolysed by acid to give the diol (XVII), which was converted into allyl 2,4,6-tri-*O*-benzyl-3-*O*-but-2-enyl-α-D-galactopyranoside (XXII) without evidence of decomposition of the but-2-enyl ether during the benzylation. The but-2-enyl group was completely eliminated from compound (XXII) by the action of potassium t-butoxide in dimethyl sulphoxide at room temperature, to give the allyl glycoside (XXIII) with only a small amount of isomerisation to the prop-1-enyl glycoside (XXIV). Further treatment of the allyl glycoside (XXIII) with potassium t-butoxide in dimethyl sulphoxide at higher temperatures gave the prop-1-enyl glycoside (XXIV) which on acid hydrolysis gave the crystalline 2,4,6-tri-*O*-benzylgalactopyranose (XXI).

To confirm the structure of compound (XXI), the prop-1-enyl glycoside (XXIV) was converted into the methyl ether (XXV). Acidic hydrolysis of compound (XXV) and subsequent hydrogenolysis gave 3-*O*-methylgalactose with properties identical to those reported previously [20] for this compound. The structure of the benzylidene derivative (XII) was also confirmed by conversion into the crystalline methyl ether (XV), which after acidic hydrolysis to 2-*O*-benzyl-3-*O*-methylgalactopyranose (XVIII) and subsequent hydrogenolysis also gave 3-*O*-methylgalactose.

2-*O*-Benzyl ethers of carbohydrates give predominantly α-glycoside linkages in glycoside synthesis; [21,22] the 2,4,6-tri-*O*-benzylgalactose (XXI) should therefore be useful for the synthesis of the α-galactoside linkages which occur [3,4] in globoside and the Forsmann antigen.

The benzyl ethers of amino-sugars have not been used to any great extent in synthetic studies, possibly owing to

[17] J. D. Roberts, W. G. Young, and S. Winstein, *J. Amer. Chem. Soc.*, 1942, **64**, 2157; A. G. Catchpole and E. D. Hughes, *J. Chem. Soc.*, 1948, 4.
[18] C. C. Price and W. H. Snyder, *J. Amer. Chem. Soc.*, 1961, **83**, 1773.
[19] R. Gigg and C. D. Warren, *J. Chem. Soc.*, 1965, 2205.
[20] J. S. Brimacombe, A. M. Mofti, and A. K. Al-Radhi, *J. Chem. Soc.* (*C*), 1971, 1363.
[21] P. W. Austin, F. E. Hardy, J. G. Buchanan, and J. Baddiley, *J. Chem. Soc.*, 1964, 2128; 1965, 1419.
[22] H. N. Flowers, *Carbohydrate Res.*, 1971, **18**, 211; M. Dejter-Juszynski and H. M. Flowers, *ibid.*, p. 219.

early reports [23] that *N*-benzylation accompanied *O*-benzylation under the conditions then used for benzylation. However, Fletcher and his co-workers [24a,b] have prepared several benzylated derivatives of *N*-acyl amino-sugars by use of benzyl bromide with barium oxide and barium hydroxide in dimethylformamide, and Jeanloz (unpublished; see ref. 23*b*) has reported the use of benzyl chloride or benzyl bromide with silver oxide in dimethylformamide to be suitable for the preparation of benzylated amino-sugar derivatives. We have found that use of benzyl chloride and sodium hydride in tetrahydrofuran gives high yields of benzyl ethers of *N*-benzoyl amino-sugars.

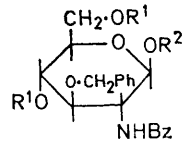
In order that new routes for the synthesis of glycosides containing amino-sugars could be investigated, the derivatives (XXXIV) and (XLI) of D-glucosamine and D-galactosamine were prepared. We have demonstrated previously [1b] that the benzamido-group in amino-sugar derivatives is stable to the conditions required for the isomerisation of the allyl group to the prop-1-enyl group with potassium t-butoxide in dimethyl sulphoxide, and compounds (XXXIV) and (XLI) were converted into the corresponding prop-1-enyl glycosides (XXXV) and (XLII) without difficulty. It was anticipated that the benzamido-groups in these derivatives could be removed by alkaline hydrolysis and that various *N*-protecting groups could be incorporated before the prop-1-enyl groups were removed under mild conditions by use of mercury(II) chloride and mercury(II) oxide as described previously.[1b]

Allyl 2-benzamido-3-*O*-benzyl-2-deoxy-β-D-glucopyranoside (XXXIII) [25] was readily converted in high yield into the tri-*O*-benzyl ether (XXXIV) by the action of benzyl chloride and sodium hydride in tetrahydrofuran, and this was isomerised to the prop-1-enyl glycoside (XXXV) under the usual conditions. Alkaline hydrolysis of the benzamido-group in compound (XXXV) however was not practicable; mainly starting material was recovered after refluxing for many hours with alkali in various solvent mixtures. Acidic hydrolysis of compound (XXXV) readily converted it into the previously [24a] described 2-benzamido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranose (XXXVI). This compound was further hydrolysed by acid to the hydrochloride (XXXVII),[24c] which on acetylation with acetic anhydride in methanol containing sodium acetate gave the known [24a] acetamido-compound (XXXVIII). The hydrochloride (XXXVII) was also converted into the *N*-2,4-dinitrophenyl derivative (XXXIX).

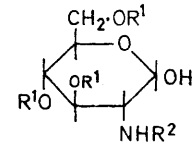
In the same way, the 2-amino-2-deoxy-D-galactose derivative (XL) [25] was converted into the corresponding prop-1-enyl glycoside (XLII), which on acid hydrolysis gave 2-benzamido-3,4,6-tri-*O*-benzyl-2-deoxy-D-galactose (XLIII). For characterisation the benzamido-group was hydrolysed with acid and the product acetylated to give the known [24a] acetamido-derivative (XLIV).

[23] (*a*) R. W. Jeanloz, *Adv. Carbohydrate Chem.*, 1958, **13**, 189; (*b*) D. Horton, in 'The Amino Sugars,' ed. R. W. Jeanloz, Academic Press, New York, 1969, vol. 1A, p. 82.

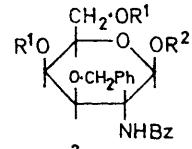
To explore further the potential of the allyl and but-2-enyl ether protecting groups in the amino-sugar series, the phenyloxazoline (XLV) was converted into the



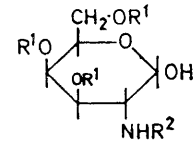
(XXXII) R^1 = Ac, R^2 = $CH_2{\cdot}CH{=}CH_2$
(XXXIII) R^1 = H, R^2 = $CH_2{\cdot}CH{=}CH_2$
(XXXIV) R^1 = CH_2Ph, R^2 = $CH_2{\cdot}CH{=}CH_2$
(XXXV) R^1 = CH_2Ph, R^2 = CH=CHMe



(XXXVI) R^1 = CH_2Ph, R^2 = Bz
(XXXVII) R^1 = CH_2Ph, R^2 = H,HCl
(XXXVIII) R^1 = CH_2Ph, R^2 = Ac
(XXXIX) R^1 = CH_2Ph R^2 = 2,4-$(NO_2)_2C_6H_3$



(XL) R^1 = Ac, R^2 = $CH_2{\cdot}CH{=}CH_2$
(XLI) R^1 = CH_2Ph, R^2 = $CH_2{\cdot}CH{=}CH_2$
(XLII) R^1 = CH_2Ph, R^2 = CH=CHMe



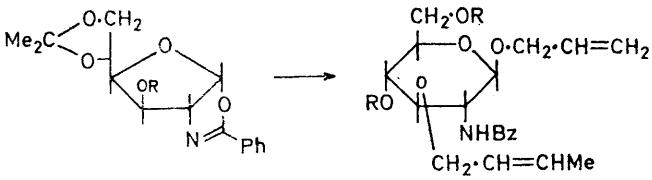
(XLIII) R^1 = CH_2Ph, R^2 = Bz
(XLIV) R^1 = CH_2Ph, R^2 = Ac

crystalline but-2-enyl ether (XLVI). Compound (XLVI) was treated with acid in allyl alcohol (as described previously [25] for the corresponding 3-*O*-benzyl ether) to give allyl 2-benzamido-3-*O*-but-2-enyl-2-deoxy-β-D-glucopyranoside (XLVII). Compound (XLVII) was purified *via* the diacetate and converted into the di-*O*-benzyl ether (XLIX). When compound (XLIX)

[24] (*a*) R. Harrison and H. G. Fletcher, *J. Org. Chem.*, 1965, **30**, 2317; (*b*) J. R. Plimmer, N. Pravdić, and H. G. Fletcher, *ibid.*, 1967, **32**, 1982; (*c*) T. D. Inch and H. G. Fletcher, *ibid.*, 1966, **31**, 1810.

[25] P. A. Gent, R. Gigg, and R. Conant, *J.C.S. Perkin I*, 1972, 277.

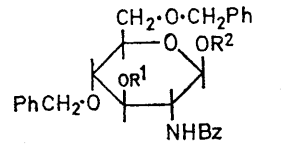
was treated with potassium t-butoxide in dimethyl sulphoxide at room temperature the but-2-enyl ether was cleaved to give allyl 2-benzamido-4,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (L), which on further treatment at higher temperatures gave the corresponding prop-1-enyl glycoside (LI). For characterisation, compound (LI) was converted into the benzyl ether (LII), which, on treatment with mercury(II) chloride, gave the previously described [24a] 2-benzamido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucose (XXXVI).



(XLV) R = H
(XLVI) R = CH_2·CH=CHMe

(XLVII) R = H
(XLVIII) R = Ac
(XLIX) R = CH_2Ph

(L) R^1 = H, R^2 = CH_2·CH=CH_2
(LI) R^1 = H, R^2 = CH=CHMe
(LII) R^1 = CH_2Ph, R^2 = CH=CHMe



In contrast to the stability of the benzamido-group in prop-1-enyl 2-benzamido-3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranoside (XXXV) to basic hydrolysis, the benzamido-group of prop-1-enyl 2-benzamido-4,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (LI) was readily hydrolysed with 2·7N-sodium hydroxide in 90% aqueous 2-methoxyethanol during 4 h. These conditions were previously [26a] found to be suitable for the hydrolysis of the benzamido-groups from methyl 2-benzamido-4,6-*O*-benzylidene-2-deoxy-α-D-galacto- and gluco-pyranosides. Each of these compounds containing readily hydrolysed benzamido-groups has a free 3-hydroxy-group. Difficulties in the hydrolysis of carbohydrate benzamido-groups have been discussed previously.[26b]

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.

Allyl 3,4-O-*Isopropylidene*-6-O-*triphenylmethyl*-α-D-*galactopyranoside* (V).—Allyl α-D-galactopyranoside [9] (20 g), dry acetone (600 ml), and toluene-*p*-sulphonic acid (1 g) were stirred at room temperature for 24 h; t.l.c. (ether) then showed complete conversion of the starting material (R_F 0) into the isopropylidene derivative (IV) (R_F 0·4). An excess of potassium carbonate was added to neutralise the acid, the acetone was evaporated off, and the residue was extracted with ether. The ether solution was dried (K_2CO_3) and evaporated and the crude product was taken up in dry pyridine (100 ml). Triphenylmethyl chloride (27 g) was added and the solution was kept at 70° for 3 h; t.l.c. (ether–light petroleum 1 : 1) then showed complete conversion into the triphenylmethyl ether (R_F 0·3). The solution was cooled, water (10 ml) and ether (300 ml) were added, and the solution was washed with ice-cold N-hydrochloric acid to remove the pyridine and then with sodium hydrogen carbonate solution and dried (K_2CO_3). Evaporation gave the crude product; for analysis a portion was chromatographed on alumina and the product was eluted with ether–methanol (10 : 1) and recrystallised from cyclohexane to give *compound* (V), m.p. 130—132°, $[\alpha]_D$ +48° (*c* 2 in $CHCl_3$) (Found: C, 74·2; H, 6·8. $C_{31}H_{34}O_6$ requires C, 74·2; H, 6·8%).

Allyl 2-O-*Benzyl*-4,6-O-*benzylidene*-α-D-*galactopyranoside* (XII).—The crude product (V) (40 g), containing some triphenylmethanol, was treated with sodium hydride and benzyl chloride in refluxing benzene until t.l.c. (ether–light petroleum 1 : 1) showed complete conversion of the starting material (R_F 0·3) into the benzyl ether (VI) (R_F 0·75). The excess of sodium hydride was decomposed with methanol, the solution was washed with water and the benzene evaporated off. A solution of the crude product in methanol (200 ml) and hydrochloric acid (12N; 2 ml) was heated under reflux for 1·5 h; t.l.c. (ether–methanol 18 : 1) then showed complete hydrolysis of the triphenylmethyl and isopropylidene groups to give the benzyl ether (IX) (R_F 0·4). The acid was neutralised with an excess of potassium carbonate and the solvent was evaporated off. The residue was extracted with ether–methanol (20 : 1) and the solution was filtered through a column of alumina (4 × 4 in). The column was eluted with the same solvent to remove the triphenylmethanol and then with methanol–water (5 : 1) to give the benzyl ether (IX). The solvents were evaporated off and the crude dry product (IX) was dissolved in benzaldehyde (200 ml) containing zinc chloride (40 g). The solution was kept at room temperature for 24 h, then poured into a mixture of ice–water and light petroleum. The crystalline product (18 g) which separated was filtered off and recrystallised from cyclohexane–benzene (2 : 1) to give *compound* (XII), m.p. 116—117°, $[\alpha]_D^{23}$ +78·6° (*c* 1 in $CHCl_3$) (Found: C, 69·7; H, 6·3. $C_{25}H_{26}O_6$ requires C, 69·3; H, 6·6%).

Allyl 3-O-*Allyl*-2-O-*benzyl*-4,6-O-*benzylidene*-α-D-*galactopyranoside* (XIII).—Compound (XII) was treated with allyl bromide and sodium hydride in refluxing benzene until t.l.c. (chloroform–ether 10 : 1) showed complete conversion of the starting material (R_F 0·35) into the allyl ether (R_F 0·8). The product was isolated in the usual way and was recrystallised from light petroleum (b.p. 60—80°) to give the *allyl pyranoside* (XIII), m.p. 69—71°, $[\alpha]_D$ +93° (*c* 1 in $CHCl_3$) (Found: C, 71·2; H, 6·6. $C_{26}H_{30}O_6$ requires C, 71·2; H, 6·9%).

2,4,6-*Tri*-O-*benzyl*-D-*galactopyranoside* (XXI).—(i) A solution of compound (XIII) (10 g) in methanol (400 ml) and N-hydrochloric acid (40 ml) was heated under reflux for 15 min; t.l.c. (chloroform–ether 10 : 1) then showed complete hydrolysis of the starting material (R_F 0·8) to a product (R_F 0·05). An excess of sodium carbonate was added to neutralise the acid and the solvents were evaporated off. Several portions of water were evaporated from the residue to remove benzaldehyde, and the crude product (XVI) was

[26] (*a*) 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; (*b*) R. D. Guthrie and G. P. B. Mutter, *J. Chem. Soc.*, 1964, 1614.

treated with sodium hydride and benzyl chloride in refluxing benzene until t.l.c. (ether–light petroleum 1 : 2) indicated complete conversion of the starting material (R_F 0) into the benzyl ether (XIX) (R_F 0·5). The product was isolated in the usual way and the excess of benzyl chloride was removed by distillation. The product was treated with potassium t-butoxide in dimethyl sulphoxide [1] until t.l.c. (as before) showed complete conversion of the diallyl derivative (XIX) into the diprop-1-enyl derivative (XX) (R_F 0·7). The product was isolated in the usual way and hydrolysed in acetone–N-hydrochloric acid (9 : 1) at reflux for 15 min. Dilution with water gave a crystalline product which was recrystallised from benzene–light petroleum (b.p. 60—80°) (1 : 1) to give the *product* (XXI), m.p. 123—124°, $[\alpha]_D$ +40·4 ⟶ +37·6° (after 24 h) (*c* 1 in $CHCl_3$) (Found: C, 72·1; H, 6·4. $C_{27}H_{30}O_6$ requires C, 72·0; H, 6·7%).

(ii) Compound (XII) (2 g) was treated with crotyl bromide and sodium hydride in refluxing benzene until t.l.c. (chloroform–ether 10 : 1) showed complete conversion of the starting material (R_F 0·35) into the but-2-enyl ether (XIV) (R_F 0·85). The product isolated in the usual way, was obtained as a syrup which was treated with methanol (80 ml) and N-hydrochloric acid (8 ml) at reflux for 15 min. T.l.c. (as before) showed complete hydrolysis to the product (XVII) (R_F 0), which was isolated as described in the previous section for compound (XVI) and converted into the tribenzyl ether (XXII) (R_F 0·8; ether–light petroleum 1 : 1) as described previously. This product was isolated in the usual way and treated with potassium t-butoxide in dimethyl sulphoxide at room temperature. The course of the reaction was followed by t.l.c. (ether–light petroleum 1 : 1); after 19 h the starting material (R_F 0·8) had been converted into the alcohol (XXIII) (R_F 0·45) together with a trace of the prop-1-enyl glycoside (XXIV) (R_F 0·63). The mixture was then kept at 70° for 3 h after which complete conversion into the prop-1-enyl glycoside (XXIV) had occurred. The oily product was isolated in the usual way and a portion was hydrolysed with acetone–N-hydrochloric acid (9 : 1) at reflux for 15 min to give 2,4,6-tri-*O*-benzyl-D-galactopyranose (XXI), m.p. and mixed m.p. 123—124°.

3-O-*Methyl*-D-*galactose*.—(i) The remainder of compound (XXIV) was treated with sodium hydride and methyl iodide in refluxing benzene until t.l.c. (ether–light petroleum 1 : 2) showed complete conversion into the methyl ether (XXV) (R_F 0·5). The methyl ether was isolated and hydrolysed with acetone–N-hydrochloric acid as already described and the product was treated with hydrogen over 10% palladium–charcoal in glacial acetic acid. When the uptake of hydrogen had ceased the solution was filtered and evaporated and the oily residue was crystallised from methanol–acetone to give 3-*O*-methyl-D-galactose, m.p. 142—144°, $[\alpha]_D$ +105° (final; *c* 0·5 in H_2O) (Found: C, 43·3; H, 7·1. Calc. for $C_7H_{14}O_6$: C, 43·3; H, 7·3%) {lit.,[20] m.p. 143—145°, $[\alpha]_D$ +106·5° (final; *c* 1·6 in H_2O)}.

(ii) Compound (XII) was treated with methyl iodide and sodium hydride in refluxing benzene until t.l.c. (chloroform–ether 10 : 1) showed complete conversion of the starting material (R_F 0·35) into the product (R_F 0·75), which was isolated in the usual way to give the *methyl ether* (XV), m.p. 120—121°, $[\alpha]_D$ +83·6° (*c* 1 in $CHCl_3$) (Found: C, 69·9; H, 6·8. $C_{24}H_{28}O_6$ requires C, 69·9; H, 6·8%). Compound (XV) was hydrolysed in 1·5N-hydrochloric acid–dioxan (2 : 1) at reflux for 2 h and the solution was evaporated to dryness. The residue was taken up in glacial acetic acid and hydrogenated as already described. The product was isolated and recrystallised from methanol–acetone to give 3-*O*-methyl-D-galactose, m.p. and mixed m.p. 142—144°.

6-O-*But*-2-*enyl*-1,2:3,4-*di*-O-*isopropylidene*-D-*galactopyranose* (XXIX).—1,2:3,4-di-*O*-isopropylidene-D-galactopyranose [27] (20 g), crotyl bromide (20 ml), and sodium hydride (5 g) in dry benzene (250 ml) were heated under reflux for 1·5 h; t.l.c. (toluene–acetone 4 : 1) then showed complete conversion of the starting material (R_F 0·4) into the product (R_F 0·8). The excess of sodium hydride was destroyed with methanol and the solution was washed with water and dried (K_2CO_3). The but-2-enyl ether (XXIX) was obtained as an oil; for analysis a portion was distilled, b.p. 125° (bath temperature) at 0·05 mmHg, $[\alpha]_D$ −69° (*c* 1 in $CHCl_3$) (Found: C, 60·7; H, 8·05. $C_{16}H_{26}O_6$ requires C, 61·1; H, 8·3%).

A portion of the product (undistilled, *i.e.* total product) was treated with potassium t-butoxide in dimethyl sulphoxide at 80° for 1 h when t.l.c. (as before) showed complete conversion of the starting material (R_F 0·8) into a product (R_F 0·4) which ran concurrently with 1,2:3,4-di-*O*-isopropylidene-D-galactopyranose.

A portion of compound (XXIX) was hydrolysed with allyl alcohol and hydrogen chloride and the product isolated as described previously [19] for the preparation of allyl 6-*O*-allyl-α-D-galactopyranoside, to give *allyl* 6-O-*but*-2-*enyl*-α-D-*galactopyranoside*, m.p. 132—134°, $[\alpha]_D$ +141·7° (*c* 1 in H_2O) (Found: C, 56·85; H, 8·2. $C_{13}H_{22}O_6$ requires C, 56·9; H, 8·1%).

1,2:3,4-*Di*-O-*isopropylidene*-6-O-(1-*methylallyl*)-D-*galactopyranose* (XXX).—1,2:3,4-Di-*O*-isopropylidene-D-galactopyranose (3 g), 1-methylallyl chloride (25 ml) (Koch–Light Ltd.), and sodium hydride (2 g) in benzene (50 ml) were heated under reflux for 12 h; t.l.c. (toluene–acetone 4 : 1) then showed complete conversion into a product (R_F 0·8). This was isolated as described in the previous section and for analysis a portion was distilled, b.p. 130° (bath temperature) at 0·05 mmHg (Found: C, 61·7; H, 8·4. Calc. for $C_{16}H_{26}O_6$: C, 61·1; H, 8·3%).

A portion of the product (undistilled, *i.e.* total product) was treated with potassium t-butoxide in dimethyl sulphoxide at 80° for 1 h; t.l.c. (as before) then showed partial conversion (*ca.* 40%) of the starting material (R_F 0·8) into a product (R_F 0·4) which ran concurrently with di-*O*-isopropylidene-D-galactose. The heating was continued for 24 h; the remaining starting material had then been converted into a new product (R_F 0·85) which was completely hydrolysed by mercury(II) chloride in the presence of mercury(II) oxide [1b] to give a product which ran concurrently with di-*O*-isopropylidene-D-galactose.

A sample of the mixture of isomers (XXIX) and (XXX) was treated with potassium t-butoxide in dimethyl sulphoxide at 50° for 1 h to decompose compound (XXIX). The products were isolated and chromatographed on alumina and the *1-methylallyl ether* (XXX) was eluted with ether–light petroleum (1 : 1) and distilled; b.p. 130° (bath temperature) at 0·05 mmHg, $[\alpha]_D$ −65·8° (*c* 1 in $CHCl_3$) (Found: C, 61·5; H, 8·3. $C_{16}H_{26}O_6$ requires C, 61·1; H, 8·3%). Compound (XXX) was treated with potassium t-butoxide in dimethyl sulphoxide at 80° for 10 h; t.l.c. (as before) then showed complete conversion into the product (R_F 0·85), which was presumed to be the enol ether (XXXI) but was not further investigated.

Allyl 2,6-*Di*-O-*benzyl*-α-D-*galactopyranoside* (X).—Allyl

[27] R. S. Tipson, *Methods Carbohydrate Chem.*, 1963, **2**, 246.

6-*O*-benzyl-3,4-*O*-isopropylidene-α-D-galactopyranoside [1a] (VII) (10 g) was converted into the di-*O*-benzyl ether (VIII) as described previously for related compounds, and the product was heated under reflux with methanol (70 ml) and N-hydrochloric acid (10 ml) for 30 min. T.l.c. (ether–light petroleum 1 : 1) then showed complete hydrolysis of the isopropylidene group from the starting material (R_F 0·75). The product was isolated and chromatographed on alumina. Elution with ether removed impurities and elution with ether–methanol (4 : 1) gave *allyl* 2,6-*di*-O-*benzyl*-α-D-*galactopyranoside* (X) as a syrup. For analysis a portion was distilled; b.p. 200° (bath temperature) at 0·005 mmHg, $[\alpha]_D$ +95·8° (*c* 0·7 in $CHCl_3$) (Found: C, 68·5; H, 7·1. $C_{23}H_{28}O_6$ requires C, 69·0; H, 7·05%).

Compound (X) (1·6 g, 4 mmol), allyl bromide (0·62 g, 5 mmol), and powdered sodium hydroxide (5 g) in benzene (25 ml) were stirred at room temperature for 24 h; t.l.c. (ether–light petroleum 1 : 1) then showed the presence of starting material (R_F 0·1), monoallyl derivative(s) (R_F 0·4), and diallyl derivative (R_F 0·75) in approximately equal proportions.

Allyl 2-*Benzamido*-3,4,6-*tri*-O-*benzyl*-2-*deoxy*-β-D-*glucopyranoside* (XXXIV).—Allyl 4,6-di-*O*-acetyl-2-benzamido-3-*O*-benzyl-2-deoxy-β-D-glucopyranoside [25] (16·5 g) was treated with N-sodium hydroxide in methanol (70 ml) at 50° for 10 min. The solution was neutralised with acetic acid and the solvents were evaporated off. The residue was triturated with water and the diol (XXXIII) was filtered off and dried thoroughly. The diol (XXXIII) was then carefully added to a mixture of benzyl chloride (40 ml) and sodium hydride (9 g) in tetrahydrofuran (300 ml) and when the initial reaction had subsided the mixture was heated under reflux for 7 h. T.l.c. (acetone–toluene 1 : 1) then indicated complete conversion of the starting material (R_F 0·4) into a product (R_F 0·85). Methanol was added to destroy the excess of sodium hydride and water (200 ml) was added. The solvents were evaporated off and the product was extracted with chloroform and recrystallised from benzene–light petroleum (b.p. 60—80°) to give *compound* (XXXIV) (14 g, 71%), m.p. 136·5—139·5°, $[\alpha]_D$ +17·1° (*c* 1 in $CHCl_3$) (Found: C, 74·4; H, 6·6; N, 2·6. $C_{37}H_{39}NO_6$ requires C, 74·85; H, 6·6; N, 2·4%).

2-*Benzamido*-3,4,6-*tri*-O-*benzyl*-2-*deoxy*-D-*glucopyranose* (XXXVI).—The allyl glycoside (XXXIV) (6 g) was added to a soluton of potassium t-butoxide (1 g) in dry dimethyl sulphoxide (50 ml). The mixture was kept at 60° for 3 h and then poured into water. The product was extracted with chloroform and heated under reflux in acetone (90 ml) and N-hydrochloric acid (10 ml) for 15 min. On cooling, the product (3·5 g) crystallised out and was recrystallised from ethanol to give compound (XXXVI), m.p. 215—217°, $[\alpha]_D$ +88·6° (*c* 0·48 in pyridine) (Found: C, 73·5; H, 6·3; N, 2·4. Calc. for $C_{34}H_{35}NO_6$: C, 73·8; H, 6·4; N, 2·5%) {lit.,[24a] m.p. 221—222°, $[\alpha]_D^{20}$ +89° (*c* 0·59 in pyridine)}.

2-*Acetamido*-3,4,6-*tri*-O-*benzyl*-2-*deoxy*-D-*glucopyranose* (XXXVIII).—A solution of compound (XXXVI) in dioxan (95 ml), water (28 ml), and concentrated hydrochloric acid (11 ml) was heated under reflux for 27 h. T.l.c. (chloroform–methanol 10 : 1) on borate-impregnated plates showed almost complete conversion of the starting material (R_F 0·8) into a major product (R_F 0·5) with only traces of other products. The mixture was diluted with water (100 ml) and evaporated to *ca.* 50 ml, and the residue was diluted with water (100 ml). The crude hydrochloride (XXXVII) [24c] (1·9 g) which separated was filtered off.

Compound (XXXVII) (650 mg) was dissolved in methanol (10 ml) and sodium acetate (200 mg) and acetic anhydride (2 ml) were added. The product which separated (400 mg) was recrystallised from methanol to give the *acetamido-derivative* (XXXVIII), m.p. 208·5—210·5°, $[\alpha]_D$ +62·1° (*c* 0·43 in pyridine) (Found: C, 70·7; H, 6·7; N, 2·6. Calc. for $C_{29}H_{33}NO_6$: C, 70·9; H, 6·8; N, 2·85%) {lit.,[24a] m.p. 218—219°, $[\alpha]_D^{20}$ +63° (*c* 0·93 in pyridine)}.

3,4,6-*Tri*-O-*benzyl*-2-*deoxy*-2-(2,4-*dinitroanilino*)-D-*glucopyranose* (XXXIX).—A mixture of the crude hydrochloride (XXXVII) (500 mg), sodium hydrogen carbonate (100 mg), and 1-fluoro-2,4-dinitrobenzene (0·15 ml) in dioxan–water (4 : 1; 20 ml) was stirred at room temperature for 4 h; t.l.c. (chloroform–methanol 10 : 1) then indicated almost complete conversion of the starting material (R_F 0·3) into a major product (R_F 0·7). The mixture was diluted with water and extracted with ether and the product was recrystallised from ether–light petroleum to give *compound* (XXXIX), m.p. 145—146°, $[\alpha]_D$ +36·9° (*c* 1 in $CHCl_3$) (Found: C, 64·3; H, 5·35; N, 6·7. $C_{33}H_{33}N_3O_9$ requires C, 64·4; H, 5·4; N, 6·8%).

Allyl 2-*Benzamido*-3,4,6-*tri*-O-*benzyl*-2-*deoxy*-β-D-*galactopyranoside* (XLI).—The diacetate (XL) [25] (4·6 g) was deacetylated and the diol was benzylated in the same way as described for the glucopyranoside derivative. The product was recrystallised from benzene–light petroleum (b.p. 60—80°) to give the *allyl galactopyranoside* (XLI) (3·7 g), m.p. 155—159°, $[\alpha]_D$ +16·6° (*c* 0·95 in $CHCl_3$) (Found: C, 74·9; H, 6·2; N, 2·3. $C_{37}H_{39}NO_6$ requires C, 74·85; H, 6·6; N, 2·4%).

2-*Benzamido*-3,4,6-*tri*-O-*benzyl*-2-*deoxy*-D-*galactopyranose* (XLIII).—Compound (XLI) (4·25 g) was isomerised with potassium t-butoxide in dimethyl sulphoxide to give the prop-1-enyl glycoside (XLII) and the product was hydrolysed with acid as described for the corresponding *gluco*-derivatives. The *galactopyranose* (XLIII) (3·7 g), recrystallised from toluene–light petroleum (b.p. 60—80°), had m.p. 175·5—179·5°, $[\alpha]_D$ +156·6 ⟶ +150·1° (after 21 h) (*c* 0·85 in $CHCl_3$) (Found: C, 74·0; H, 6·4; N, 2·4. $C_{34}H_{35}NO_6$ requires C, 73·8; H, 6·4; N, 2·5%).

2-*Acetamido*-3,4-6-*tri*-O-*benzyl*-2-*deoxy*-D-*galactopyranose* (XLIV).—The benzamido-derivative (XLIII) was hydrolysed to the hydrochloride and the product acetylated (as described for the *gluco*-derivative) to give the acetamido-derivative (XLIV), m.p. 183—185°, $[\alpha]_D$ +69·7° (*c* 1 in $CHCl_3$) (Found: C, 70·5; H, 6·5; N, 2·7. Calc. for $C_{29}H_{33}NO_6$: C, 70·9; H, 6·8; N, 2·85%) {lit.,[24a] m.p. 184—185°, $[\alpha]_D^{20}$ +72° (*c* 0·5 in $CHCl_3$)}

3-O-*But*-2-*enyl*-1,2-*dideoxy*-5,6-O-*isopropylidene*-2′-*phenyl*-β-D-*glucofuranoso*[2,1-d]-Δ²′-*oxazoline* (XLVI).—The oxazoline (XLV) [28] (5 g), but-2-enyl bromide (5 ml), and sodium hydride (1 g) in dry benzene (100 ml) were heated under reflux for 3 h; t.l.c. (ether–light petroleum 1 : 1) then indicated complete conversion of the starting material (R_F 0·25) into the product (R_F 0·8). Methanol was added to destroy the excess of sodium hydride and the solution was washed with water and dried (K_2CO_3). The product was recrystallised from light petroleum (b.p. 60—80°) to give the *phenyloxazoline* (XLVI) (4·5 g), m.p. 93—95°, $[\alpha]_D$ −0·5° (*c* 1 in $CHCl_3$) (Found: C, 66·7; H, 6·9; N, 4·0. $C_{20}H_{25}NO_5$ requires C, 66·8; H, 7·0; N, 3·9%).

[28] R. Gigg and C. D. Warren, *J. Chem. Soc.*, 1965, 1351; S. Konstas, I. Photaki, and L. Zervas, *Chem. Ber.*, 1959, **92**, 1288; B. Lindberg and H. Agback, *Acta Chem. Scand.*, 1964, **18**, 185.

Allyl 4,6-*Di*-O-*acetyl*-2-*benzamido*-3-O-*but*-2-*enyl*-2-*deoxy*-β-D-*glucopyranoside* (XLVIII).—The phenyloxazoline. (XLVI) (3 g) in allyl alcohol (60 ml) containing toluene-*p*-sulphonic acid (1·1 g) was kept at room temperature for 3 h; t.l.c. (toluene–acetone 1 : 1) then indicated complete conversion of the starting material (R_F 0·9) into a new product (R_F 0·4). An excess of sodium hydrogen carbonate was added and the allyl alcohol was evaporated off. The residue was extracted with hot ethyl acetate (100 ml); evaporation of the solvent gave the crude diol (XLVII), which was acetylated with acetic anhydride in pyridine (1 : 2) at 50° for 3 h. The mixture was poured into water and the product was filtered off and recrystallised from benzene–light petroleum (b.p. 60—80°) to give the *diacetate* (XLVIII) (3 g), m.p. 165—167°, $[\alpha]_D$ +31·2° (*c* 1 in $CHCl_3$) (Found: C, 62·7; H, 6·6; N, 3·1. $C_{24}H_{31}NO_8$ requires C, 62·5; H, 6·8; N, 3·0%).

Allyl 2-*Benzamido*-4,6-*di*-O-*benzyl*-3-O-*but*-2-*enyl*-2-*deoxy*-β-D-*glucopyranoside* (XLIX).—The diacetate (XLVIII) (1·5 g), dissolved in N-sodium hydroxide in methanol (20 ml), was kept at 50° for 15 min. An excess of acetic acid was added and the solution was evaporated to dryness. Water (10 ml) was added and the diol (XLVII) was filtered off and dried thoroughly. It was then dissolved in tetrahydrofuran (50 ml) and sodium hydride (2 g) was added slowly. Benzyl chloride (3 ml) was added and the solution was heated under reflux for 3 h. T.l.c. (toluene–acetone 2 : 1) then showed complete conversion of the starting material (R_F 0·25) into a product (R_F 0·75). Methanol was added to decompose the excess of sodium hydride and water (50 ml) was added. The mixture was evaporated to *ca.* 20 ml and light petroleum (50 ml) was added. The solid product was collected and recrystallised from benzene–petroleum (b.p. 60—80°) to give *compound* (XLIX) (1·5 g), m.p. 142—144°, $[\alpha]_D$ +17·6° (*c* 1 in $CHCl_3$) (Found: C, 73·6; H, 7·1; N, 2·8. $C_{34}H_{39}NO_6$ requires C, 73·2; H, 7·05; N, 2·5%).

Prop-1-*enyl* 2-*Benzamido*-4,6-*di*-O-*benzyl*-2-*deoxy*-β-D-*glucopyranoside* (LI).—The allyl glycoside (XLIX) (200 mg) was added to a solution of potassium t-butoxide (200 mg) in dimethyl sulphoxide (5 ml) at room temperature and the course of the reaction was followed by t.l.c. (toluene–acetone 2 : 1) (for this purpose a portion of the solution was diluted with water and the products were extracted with ethyl acetate). After 10 h the starting material (R_F 0·75) had been completely converted into the alcohol (L) (R_F 0·55). When the ethyl acetate solution was treated with mercury(II) chloride [1b] (to hydrolyse any prop-1-enyl ether) only a trace of a slower moving product (R_F 0·45) was visible, indicating that little isomerisation of the allyl group to the prop-1-enyl group had occurred. The solution was then heated at 80° for 4 h; t.l.c. [as before including the mercury(II) chloride treatment] indicated complete conversion into the prop-1-enyl glycoside (LI). The solution was cooled and poured into water and the product was filtered off and recrystallised from aqueous methanol to give the *prop*-1-*enyl glycoside* (LI) (100 mg), m.p. 165—167°, $[\alpha]_D$ −17·1° (*c* 0·9 in $CHCl_3$) (Found: C, 71·5; H, 6·3; N, 2·6. $C_{30}H_{33}NO_6$ requires C, 71·55; H, 6·6; N, 2·8%).

Prop-1-*enyl* 2-*Benzamido*-3,4,6-*tri*-O-*benzyl*-2-*deoxy*-β-D-*glucopyranoside* (LII).—The prop-1-enyl glycoside (LI) (200 mg) was treated with benzyl chloride and sodium hydride in refluxing tetrahydrofuran for 3 h; t.l.c. (acetone–toluene 3 : 1) then showed complete conversion of the starting material (R_F 0·5) into the product (R_F 0·77). Isolation in the usual way and recrystallisation from light petroleum (b.p. 60—80°) gave the product (LII) (150 mg), m.p. 173—175°, $[\alpha]_D$ 0 ± 1° (*c* 1 in $CHCl_3$) (Found: C, 75·1; H, 6·7; N, 2·4. $C_{37}H_{39}NO_6$ requires C, 74·85; H, 6·6; N, 2·4%). The compound was hydrolysed with mercury(II) chloride in aqueous acetone [1b] and the product was recrystallised from ethanol to give 2-benzamido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranose (XXXVI), m.p. and mixed m.p. (with the material prepared as already described) 215—217°.

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