Nitrogen-containing Carbohydrate Derivatives. Part XXX.† Preparation and Reactions of Methyl 4,6-*O*-Benzylidene-2,3-dideoxy-2,3-epimino-D-gulo- and -D-talopyranosides

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Methyl 4,6-*O*-benzylidene-α- and β-galactopyranosides have been converted into the α- and β-anhydro-gulosides and -talosides, which in turn have been subjected to azidolysis conditions. The major products were azido-idosides, but minor products were isolated in some cases and their structures were investigated. The azido-idosides were sulphonylated and treated with lithium aluminium hydride to give the title compounds (α- and β-*gulo*- and β-*talo*-). Deamination of the epimines gave 2,3-unsaturated sugars. Azidolysis of the α-*talo*-epimine and subsequent reactions gave methyl 2,3-acetamido-4,6-*O*-benzylidene-2,3-dideoxy-α-D-idopyranoside.

METHYL 4,6-*O*-BENZYLIDENE-2,3-DIDEOXY-2,3-EPIMINO-α-D-ALLO- AND -MANNO-PYRANOSIDES have been prepared previously from azido-sulphonates, and the reactions of these compounds with a variety of nucleophiles have been used for the synthesis of 2,3-difunctional nitrogen-containing derivatives of D-glucose and D-altrose. The aim of the work now described was to synthesise the corresponding 2,3-epimino-derivatives in the D-gulose and D-talose series.

Many of the methods used for the synthesis of the *allo*- and *manno*-epimines were not suitable for this work. In particular, the routes through *trans*-diequatorial precursors could not be used since the 2- and 3-amino-deoxy-D-galactose derivatives which would be necessary are much less readily available than are their counterparts in the *gluco*-series. The 2- (or 3-) sulphonates of D-idosides having a nitrogen function at C-3 (or C-2) were therefore selected as precursors. These have the advantage of reasonable accessibility, and have the substituents at C-2 and C-3 in a (formal) *trans*-diaxial orientation, that is, in a stereochemical situation favourable for ring closure.

Methyl α- and β-D-galactopyranosides were prepared from the free sugar by the highly efficient method of Frahn and Mills,[1] so that subsequent syntheses could be carried out in both anomeric series. Methyl 4,6-*O*-benzylidene-α- and β-D-galactopyranoside were prepared by treatment of the glycosides with benzaldehyde and zinc chloride; the published procedure[2] was modified slightly to allow the use of the monohydrate of the α-galactoside, thus avoiding the tedious procedure required to prepare anhydrous material. The physical characteristics of the α-product were in agreement with those reported by Bell and Greville,[3] rather than with

† Part **XXIX**, R. D. Guthrie and G. J. Williams, *J.C.S. Perkin I*, 1972, 2619.

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[1] J. L. Frahn and J. A. Mills, *Austral. J. Chem.*, 1965, **18**, 1303.

[2] E. Sorkin and T. Reichstein, *Helv. Chim. Acta*, 1945, **28**, 1.

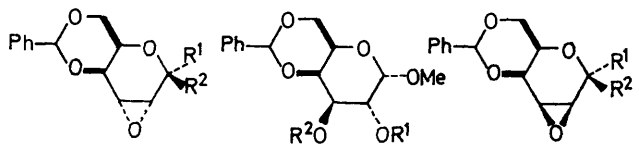
[3] D. J. Bell and G. D. Greville, *J. Chem. Soc.*, 1955, 1136.

those originally claimed [2] (which have since been conceded [4] to be incorrect).

Published procedures exist for the preparation of methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-gulopyranoside (1) *via* the 2-*O*-benzoyl-3-*O*-tosyl-galactoside (3),[5] and of methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-talopyranoside (6) *via* the 3-*O*-benzoyl-2-*O*-tosyl-galactoside (4) [5] or the 2-monotosylate (5).[6] Since both anhydrosugars were required, however, it was considered more convenient to treat methyl 4,6-*O*-benzylidene-2,3-di-*O*-tosyl-α-D-galactopyranoside with methanolic sodium methoxide, which gave a separable mixture of the anhydroguloside (1) and the anhydrotaloside (6) as reported [5] (and not the single major product described in the earlier paper [2]). When methyl 4,6-*O*-benzylidene-α-D-galactopyranoside was treated with 1 equiv. of tosyl chloride in pyridine a mixture was obtained from which the ditosylate was readily separated. The remainder, which contained, presumably, a mixture of the 2- and 3-tosylates, was treated with sodium methoxide to give a mixture of composition similar to that obtained by similar treatment of the ditosylate.

Methyl 4,6-*O*-benzylidene-2,3-di-*O*-tosyl-β-D-galactopyranoside gave only methyl 2,3-anhydro-4,6-*O*-benzylidene-β-D-talopyranoside (7) when treated with sodium methoxide, as previously reported.[2,7] The low yield (33%) of epoxide was presumably due, at least in part, to attack by methoxide ion on anhydro-sugar already formed to give methyl 4,6-*O*-benzylidene-3-*O*-methyl-β-D-idopyranoside, a reaction known to occur readily.[7]

Treatment of methyl 4,6-*O*-benzylidene-3-*O*-tosyl-β-D-galactopyranoside with sodium methoxide gave the

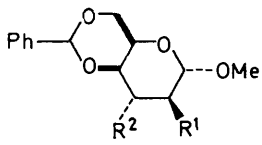


(1) R^1 = OMe, R^2 = H (3) R^1 = Bz, R^2 = Ts (6) R^1 = OMe, R^2 = H
(2) R^1 = H, R^2 = OMe (4) R^1 = Ts, R^2 = Bz (7) R^1 = H, R^2 = OMe
(5) R^1 = Ts, R^2 = H

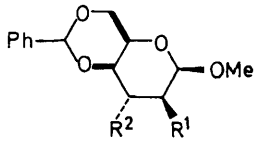
2,3-anhydro-β-gulopyranoside (2),[2] but a more convenient procedure, in which the crude product from the partial tosylation was treated directly with sodium methoxide, was also used.

The four azido-idopyranosides were prepared by treatment of the appropriate 2,3-epoxides with sodium azide and ammonium chloride in boiling 2-methoxyethanol. Treatment of the α-*talo*-epoxide (6) in this way had been found [8] to give the 3-azido-3-deoxy-α-D-idoside (8). Reduction gave the amino-alcohol (10), which was by conversion into the amide (11), previously prepared [9,10] by ammonolysis of the anhydro-taloside (6) followed by *N*-acetylation. The previous assignment [9] of configuration to this series rested on the fact that the acetamido-compound (11) was different from methyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-galactopyranoside, the only other compound which was likely to have resulted from the epoxide (6). Positive evidence for the D-*ido*-configuration of (10) was obtained from the c.d. spectrum of the cuprammonium complex,[11] which showed a negative band at 600 nm.

Azidolysis of the 2,3-anhydro-α-guloside (1) gave the



	R^1	R^2
(8)	OH	N_3
(9)	OTs	N_3
(10)	OH	NH_2
(11)	OH	NHAc
(12)	N_3	OH
(13)	N_3	OTs
(14)	NH_2	OH
(15)	NHAc	OH
(16)	NHAc	OAc
(17)	NH_2	OTs
(18)	NHAc	OTs
(19)	NHBz	OTs



	R^1	R^2
(20)	OH	N_3
(21)	OH	NH_2
(22)	OH	NHAc
(23)	OAc	NHAc
(24)	OTs	N_3
(25)	OMs	N_3
(26)	OAc	N_3
(27)	N_3	OH
(28)	NH_2	OH
(29)	NHAc	OH

2-azido-2-deoxy-α-D-idoside (12), catalytic hydrogenation of which gave the 2-amino-2-deoxy-idoside (14), a hygroscopic compound, that was characterised as its known *N*-acetyl derivative (15) [10] and its *NO*-diacetyl derivative (16), previously prepared by alternative routes.[9,10] The D-*ido*-configuration of this series had already been established by a degradative method: [9] c.d. studies on the cuprammonium complex of (14) confirmed this (negative band at 590 nm).[11] Catalytic hydrogenation of the tosylate (13) of (12) gave syrupy methyl 2-amino-4,6-*O*-benzylidene-2-deoxy-3-*O*-tosyl-α-D-idopyranoside (17), which was characterised as its crystalline *N*-acetyl and *N*-benzoyl derivatives, (18) and (19). The acetamido-tosylate (18) was also prepared by tosylation of methyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-idopyranoside (15).

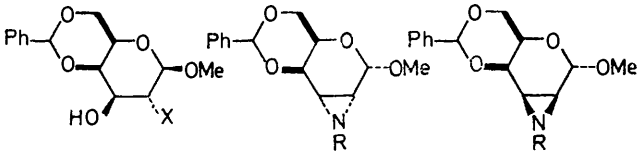
Two compounds were produced when the β-anhydrotaloside (7) was subjected to azidolysis conditions. Both showed i.r. absorptions in the 2100 and 3300 cm^{-1} regions, characteristic of azido-hydroxy-compounds, and the major product was tentatively assigned the β-D-idopyranoside structure (20) by analogy with the assignments made for the structures of the main products obtained [7] by ring-opening of the same epoxide with other nucleophiles. The 3-amino-idoside (21) was obtained by catalytic hydrogenation of the azide, and characterised as its *N*-acetyl (22) and *NO*-diacetyl

[4] T. Reichstein, quoted in ref. 3.
[5] M. Gyr and T. Reichstein, *Helv. Chim. Acta*, 1945, **28**, 226.
[6] F. Reber and T. Reichstein, *Helv. Chim. Acta*, 1945, **28**, 1164.
[7] L. G. Wiggins, *J. Chem. Soc.*, 1944, 522.
[8] S. Hanessian and T. H. Haskell, *J. Org. Chem.*, 1965, **30**, 1080.
[9] J. G. Buchanan and K. J. Miller, *J. Chem. Soc.*, 1960, 3392.
[10] R. W. Jeanloz, Z. Tarasiejska Glazer, and D. A. Jeanloz, *J. Org. Chem.*, 1961, **26**, 532.
[11] R. D. Guthrie and J. A. Liebmann, to be published.

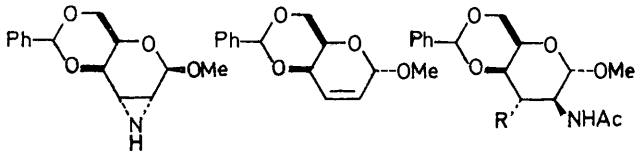
(23) derivatives. The latter has been prepared by Wiggins,[7] without proof of configuration, by ammonolysis of the epoxide (7) followed by acetylation. The *ido*-configuration for the series was again confirmed by c.d. studies of the cuprammonium complex of (21) (no measurable effect around 590 nm).[11]

A minor product was obtained in less than 2% yield and no physical characteristics, other than the i.r. spectrum, were recorded. It seems likely, however, that this compound was methyl 2-azido-4,6-*O*-benzylidene-2-deoxy-β-D-galactopyranoside (30). The 2-*O*-methyl-galactoside (31) has been isolated by Wiggins[7] as the minor product from the reaction of the epoxide (7) with sodium methoxide.

Attempts to prepare the tosylate (24) of the azido-idoside (20) gave a compound which, although it had the expected i.r. spectrum, could be crystallised only with difficulty, and failed to give satisfactory analytical figures. A crystalline 2-*O*-mesyl-derivative (25) was prepared, however.



(30) X = N_3 (32) R = H (34) R = H
(31) X = OMe (33) R = Ac (35) R = Ac



(36) (37) (38) R = N_3
(39) R = NHAc

Azidolysis of the 2,3-anhydro-β-guloside (2) gave a mixture from which the 2-azido-2-deoxy-β-D-idoside (27) was obtained in 40% yield. Reduction gave a syrupy amine (28), characterised as its *N*-acetyl derivative (29). Studies[11] of the cuprammonium complex of (28) confirmed the *ido*-configuration.

The minor product, corresponding to about 20% of the starting material, showed no i.r. absorption due to azido-groups and was shown (t.l.c.) to contain two components in approximately equal amounts. These were not identified. The mass spectrum contained peaks at *m/e* values up to 545 and it therefore seems likely that a dimeric substance was present.

Treatment of the azide (27) with tosyl chloride in pyridine, even at elevated temperature, resulted in no reaction. Mesyl chloride in pyridine at −20° caused partial conversion of the azido-alcohol into a more mobile compound (t.l.c.) after 1 day. Re-treatment of the resulting mixture at 0° for a further day gave a semicrystalline material after the usual work-up, but t.l.c. showed this to contain only highly polar material, presumably arising from decomposition.

Jeanloz *et al.* have prepared a mixture of the 2- and 3-acetamido-idosides (15) and (11) by acetylation of the material obtained from treatment of methyl 4,6-*O*-benzylidene-2,3-di-*O*-tosyl-α-D-galactopyranoside with ammonia in methanol containing sodium methoxide.[10] In a similar attempt to by-pass the isolation of the epoxide, methyl 4,6-*O*-benzylidene-2,3-di-*O*-tosyl-β-D-galactopyranoside was treated with sodium azide in methanol containing sodium methoxide. A low yield of a crystalline material was obtained, shown by i.r. spectroscopy to contain azido- and hydroxy-groups. The spectrum was similar to that of methyl 3-azido-4,6-*O*-benzylidene-3-deoxy-β-D-idopyranoside (20), but neither the m.p. of the compound, nor its chromatographic properties coincided with those of the authentic material or of the 2-azido-idoside (27). It was not further investigated.

The azido-sulphonates (9), (13), and (25) are potential precursors of 2,3-epimino-sugars; *vic*-azido-sulphonates have previously been converted into 2,3-epimino-pyranosides[12-14] and other epimino-sugar derivatives.[15-25] The Raney nickel–hydrazine hydrate reagent first used to effect the conversion[13,26] can give rise to low yields of epimine,[14] complex mixtures,[18] and reduced compounds.[27] This is doubtless due to the lability of the epimine ring towards the reagent. Lithium aluminium hydride appears to be the reagent of choice for the ring closure reaction: the heterocyclic ring, once formed, remains unaffected by the hydride.

Thus, methyl 3-azido-4,6-*O*-benzylidene-3-deoxy-2-*O*-tosyl-α-D-idopyranoside (9), when treated with lithium aluminium hydride in boiling tetrahydrofuran, gave the 2,3-epimino-α-D-gulopyranoside (32) in 68% yield, characterised by the sharp absorption band at 3270 cm^{-1} due to the stretching vibration of the weak N–H bond,[28] and by the appearance of a two-proton n.m.r.

[12] R. D. Guthrie, D. Murphy, D. H. Buss, L. Hough, and A. C. Richardson, *Proc. Chem. Soc.*, 1963, 84.
[13] R. D. Guthrie and D. Murphy, *J. Chem. Soc.*, 1963, 5288.
[14] G. J. Williams, D.Phil. Thesis, University of Sussex, 1970.
[15] J. Cleophax, S. D. Gero, J. Hildesheim, R. D. Guthrie, and C. W. Smith, *Chem. and Ind.*, 1969, 784.
[16] J. Cleophax, S. D. Gero, J. Hildesheim, A. M. Sepulchre, R. D. Guthrie, and C. W. Smith, *J. Chem. Soc.* (*C*), 1970, 1385.
[17] J. Cleophax, J. Hildesheim, A. M. Sepulchre, and S. D. Gero, *Bull. Soc. chim. France*, 1969, 153.
[18] J. Cleophax, S. D. Gero and J. Hildesheim, *Chem. Comm.*, 1968, 94; J. Hildesheim, J. Cleophax, A. M. Sepulchre and S. D. Gero, *Carbohydrate Res.*, 1969, **9**, 315.
[19] J. Cleophax, J. Hildesheim, A. M. Sepulchre, and S. D. Gero, *Compt. rend.*, 1968, **226***C*, 720.
[20] H. Saeki, T. Iwashige, and H. Ohki, *Chem. and Pharm. Bull.* (*Japan*), 1968, **16**, 188.
[21] H. Saeki and E. Ohki, *Chem. and Pharm. Bull.* (*Japan*), 1968, **16**, 2471.
[22] H. Saeki and E. Ohki, *Chem. and Pharm. Bull.* (*Japan*), 1969, **17**, 1664.
[23] H. Saeki and E. Ohki, *Chem. and Pharm. Bull.* (*Japan*), 1968, **16**, 2477.
[24] A. D. Barford and A. C. Richardson, *Carbohydrate Res.*, 1970, **14**, 217.
[25] A. D. Barford and A. C. Richardson, *Carbohydrate Res.*, 1970, **14**, 231.
[26] W. Meyer zu Reckendorf, *Chem. Ber.*, 1965, **98**, 93.
[27] C. F. Gibbs and L. Hough, *Chem. Comm.*, 1969, 1210.
[28] D. H. Buss, L. Hough, and A. C. Richardson, *J. Chem. Soc.*, 1963, 5295.

signal due to the aziridine ring protons at high field.[29,30] Further characterisation was achieved by conversion of the epimine into its *N*-acetyl derivative (33).

Treatment of methyl 2-azido-4,6-*O*-benzylidene-2-deoxy-3-*O*-tosyl-α-D-idopyranoside (13) with lithium aluminium hydride, as for the 3-azido-compound (9), gave the 2,3-epimino-α-D-talopyranoside (34), which was isolated in 19% yield and characterised like the *gulo*-epimine (32). A higher yield of product was isolated when the mixture obtained after removal of the excess of lithium aluminium hydride and the resulting inorganic by-products was treated with acetic anhydride in pyridine. A 45% yield of *N*-acetylepimine (35) was obtained in this way. Treatment of (35) with a trace of sodium in methanol gave the free epimine (34).

Two by-products were isolated by p.l.c. from the acetylated mixture, one of which was methyl 2-acetamido-3-*O*-acetyl-4,6-*O*-benzylidene-2-deoxy-α-D-idopyranoside (16); a second, syrupy compound was also isolated but no conclusive assignments could be made. It is thus clear that the low yield of epimine produced from the 2-azido-3-tosyl-idoside (13) is due, at least in part, to competition from side-reactions: hydrolysis of the sulphonate-group in the reaction medium evidently competes with the internal displacement reaction. There is no reason to suppose that the displacement reaction itself should be less favourable in this case than for the 3-azido-2-tosylate (9): the opposite would indeed be expected, since it is well known that displacement of sulphonyloxy-groups at C-2 proceeds only with difficulty. It seems therefore that the 3-*O*-tosyl group must be particularly susceptible to hydrolysis.

Methyl 2-amino-4,6-*O*-benzylidene-2-deoxy-3-*O*-tosyl-α-D-idopyranoside (17) and its *N*-acetyl and *N*-benzoyl derivatives, (18) and (19), should also be suitable precursors of the *talo*-epimine (34). Lithium aluminium hydride in tetrahydrofuran has been found to be a good reagent for conversion of *trans*-acylamino-sulphonates into epimines;[12,28,31,32] on treatment with this reagent methyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-3-*O*-tosyl-α-D-idopyranoside (18) gave a mixture which was shown by t.l.c. to contain about 80% of the epimine (34).

In the β-series only methyl 3-azido-4,6-*O*-benzylidene-3-deoxy-2-*O*-mesyl-β-D-idopyranoside (25) was available as a precursor for epimine synthesis. Treatment of this compound with lithium aluminium hydride in tetrahydrofuran gave the 2,3-epimino-β-D-gulopyranoside (36) in 82% yield, which was characterised, as before, by i.r. and n.m.r. spectra.

It has been found[33] that treatment of methyl 4,6-*O*-benzylidene-2,3-dideoxy-2,3-epimino-α-D-allo- and -manno-pyranosides with sodium nitrite in aqueous acetic acid causes loss of the epimine group and smooth conversion into the corresponding 2,3-unsaturated sugar. This reaction was applied to the 2,3-dideoxy-2,3-epimino-α-D-gulo- and -talo-sides, (32) and (34), both of which gave the known[34] methyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-*threo*-hex-2-enopyranoside (37). The yellow *N*-nitroso-intermediate formed from the *gulo*-epimine (32) was found to decompose more readily than that formed from the *talo*-epimine (34).

Treatment of methyl 4,6-*O*-benzylidene-2,3-dideoxy-2,3-epimino-α-D-talopyranoside (34) with sodium azide and ammonium chloride gave, after acetylation, the 2-acetamido-3-azido-2,3-dideoxy-α-D-idoside (38), the configuration of which was assigned by analogy with openings of the corresponding epoxide and of the *manno*-epimine.[14,35] Hydrogenation of (38) and *N*-acetylation gave methyl 2,3-diacetamido-4,6-*O*-benzylidene-2,3-dideoxy-α-D-idopyranoside (39), the first derivative of 2,3-diamino-2,3-dideoxyidose to have been synthesised.

Attempted azidolysis of the α-*gulo*-epimine (32) under the same conditions resulted in essentially no change. This low reactivity is in keeping with the low reactivity of the corresponding epoxide in comparison with other similar epoxides.[11]

EXPERIMENTAL

All organic extracts were washed, dried ($MgSO_4$), and evaporated *in vacuo* at $<50°$. T.l.c. and p.l.c. were performed on silica gel (Merck GF_{254}). Compounds were identified where necessary by m.p., $[\alpha]_D$, i.r., n.m.r., and t.l.c. comparisons. Optical rotations are recorded for solutions in chloroform unless otherwise stated, and were determined at 20—24°. Spectral data (n.m.r. and i.r.) were consistent with the assigned structures: any special features are mentioned in the Discussion section. Detailed n.m.r. data are available in Supplementary Publication No. SUP 20894 (8 pp.).*

Partial Tosylation of Methyl 4,6-O-*Benzylidene-α-galactopyranoside and Treatment of the Product with Sodium Methoxide.*—Methyl 4,6-*O*-benzylidene-α-D-galactopyranoside[2] (5 g) in dry pyridine (25 ml) was treated at −5° with tosyl chloride (3·5 g) in dry pyridine (15 ml). After 6 h at 5° followed by 4 days at 20° the mixture was poured on ice (*ca.* 50 g) and the resulting mixture was extracted with chloroform. Extraction of the resulting white solid with methanol and filtration of the cooled extract gave the ditosylate (13%) [identical (t.l.c. in 5% methanol–chloroform) with authentic material]. The white syrup obtained by evaporation of the methanolic solution was redissolved in methanol (50 ml) and treated with methanol (18 ml) containing sodium (1·1 g). The solution was boiled for 18 h, then poured on ice (*ca.* 150 g), and the aqueous mixture was extracted with 1,2-dichloroethane (3 × 100 ml) to yield the anhydrotaloside (6) (6%), m.p. 234—235° (from benzene). Recrystallisation of the residual material from ethyl acetate gave the anhydro-guloside (1) (12%),

* For details of Supplementary Publications see Notice to Authors No. 7 [*J. Chem. Soc.* (*A*), 1970, Index Issue].

[29] D. H. Buss, L. Hough, L. D. Hall, and J. F. Manville, *Tetrahedron*, 1965, **21**, 69.
[30] F. Sweet and R. K. Brown, *Canad. J. Chem.*, 1968, **46**, 1481.
[31] Y. Ali, A. C. Richardson, C. F. Gibbs, and L. Hough, *Carbohydrate Res.*, 1968, **7**, 255.
[32] C. F. Gibbs, L. Hough, and A. C. Richardson, *Carbohydrate Res.*, 1965, **1**, 290.
[33] R. D. Guthrie and D. King, *Carbohydrate Res.*, 1966, **3**, 128.
[34] R. U. Lemieux, E. Fraga, and K. A. Watanabe, *Canad. J. Chem.*, 1968, **46**, 61.
[35] R. D. Guthrie and D. Murphy, *J. Chem. Soc.*, 1965, 3828.

m.p. 164—166°, slightly contaminated with anhydro-taloside (6) (t.l.c.). The residual material was shown (t.l.c. in chloroform) to contain mainly (*ca.* 70%) anhydro-guloside (1), together with some anhydro-taloside (6) and material of lower R_F value.

Methyl 2,3-*Anhydro*-4,6-O-*benzylidene*-β-D-*gulopyranoside* (2).—Methyl 4,6-*O*-benzylidene-β-D-galactopyranoside [2] (10 g) in anhydrous pyridine (50 ml) was treated at −10° with tosyl chloride (7 g) in anhydrous pyridine (30 ml). After storage for 1 h at 0° and then for 48 h at 5°, the mixture was poured on ice (50 g), filtered, and extracted with ether. The white solid obtained after removal of solvent was dissolved in methanol (500 ml) containing sodium (12 g) and the solution was boiled 1·25 h, then poured on ice (250 g). The material which crystallised from the aqueous mixture was collected and recrystallised from chloroform–light petroleum to give compound (2) (29%), m.p. 140—141°, $[\alpha]_D$ −113° (*c* 0·4), {lit.,[2] m.p. 146—147°, $[\alpha]_D^{20}$ −118·5° (*c* 1·2)}.

Methyl 3-*Azido*-4,6-O-*benzylidene*-3-*deoxy*-α-D-*idopyranoside* (8).—Prepared as described in ref. 8, this had m.p. 152—153°, $[\alpha]_D$ +106° (*c* 1·2) {lit.,[8] m.p. 153—154°, $[\alpha]_D^{27}$ +105° (*c* 0·94)}. Treatment of the azide with tosyl chloride in pyridine (10 days at 5°) gave, after normal work-up followed by recrystallisation from chloroform–light petroleum, *methyl* 3-*azido*-4,6-O-*benzylidene*-3-*deoxy*-2-O-*tosyl*-α-D-*idopyranoside* (9), m.p. 126—127°, $[\alpha]_D$ +63° (*c* 1·1) (Found: C, 54·8; H, 5·2; N, 9·0; $C_{21}H_{23}N_3O_7S$ requires C, 54·7; H, 5·0; N, 9·1%).

Methyl 3-*Amino*-4,6-O-*benzylidene*-3-*deoxy*-α-D-*idopyranoside* (10).—The azido-alcohol (8) (500 mg) and Adams catalyst, suspended in absolute ethanol (50 ml), were shaken for 1·5 h under a stream of hydrogen. The catalyst was filtered off leaving a clear filtrate which, on evaporation, gave a white solid. Recrystallisation from ethyl acetate gave *compound* (10) (61%), m.p. 140—141°, $[\alpha]_D$ +65° (*c* 0·8) (Found: C, 60·0; H, 6·7; N, 5·1. $C_{14}H_{19}NO_5$ requires C, 59·8; H, 6·8; N, 5·0%). Acetylation with acetic anhydride in methanol gave methyl 3-acetamido-4,6-*O*-benzylidene-3-deoxy-α-D-idopyranoside (11), m.p. 216—218° (from ethanol), $[\alpha]_D$ +46° (*c* 0·8) {lit.,[9] m.p 226°, $[\alpha]_D^{24}$ +47·0° (*c* 0·98)}.

Methyl 2-*Azido*-4,6-O-*benzylidene*-2-*deoxy*-α-D-*idopyranoside* (12).—Methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-gulopyranoside [5] (1) (9 g), sodium azide (9 g), and ammonium chloride (3·6 g) in 80% aqueous 2-methoxyethanol (108 ml) were heated for 8·5 h at reflux. The residue obtained after removal of solvent was dissolved in chloroform–water. The chloroform phase gave, after recrystallisation, the *product* (12) (76%), m.p. 155—156°, $[\alpha]_D$ +96° (*c* 1·0) (Found: C, 55·1; H, 5·8; N, 13·6. $C_{14}H_{17}N_3O_5$ requires C, 54·7; H, 5·6; N, 13·7%).

Tosylation and recrystallisation of the product from benzene–light petroleum gave *methyl* 2-*azido*-4,6-O-*benzylidene*-2-*deoxy*-3-O-*tosyl*-α-D-*idopyranoside* (13), m.p. 139—140°, $[\alpha]_D$ +41° (*c* 0·6) (Found: C, 55·0; H, 5·1; N, 9·1. $C_{21}H_{23}N_3O_7S$ requires C, 54·7; H, 5·0; N, 9·1%).

Reduction of Methyl 2-*Azido*-4,6-O-*benzylidene*-2-*deoxy*-α-D-*idopyranoside* (12).—The azido-alcohol (12) (500 mg) and Adams catalyst, suspended in absolute ethanol (25 ml), were shaken for 1·5 h under a stream of hydrogen. The catalyst was removed and the filtrate evaporated to a thick syrup that slowly became crystalline. The solid obtained on recrystallisation from ethanol became syrupy when filtered. The crystalline material was pure as judged by t.l.c. (ethyl acetate; ninhydrin-positive) and presumably was methyl 2-amino-4,6-*O*-benzylidene-2-deoxy-α-D-idopyranoside (14), $[\alpha]_D$ +48° (*c* 0·8).

Treatment of the product with acetic anhydride in methanol gave methyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-idopyranoside (15) [yield from amino-alcohol obtained by hydrogenation of azido-alcohol (500 mg) was 86%], m.p. 195—196° (from ethyl acetate), $[\alpha]_D$ −12° (*c* 0·7) {lit.,[10] m.p. 201—202°, $[\alpha]_D$ −18° (*c* 1·08)} (Found: C, 59·3; H, 6·4; N, 4·2. Calc. for $C_{16}H_{21}NO_6$: C, 59·4; H, 6·5; N, 4·3%).

Acetylation of the amino-alcohol (14) (190 mg) with acetic anhydride in pyridine gave methyl 2-acetamido-3-*O*-acetyl-4,6-*O*-benzylidene-2-deoxy-α-D-idopyranoside (16) (95%), m.p. 193° (from ethyl acetate–light petroleum), $[\alpha]_D$ +49° (*c* 1·0) {lit.,[10] m.p. 192—193°, $[\alpha]_D$ +48° (*c* 0·66)}.

Methyl 2-*Acetamido*-4,6-O-*benzylidene*-2-*deoxy*-3-O-*tosyl*-α-D-*idopyranoside* (18).—Methyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-idopyranoside (15) was treated with tosyl chloride in pyridine to give *compound* (18), m.p. 152—154°, $[\alpha]_D$ 0° (*c* 0·8) (Found: C, 57·6; H, 5·6; N, 3·1. $C_{23}H_{27}NO_8S$ requires C, 57·9; H, 5·7; N, 2·9%).

Hydrogenation of Methyl 2-*Azido*-4,6-O-*benzylidene*-2-*deoxy*-3-O-*tosyl*-α-D-*idopyranoside* (13).—The azido-tosylate (13) (685 mg), suspended in absolute ethanol (50 ml), was shaken with 10% palladium–charcoal under a stream of hydrogen. After 6 h the catalyst was removed leaving a clear solution (one component; t.l.c. in ethyl acetate) from which solvent was removed leaving a white foam, $\nu_{max.}$ (film) 3410 cm^{-1}. One half of this material, dissolved in methanol (10 ml), was treated with acetic anhydride (0·5 ml). Work-up gave a white, amorphous solid (76% as acetamido-tosylate) which appeared (t.l.c. in ethyl acetate) to contain predominantly one component (*ca.* 80%; R_F 0·5) together with other compounds of lower R_F value. P.l.c. gave the acetamido-tosylate (18) (50 mg), m.p. and mixed m.p. 150—152° (from ethyl acetate), identical (t.l.c. in ethyl acetate–chloroform) with the sample prepared before.

The remaining half of the reduced material was treated with benzoic anhydride in methanol to give *methyl* 2-*benzamido*-4,6-*O*-*benzylidene*-2-*deoxy*-3-O-*tosyl*-α-D-*idopyranoside* (19) (49%), m.p. 164—165° (from chloroform–ether, $[\alpha]_D$ −39° (*c* 0·7) (Found: C, 62·0; H, 5·4; N, 2·4. $C_{28}H_{29}NO_8S$ requires C, 62·3; H, 5·4; N, 2·6%).

Azidolysis of Methyl 2,3-*Anhydro*-4,6-O-*benzylidene*-β-D-*talopyranoside* (7).—The anhydro-taloside [2] (7) (495 mg), sodium azide (1·01 g), and ammonium chloride (0·10 g) in 2-methoxyethanol (50 ml) were heated under reflux. After 45 min the mixture was cooled, and the solvent removed. The residue was extracted with chloroform, and the material obtained by evaporation of the extracts recrystallised from chloroform–light petroleum to give *methyl* 3-*azido*-4,6-O-*benzylidene*-3-*deoxy*-β-D-*idopyranoside* (20) (54%), m.p. 134—135°, $[\alpha]_D$ −40° (*c* 1·0), $[\alpha]_D$ −42° (*c* 0·5 in EtOH) (Found: C, 54·7; H, 5·6; N, 13·8. $C_{14}H_{17}N_3O_5$ requires C, 54·7; H, 5·6; N, 13·7%). The mother liquors from the recrystallisation were worked-up by p.l.c. (30% chloroform–benzene). Two bands were visible under u.v. light; extraction of the more mobile component gave more 3-azido-idoside (20) (4%), identical (t.l.c.) with the material obtained by crystallisation; extraction of the less mobile component gave a minute amount of a white crystalline solid [tentatively identified as methyl

2-azido-4,6-*O*-benzylidene-2-deoxy-β-D-galactopyranoside (30)], pure as judged by t.l.c.

Reduction of Methyl 3-Azido-4,6-O-benzylidene-3-deoxy-β-D-idopyranoside (20).—The azido-idoside (20) (200 mg), suspended in absolute ethanol, was shaken for 1 h under a stream of hydrogen in the presence of Adams catalyst. Removal of the catalyst and evaporation left, as a syrup, impure methyl 3-amino-4,6-*O*-benzylidene-3-deoxy-β-D-idopyranoside (21), $[\alpha]_D$ −88° (*c* 0·7). The impurity amounted to 10—20% as estimated by t.l.c. in 10% methanol–chloroform, which showed major spot at R_F 0·1 with minor spot, rendered invisible by u.v. masking, at R_F 0·3.

Acetylation of the amino-alcohol (21) with acetic anhydride in methanol gave *methyl 3-acetamido-4,6-O-benzylidene-3-deoxy-β-D-idopyranoside* (22) (76%), m.p. 100—103°, $[\alpha]_D$ −52° (*c* 0·8) (Found: C, 59·5; H, 6·8; N, 4·4. $C_{16}H_{21}NO_6$ requires C, 59·4; H, 6·5; N, 4·3%).

Treatment of the amide (22) with acetic anhydride in pyridine gave methyl 3-acetamido-2-*O*-acetyl-4,6-*O*-benzylidene-3-deoxy-β-D-idopyranoside (23), m.p. 237—238°, $[\alpha]_D$ −19° (*c* 0·4) {lit.,[7] m.p. 234°, $[\alpha]_D$ −13·1° (*c* 0·85)}.

Esters of Methyl 3-Azido-4,6-O-benzylidene-3-deoxy-β-D-idopyranoside (20).—(a) *Methyl 3-azido-4,6-O-benzylidene-3-deoxy-2-O-mesyl-β-D-idopyranoside* (25), prepared by treatment of the azido-alcohol (20) with mesyl chloride in pyridine, had m.p. 166—168° (from chloroform–light petroleum), $[\alpha]_D$ −21° (*c* 0·6) (Found: C, 47·1; H, 5·2; N, 10·9. $C_{15}H_{19}N_3O_7S$ requires C, 46·7; H, 5·0; N, 10·9%).

(b) *Methyl 2-O-acetyl-3-azido-4,6-O-benzylidene-3-deoxy-β-D-idopyranoside* (16), prepared by treatment of the azido-alcohol (20) with acetic anhydride in pyridine, had m.p. 120—121° (from light petroleum), $[\alpha]_D$ −16° (*c* 0·5) (Found: C, 55·5; H, 5·5; N, 12·1. $C_{16}H_{19}N_3O_6$ requires C, 55·0; H, 5·5; N, 12·0%).

Azidolysis of Methyl 2,3-Anhydro-4,6-O-benzylidene-β-D-gulopyranoside (2).—The anhydro-guloside (2) (3 g), sodium azide (3 g), and ammonium chloride (1·2 g) in 84% aqueous 2-methoxyethanol (36 ml) were boiled for 5 h under reflux. The residue obtained after removal of solvent was dissolved in chloroform–water, and the dried chloroform fraction was evaporated to a thick syrup that was crystallised from chloroform–light petroleum to give pure (t.l.c. in 5% methanol–chloroform) *methyl 2-azido-4,6-O-benzylidene-2-deoxy-β-D-idopyranoside* (27) (660 mg, 19%), m.p. 187—189°, $[\alpha]_D$ −110° (*c* 0·4) (Found: C, 54·7; H, 5·5; N, 13·5. $C_{14}H_{17}N_3O_5$ requires C, 54·7; H, 5·6; N, 13·7%).

P.l.c. of the remaining material (10% methanol–toluene) gave a further crop of azide (27) (14%), identical (t.l.c. in ethyl acetate–chloroform) with the material obtained by crystallisation, and amorphous material (580 mg) containing two components (t.l.c. in ethyl acetate–chloroform and in 10% methanol–chloroform), neither of which corresponded to the azide (27).

A mixture obtained by azidolysis of the epoxide (2) (1 g) under similar conditions was dissolved in the minimum quantity of warm methanol and the crystals which were deposited from the cooled solution were collected. Crystallisation of the residual material from chloroform–light petroleum gave the azide (27) (25%); the i.r. spectrum was identical with that of the material prepared as already described.

Recrystallisation of the mixture obtained from the methanolic solution gave a mixture, m.p. 237—238° (from ethyl acetate–light petroleum), $[\alpha]_D$ −77° (*c* 1·05); t.l.c. showed two components (saturated aqueous butanol; 10% methanol–chloroform) in approximately equal amounts, $\nu_{max.}$ (Nujol) 3460b, 3360b, 1650br,w, and 1415 cm^{-1} (Found: C, 61·0; H, 6·6; N, 2·8). Treatment of this material with acetic anhydride in pyridine gave, after removal of volatile material, an amorphous solid, $\nu_{max.}$ (Nujol) 1740, 1340, and 1235 cm^{-1}.

Reduction of Methyl 2-Azido-4,6-O-benzylidene-2-deoxy-β-D-idopyranoside (27).—The azide (27) (200 mg) in absolute ethanol (25 ml) was shaken for 1 h under a stream of hydrogen in the presence of Adams catalyst. The clear solution obtained after removal of the catalyst was evaporated to dryness to give syrupy methyl 2-amino-4,6-*O*-benzylidene-2-deoxy-β-D-idopyranoside (28) [impure: t.l.c. in ethyl acetate showed one major component (>90%; R_F <0·1), and minor components, visible by charring only (R_F 0·5—0·8); t.l.c. in 10% methanol–chloroform showed onr major component (>90%; R_F 0·5), and minor components (R_F 0·8—0·9)], $[\alpha]_D$ −55° (*c* 0·7).

Treatment of the amine (28) with acetic anhydride in methanol gave, after two recrystallisations from chloroform–light petroleum, *methyl 2-acetamido-4,6-O-benzylidene-2-deoxy-β-D-idopyranoside* (29) (69%) (Found: C, 59·3; H, 6·5; N, 4·3. $C_{16}H_{21}NO_6$ requires: C, 59·4; H, 6·5; N, 4·3%).

Attempted Preparation of Azido-idosides from Methyl 4,6-O-Benzylidene-2,3-di-O-tosyl-β-D-galactopyranoside.—The ditosylate (1 g) was treated for 9 h with sodium azide (3 g) in refluxing methanol (50 ml) containing sodium (0·3 g). After treatment with water (100 ml), methanol was removed from the solution and the resulting aqueous mixture was extracted with chloroform. Evaporation of the extract to dryness gave a white solid which was shown (t.l.c. in 5% methanol–toluene) to be free of starting material. Extraction with hot light petroleum and cooling of the extract gave a crystalline solid (40 mg), m.p. 93—95° with different mobility from both the 2-azido-idoside (27) and the 3-azido-idoside (20).

Methyl 4,6-O-Benzylidene-2,3-dideoxy-2,3-epimino-α-D-gulopyranoside (32).—Methyl 3-azido-4,6-*O*-benzylidene-3-deoxy-2-*O*-tosyl-α-D-idopyranoside (9) (1·1 g), dissolved in dry tetrahydrofuran (100 ml), was cautiously treated with lithium aluminium hydride (1·1 g). The mixture was boiled for 2·7 h under reflux, and then cooled to 0°. Water (5 ml) was cautiously added to the vigorously stirred and cooled solution: the rate of addition was adjusted to maintain the temperature of the mixture below 10°. The mixture was filtered, the residue was washed with methanol and chloroform, and the combined filtrate and washings were evaporated. The white mass obtained was extracted with chloroform, insoluble material was removed by filtration, and the filtrate was evaporated to a white solid which gave the *epimine* (32) (68%), m.p. 202—204° (from ethyl acetate–light petroleum), $[\alpha]_D$ +13° (*c* 2·4) (Found: C, 63·9; H, 6·5; N, 5·3. $C_{14}H_{17}NO_4$ requires C, 63·9; H, 6·5; N, 5·3%), τ ($CDCl_3$) 4·42 (1H, s, PhC*H*), 4·86 (1H, d, H-1, $J_{1,2}$ 2·5 Hz), 5·70—6·40 (4H, H-4,5,6,6'), 6·52 (3H, s, OCH_3), 7·2—7·35 (2H, H-2,3), and 9·08br (1H, s, NH).

Treatment of the epimine (32) with acetic anhydride in pyridine for 16 h gave, after removal of solvent and recrystallisation from ethanol, *methyl 2,3-acetylepimino-4,6-O-benzylidene-2,3-dideoxy-α-D-gulopyranoside* (33), m.p. 145—147°, $[\alpha]_D$ +88° (*c* 1·4) (Found: C, 63·1; H, 6·3; N, 4·8. $C_{16}H_{19}NO_5$ requires C, 62·9; H, 6·3; N, 4·6%),

τ 4·40 (1H, s, PhC*H*), 4·86 (1H, d, H-1, $J_{1,2}$ 3·5 Hz), 5·6—6·0 (4H, H-4,5,6,6'), 6·50 (3H, s, OCH_3), 6·86—7·00 (2H, H-2,3), and 7·78 (3H, s, NAc).

Methyl 4,6,O-*Benzylidene*-2,3-*dideoxy*-2,3-*epimino*-α-D-*talopyranoside* (34).—Methyl 2-azido-4,6-*O*-benzylidene-2-deoxy-3-*O*-tosyl-α-D-idopyranoside (13) (5 g), dissolved in tetrahydrofuran (100 ml), was treated with lithium aluminium hydride (3·3 g) and the solution was boiled for 3 h under reflux. The excess of reagent was destroyed as before and the solid material was collected and washed with methanol; the washings and filtrate were evaporated to leave a light yellow solid. Recrystallisation from ethanol–light petroleum and then from propan-1-ol gave the *epimine* (34) (19%), m.p. 166—168°, $[\alpha]_D$ −35° (*c* 0·83) (Found: C, 64·0; H, 6·9; N, 5·4. $C_{14}H_{17}NO_4$ requires C, 63·9; H, 6·5; N, 5·3%). τ 4·40 (1H, s, PhC*H*), 5·00 (1H, s, H-1), 5·6—6·34 (4H, H-4,5,6,6'), 6·54 (3H, s, OCH_3), 7·38 (1H, q, H-3, $J_{2,3}$ 5·0, $J_{3,4}$ 7·0 Hz), 7·82 (1H, d, H-2), and 8·84br (1H, s, NH).

Treatment of the crude product for 16 h with acetic anhydride (16 ml) in pyridine (40 ml), evaporation, and recrystallisation from ethyl acetate–light petroleum gave the N-*acetylepimine* (35) (45%), m.p. 204—206°, $[\alpha]_D$ +20° (*c* 0·8) (Found: C, 62·7; H, 6·3: N, 4·9. $C_{16}H_{19}NO_5$, requires C, 62·9; H, 6·3; N, 4·6%), τ 4·40 (1H, s, PhC*H*), 4·94 (1H, s, H-1), 5·54—6·40 (4H, H-4,5,6,6'), 6·56 (3H, s, OCH_3), 6·90 (1H, t, $J_{2,3} = 6·0$ Hz $= J_{3,4}$, H-3), 7·20 (1H d, H-2), and 7·80 (3H, s, Ac).

The *N*-acetylepimine (35) was dissolved in dry methanol to which were added a few chips of sodium metal. After 16 h the solution was neutralised with ion-exchange resin (Amberlite IR120; H^+ form) and evaporated to leave a white solid. Recrystallisation from ethyl acetate–petroleum gave the free epimine (34), m.p. 161—163°.

Separation of the mixture obtained after acetylation of the crude reaction product was also carried out by p.l.c. (chloroform). The two most mobile bands were extracted and the oily materials obtained were combined and dissolved in benzene. The solution was filtered and evaporated to leave an impure syrup [35 mg from 590 mg of (13)]. The third band was extracted to give the *N*-acetylepimine (35) [120 mg (34%) from 590 mg of (13)] (590 mg). The fourth band gave, on extraction, a syrup (25 mg) which crystallised from chloroform–ether to give methyl 2-acetamido-3-*O*-acetyl-4,6-*O*-benzylidene-2-deoxy-α-D-idopyranoside (16).

Reaction of Methyl 2-*Amino*-4,6-O-*benzylidene*-2-*deoxy*-3-O-*tosyl*-α-D-*idopyranoside* (17) *with Sodium Hydroxide*.—Syrupy amino-tosylate (17) (130 mg) was dissolved in 95% aqueous 2-methoxyethanol (10 ml) containing sodium hydroxide (480 mg); the solution was boiled for 3 h under reflux, then poured into water (*ca.* 20 ml) and extracted with chloroform. The syrup obtained by evaporation of the extract was treated with acetic anhydride in pyridine, to give methyl 2,3-*N*-acetylepimino-4,6-*O*-benzylidene-2,3-dideoxy-α-D-talopyranoside (35) (38%), m.p. 201—203° (from ethanol).

Treatment of Methyl 2-*Benzamido*-4,6-O-*benzylidene*-2-*deoxy*-3-O-*tosyl*-α-D-*idopyranoside* (19) *with Potassium Hydroxide*.—The benzamido-tosylate (19) (96 mg) was dissolved in 90% aqueous 2-methoxyethanol (10 ml) containing potassium hydroxide (300 mg) and the mixture was boiled 1·5 h under reflux. The solid obtained after removal of solvent was taken up in chloroform; the solution was filtered and evaporated to give methyl 4,6-*O*-benzylidene-2,3-dideoxy-2,3-epimino-α-D-idopyranoside (34), m.p. 169—170°.

Treatment of Methyl 2-*Acetamido*-4,6-O-*benzylidene*-2-*deoxy*-3-O-*tosyl*-α-D-*idopyranoside* (18) *with Lithium Aluminium Hydride*.—The acetamido-tosylate (18) (70 mg) in tetrahydrofuran (4 ml) was treated with lithium aluminium hydride (70 mg) and the mixture was boiled for 3 h under reflux. The excess of reagent was destroyed by cautious addition of water to the cooled mixture and solid material was filtered off, leaving a clear filtrate. Evaporation gave a clear syrup (50 mg), shown by t.l.c. (ethyl acetate; saturated aqueous butan-1-ol) to contain *ca.* 80% of one component running alongside authentic epimine (34), together with impurities of higher R_F value.

Methyl 4,6-O-*Benzylidene*-2,3-*dideoxy*-2,3-*epimino*-β-D-*gulopyranoside* (38).—Methyl 3-azido-4,6-*O*-benzylidene-3-deoxy-2-*O*-mesyl-β-D-idopyranoside (25) (0·5 g) in tetrahydrofuran (50 ml) was treated with lithium aluminium hydride (0·5 g) and the mixture was heated for 3 h under reflux. The excess of reagent was destroyed as before and the clear filtrate obtained after removal of insoluble material was evaporated to leave a white mass. Recrystallisation from chloroform–light petroleum gave white plates of the *epimine* (36) (82%), m.p. 155—156°, $[\alpha]_D$ −91° (*c* 0·8) (Found: C, 64·2; H, 6·7; N, 5·5. $C_{14}H_{17}NO_4$ requires C, 63·9; H, 6·5; N, 5·3%), τ 4·44 (1H, s, PhC*H*) 5·24 (1H, s, H-1), 5·6—6·7 (4H, H-4,5,6,6'), 6·40 (3H, s, OCH_3), 7·36—7·60 (2H, H-2,3), and 9·02br (1H, s, NH).

Deamination of Methyl 4,6-O-*Benzylidene*-2,3-*dideoxy*-2,3-*epimino*-α-D-*gulopyranoside* (32).—The epimine (32) (100 mg) was dissolved in 50% aqueous acetic acid (4 ml) and treated with sodium nitrite (40 mg) in water (2 ml) at room temperature. A yellow colour was immediately formed and, after a few seconds, a yellow solid was precipitated. After 2 min the solution was made alkaline with 2N-sodium hydroxide, causing rapid decolourisation of the solution and solid. Chloroform was added to dissolve the white solid remaining and the dried chloroform phase was evaporated to a white solid, which gave methyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-*threo*-hex-2-enopyranoside (37) (60 mg, 64%), m.p. 160—162° (from ethanol), $[\alpha]_D$ −143° (*c* 0·46) {lit.,[34] m.p. 163—164°, $[\alpha]_D^{25}$ −130° (*c* 3·0)}.

Deamination of Methyl 4,6-O-*Benzylidene*-2,3-*dideoxy*-2,3-*epimino*-α-D-*talopyranoside* (34).—The epimine (34) (20 mg) was treated similarly. The solution immediately became yellow and a thick yellow precipitate had formed within 5 s. After addition of 2N-sodium hydroxide to make the solution alkaline the yellow colour persisted but finally disappeared when the solution was kept at 40° for 5 min. The solid was filtered off and dried to give methyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-*threo*-hex-2-enopyranoside (37), m.p. 159—161°, identical with the sample just described.

Azidolysis of Methyl 4,6-O-*Benzylidene*-2,3-*dideoxy*-2,3-*epimino*-α-D-*talopyranoside* (34).—The epimine (34) (100 mg), sodium azide (100 mg), and ammonium chloride (15 mg) were dissolved in 80% aqueous 2-methoxyethanol (1 ml) and the mixture was boiled for 3 h under reflux. The solid obtained after removal of solvent was extracted with chloroform and the extract, on evaporation, gave brown syrupy methyl 2-amino-3-azido-4,6-*O*-benzylidene-2,3-dideoxy-α-D-idopyranoside, $[\alpha]_D$ +60° (*c* 0·5), contaminated with *ca.* 10% of starting material as shown by t.l.c. (aqueous butan-1-ol; ethyl acetate).

Treatment of the syrupy amine with acetic anhydride

in methanol gave a crystalline product. Recrystallisation from methanol gave *methyl 2-acetamido-3-azido-4,6-O-benzylidene-2,3-dideoxy-α-D-idopyranoside* (38) (26%), m.p. 231—233°, $[\alpha]_D$ +56° (*c* 0·55) (Found: C, 55·0; H, 5·8; N, 16·3. $C_{16}H_{20}N_4O_5$ requires C, 55·2; H, 5·8; N, 16·1%).

Methyl 2,3-Diacetamido-4,6-O-benzylidene-2,3-dideoxy-α-D-idopyranoside (39).—Methyl 2-acetamido-3-azido-4,6-*O*-benzylidene-2,3-dideoxy-α-D-idopyranoside (38) (110 mg), suspended in absolute ethanol (25 ml), was shaken for 1·5 h under a stream of hydrogen in the presence of Adams catalyst. The catalyst was filtered off and the clear filtrate was evaporated to a syrup which was redissolved in methanol (3 ml) and treated with acetic anhydride (1 ml). A white solid began to precipitate from the solution after a few minutes at room temperature. After 1·5 h the solid was filtered off and washed with methanol to give the *diamide* (39) (74%), m.p. 304—305°, $[\alpha]_D$ +39° (*c* 0·7) (Found: C, 59·2; H, 6·7; N, 7·8. $C_{18}H_{24}N_2O_6$ requires C, 59·3; H, 6·6; N, 7·7%).

We thank the S.R.C. for a studentship (to J. A. L.).

[2/2610 *Received*, 17*th November*, 1972]