Branched-chain Sugars. Part II.[1] Characterization of Methyl 2,4-Di-*O*-acetyl-3,6-dideoxy-3-*C*-methyl-3-nitro-α-L-glucopyranoside and Some of its Chemical Transformations

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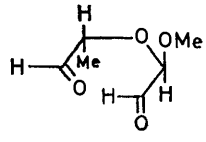
One of the nitro-acetates obtained by cyclization with nitroethane of the dialdehyde (1) (prepared by oxidation of methyl α-L-rhamnopyranoside with sodium periodate) followed by acetylation has been unambiguously characterized as methyl 2,4-di-*O*-acetyl-3,6-dideoxy-3-*C*-methyl-3-nitro-α-L-glucopyranoside (2). The configuration at the tertiary centre of the latter compound was established with reasonable certainty by the ready solvolysis of both sulphonyloxy-groups from the derived methyl 3-acetamido-3,6-dideoxy-3-*C*-methyl-2,4-di-*O*-methylsulphonyl-α-L-glucopyranoside (7) under conditions requiring participation by the neighbouring 3-acetamido-group. Chemical transformations of the nitro-acetate (2) and methyl 3-acetamido-3,6-dideoxy-3-*C*-methyl-α-L-glucopyranoside (6), aimed at making a 2-deoxy-derivative, are described.

In contrast to the base-catalysed cyclizations of sugar 'dialdehydes' with nitromethane, introduced by Baer and Fischer[2,3] in 1958, there are comparatively few examples of corresponding cyclizations with nitroethane leading to branched-chain nitro-glycosides. One of the reasons for this is undoubtedly the difficulty in assigning the configuration of the products at the tertiary carbon atom. The dialdehyde (1), obtained by oxidation of methyl α-L-rhamnopyranoside with aqueous sodium periodate, has been cyclized[4] with nitroethane to a mixture of products from which a crystalline methyl 2,4-di-*O*-acetyl-3,6-dideoxy-3-*C*-methyl-3-nitrohexopyranoside {m.p. 137·5—138°, $[\alpha]_D$ −133° (*c* 1·44 in $CHCl_3$)} was isolated, in 12% yield, after acetylation. ^1H N.m.r. spectroscopy established an α-L-*gluco*- or α-L-*allo*-configuration for this crystalline nitro-derivative, and the chemical shift of the acetamido methyl protons in the corresponding 3-acetamido-derivative (3) has been interpreted in favour of the equatorial disposition of this group, commensurate with an α-L-*gluco*-configuration. This empirical ^1H n.m.r. method was developed by Lichtenthaler *et al.*,[5] who were able to show that the chemical shift of an acetamido-group falls within one of two reasonably well-defined ranges, depending on whether the group is equatorially or axially disposed. Lichtenthaler's method has been used retrospectively in assigning configurations to branched-chain acetamido-sugars obtained[3,6] *via* cyclizations with nitroethane of the dialdehydes derived from methyl α- and β-D-glucopyranosides. The great care that must be exercised in assigning configurations to the products of such cyclizations is well exemplified by the latter reactions, since partial epimerization of the dialdehydes at C-5 was demonstrated to occur prior to the cyclization reaction; such epimerization does not appear to be prevalent in base-catalysed cyclizations with nitromethane.[7] Cyclizations with nitroethane have also been performed[7,8] on the nucleoside dialdehyde derived from uridine, and, in this instance, configurational assignments based on n.m.r. spectroscopy have been confirmed by chemical evidence similar to that described later.



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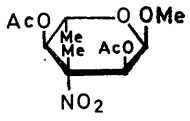

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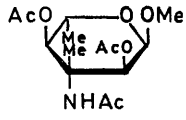

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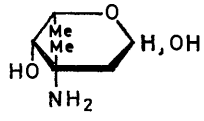

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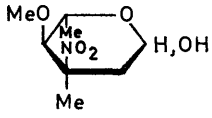

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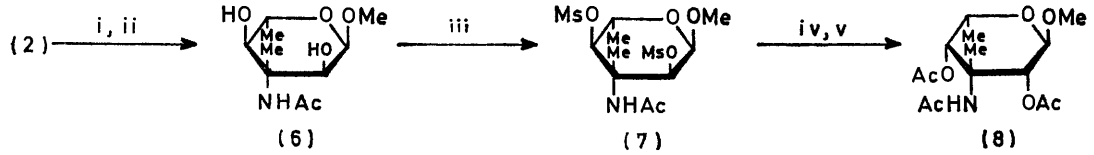
Our interest in the cyclization of the dialdehyde (1) with nitroethane was aroused by the recent discovery of two unusual branched-chain sugars, 3-amino-2,3,6-trideoxy-3-*C*-methyl-L-*lyxo*-hexose (vancosamine) (4)[9] and 2,3,6-trideoxy-3-*C*,4-*O*-dimethyl-3-nitro-L-*ribo*-hexose (evernitrose) (5),[10] as components of the antibiotics vancomycin[11] and everninomicin,[10] respectively. Although these antibiotic sugars have been fully characterized by chemical and spectroscopic methods,[9,10] their synthesis presents a challenge. A promising approach to vancosamine and evernitrose appeared to be offered

[1] Part I, J. S. Brimacombe, A. J. Rollins, and S. W. Thompson, *Carbohydrate Res.*, in the press.
[2] H. H. Baer and H. O. L. Fischer, *Proc. Nat. Acad. Sci. U.S.A.*, 1958, **44**, 991.
[3] For reviews on nitro-sugars see H. H. Baer, *Adv. Carbohydrate Chem.*, 1969, **24**, 67; F. W. Lichtenthaler, *Fortschr. Chem. Forsch.*, 1970, **14**, 556.
[4] S. W. Gunner, W. G. Overend, and N. R. Williams, *Chem. and Ind.*, 1964, 1523.
[5] F. W. Lichtenthaler and P. Emig, *Tetrahedron Letters*, 1967, 577; *Carbohydrate Res.*, 1968, **7**, 121; F. W. Lichtenthaler, G. Bambach, and P. Emig, *Chem. Ber.*, 1969, **102**, 994.
[6] H. H. Baer and G. V. Rao, *Annalen*, 1965, **686**, 210.
[7] F. W. Lichtenthaler and H. Zinke, *Angew. Chem. Internat. Edn.*, 1966, **5**, 737.
[8] F. W. Lichtenthaler and H. Zinke, *J. Org. Chem.*, 1972, **37**, 1612.
[9] W. D. Weringa, D. H. Williams, J. Feeney, J. P. Brown, and R. W. King, *J.C.S. Perkin I*, 1972, 443; A. W. Johnson, R. M. Smith, and R. D. Guthrie, *J.C.S. Chem. Comm.*, 1972, 361; *J.C.S. Perkin I*, 1972, 2153.
[10] A. K. Ganguly, O. Z. Sarre, and H. Reimann, *J. Amer. Chem. Soc.*, 1968, **90**, 7129; see also ref. 8, p. 1618.
[11] M. H. McCormick, W. M. Stark, G. E. Pittenger, R. C. Pittenger, and J. M. McGuire, 'Antibiotics Annual (1955—1956),' Medical Encyclopaedia Inc., New York, 1956, p. 606.

by the cyclization of the dialdehyde (1) with nitroethane, provided that the configuration at the tertiary centre of the products could be reliably determined. We report an unambiguous characterization of the crystalline branched-chain nitroglycoside (2) formed in this cyclization, and also describe a number of chemical transformations of this sugar that were aimed at making a 2-deoxy-derivative.

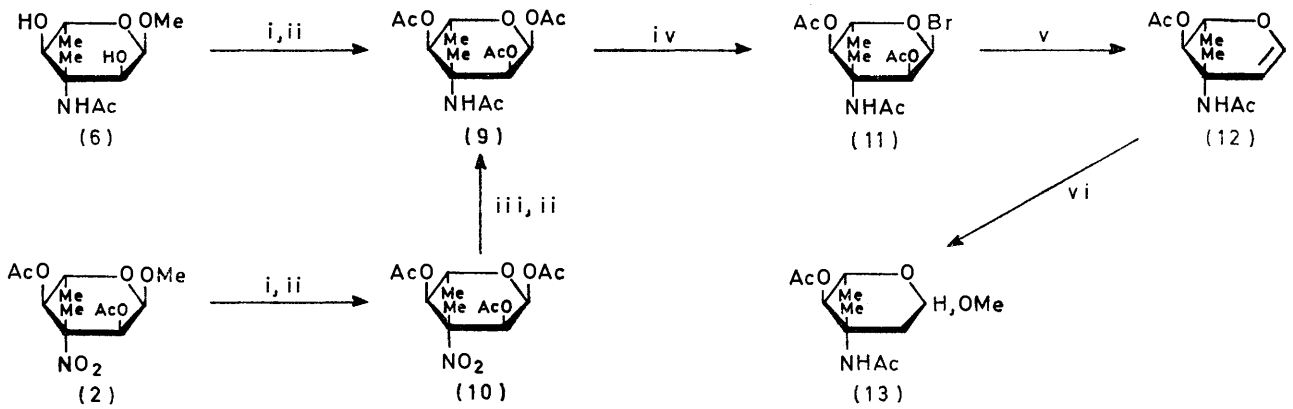
Cyclization of the dialdehyde (1) with nitroethane gave, after acetylation and chromatography on silica gel, a number of crystalline products (see Experimental section), one of which {m.p. 137—138°, $[\alpha]_D$ −130° (*c* 1 in $CHCl_3$), 19%} was identical with that reported [4] previously. Since the configurations of this branched-chain nitroglycoside (2) at C-1 and C-2 ($J_{1,2}$ 4·5 Hz; *cis*) and C-4 and C-5 ($J_{4,5}$ 10 Hz; *trans*) can readily be assigned [4] from ^{1}H n.m.r. spectroscopy, only the configuration at the tertiary centre at C-3 remains to be established. This was achieved as shown in Scheme 1,



SCHEME 1 i, Ni–H_2; ii, Ac_2O–MeOH; iii, MsCl–C_5H_5N; iv, NaOAc–MeO·CH_2·CH_2·OH–H_2O; v, Ac_2O–C_5H_5N

with the correct configurations assumed. Reduction of the nitro-group over Raney nickel occurred with concomitant deacetylation to give, after *N*-acetylation, methyl 3-acetamido-3,6-dideoxy-3-*C*-methyl-α-L-glucopyranoside (6), which was converted into the bismethanesulphonate (7). Solvolysis of the latter compound in moist 95% 2-methoxyethanol in the presence of sodium acetate resulted in the loss of both sulphonyloxy-groups to yield, after acetylation, methyl 3-acetamido-2,4-di-*O*-acetyl-3,6-dideoxy-3-*C*-methyl-α-L-talopyranoside (8). Solvolysis of the methylsulphonyloxy-groups under these extremely mild conditions logically requires [12] participation by the neighbouring 3-acetamido-group, which perforce must be located *trans* to the groups at C-2 and C-4. Hence, the bismethanesulphonate (7) can be assumed to have the α-L-*gluco*-configuration and the structures of the other compounds in the sequence are as assigned. The changes in configuration at C-2 and C-4 were also evident from the ^{1}H n.m.r. spectrum of the di-*O*-acetate (8); H-2 and H-4 showed little coupling with their neighbouring proton and appeared as slightly broadened singlets at τ 5·03 and 4·80, respectively, whereas doublets with $J_{1,2}$ 4·5 and $J_{4,5}$ 10 Hz have been observed [4] for methyl 3-acetamido-2,4-di-*O*-acetyl-3,6-dideoxy-3-*C*-methyl-α-L-glucopyranoside (3). A combination of ^{1}H n.m.r. spectroscopy [5] and the foregoing type of procedure appears, therefore, to offer a serviceable method for assigning configurations to branched-chain nitro-glycosides. However, attempts to interrupt the solvolysis of (7) at an intermediate stage, when only one of the sulphonyloxy-groups had been removed, were unsuccessful (*cf.* ref. 13).

We next attempted to make 2-deoxy-derivatives of these branched-chain sugars, since this is a feature of the structures of both vancosamine (4) [9] and evernitrose (5).[10] In the initial approach used (Scheme 2), methyl 3-acetamido-3,6-dideoxy-3-*C*-methyl-α-L-glucopyranoside (6) was hydrolysed with dilute hydrochloric acid to give, after acetylation, 3-acetamido-1,2,4-tri-*O*-acetyl-3,6-dideoxy-3-*C*-methyl-α-L-glucopyranose (9). However, the overall yield for these steps was only 30%. A considerable improvement in the yield of the tetra-acetate (9) resulted from hydrolysis of methyl 2,4-di-*O*-acetyl-3,6-dideoxy-3-*C*-methyl-3-nitro-α-L-glucopyranoside (2) with dilute hydrochloric acid and acetylation of the free nitro-sugar to give 1,2,4-tri-*O*-acetyl-3,6-dideoxy-3-*C*-methyl-3-nitro-α-L-glucopyranose (10). Conversion of



SCHEME 2 Reagents: i, dil. HCl; ii, Ac_2O–C_5H_5N; iii, Pd–C/H_2; iv, HBr–HOAc–Ac_2O; v, Zn–Cu; vi, MeOH–BF_3

[12] L. Goodman, *Adv. Carbohydrate Chem.*, 1967, **22**, 109; B. Capon, *Chem. Rev.*, 1969, **69**, 471.

[13] A. C. Richardson and K. A. McLauchlan, *J. Chem. Soc.*, 1962, 2499.

the latter compound into the tetra-acetate (9) was then accomplished by reduction of the nitro-group over palladised carbon, followed by acetylation of the resulting amine. The 2-deoxy-derivative was then approached by means of a conventional glycal route. Thus, the acetylated derivative (9) was converted *in situ* into the acetobromo-compound (11) by treatment with hydrogen bromide in glacial acetic acid and acetic anhydride, whereafter treatment with a zinc–copper couple afforded 3-acetamido-4-*O*-acetyl-3,6-dideoxy-3-*C*-methyl-α-L-glucal (12) in moderate yield. Boron trifluoride-catalysed addition of methanol to the glycal (12) in methylene chloride gave a virtually quantitative yield of methyl 3-acetamido-4-*O*-acetyl-2,3,6-trideoxy-3-*C*-methyl-αβ-L-*arabino*-hexopyranoside (13) (a derivative of *epi*-vancosamine), which ^{1}H n.m.r. spectroscopy showed to contain the α- and β-anomers in the ratio **3 : 1**, respectively. Inversion of configuration at C-4 of the glycosides (13) should yield derivatives of natural vancosamine (4),[9] and investigations along these lines are in progress. Moreover, application of the glycal route to methyl 3-acetamido-2,4-di-*O*-acetyl-3,6-dideoxy-3-*C*-methyl-α-L-talopyranoside (8) offers an alternative approach to vancosamine and has the advantage that the C-4 substituent already possesses the requisite configuration.

Attempts to apply the glycal method to 1,2,4-tri-*O*-acetyl-3,6-dideoxy-3-*C*-methyl-3-nitro-α-L-glucopyranose (10) were unsuccessful. Although conversion into the corresponding acetobromo-derivative could be achieved, the nitro-group did not appear to survive the conditions used to introduce the double bond; the reaction yielded an intractable mixture of products, none of which showed evidence (i.r. spectroscopy) for the presence of a nitro-group. The direct application of the glycal route in a synthesis of evernitrose (5) thus seems to be ruled out. However, the ability of peroxy-acids to transform [14] amino-groups into nitro-groups holds prospects for future developments.

EXPERIMENTAL

T.l.c. was performed on Kieselgel G, and spots were detected with vanillin–sulphuric acid.[15] I.r. spectra were recorded for Nujol mulls with a Perkin-Elmer Infracord spectrophotometer and n.m.r. spectra were determined for solutions in deuteriochloroform (1% tetramethylsilane as internal standard) with either a Perkin-Elmer R10 or a Bruker (90 MHz) spectrometer. Optical rotations were measured at ambient temperature with a Perkin-Elmer 141 automatic polarimeter. Light petroleum refers to the fraction having b.p. 60—80°.

Methyl 2,4-*Di*-O-*acetyl*-3,6-*dideoxy*-3-C-*methyl*-3-*nitro*-α-L-*glucopyranoside* (2).—A stirred solution of syrupy methyl α-L-rhamnopyranoside [16] (100 g; probably containing some β-glycoside) in water (1 l) was treated in portions with sodium periodate (200 g) while crushed ice was added to maintain a temperature of 20—30°. After 3 h, sodium hydrogen carbonate was cautiously added to neutralize the acid, the mixture was poured into ethanol (4 l), and insoluble material was filtered off. The filtrate was concentrated to a syrup that was extracted with hot ethanol (1 l). The extract was cooled, filtered, set aside overnight, filtered again, and treated with nitroethane (100 ml) followed by a solution prepared from sodium (12 g) and ethanol (750 ml). This reaction mixture was kept at room temperature for 4 h, after which it was neutralized with solid carbon dioxide. Insoluble material was filtered off and the filtrate was concentrated to a syrup that was dissolved in ethanol (1 l) and set aside overnight to precipitate inorganic material. After filtration, the solution was concentrated and the residue was taken up in pyridine (400 ml) and treated with acetic anhydride (300 ml) for 12 h at room temperature. Work-up in the usual manner afforded a solution of the products in methylene chloride, which t.l.c. (light petroleum–acetone, 9 : 1) showed to contain at least four components. Removal of the solvent left a syrup that was dissolved in ether–light petroleum (1 : 1; 500 ml) and left in a refrigerator. The first crop of crystals (highest R_F) was identified as the α-L-*glucoside derivative* (2) (36 g, 19%), m.p. 137—138°, $[\alpha]_D$ −130° (*c* 1 in $CHCl_3$) (Found: C, 46·9; H, 6·2; N, 4·9. $C_{12}H_{19}NO_8$ requires C, 47·2; H, 6·2; N, 4·6%), τ 4·32 (1H, d, $J_{1,2}$ 4·5 Hz, H-2), 4·59 (1H, d, $J_{4,5}$ 10 Hz, H-4), 4·90 (1H, d, H-1), 6·05 (1H, m, H-5), 6·54 (3H, s, OMe), 7·91 (6H, s, 2 × OAc), 8·10 (3H, s, 3-Me), and 8·77 (3H, d, $J_{5,6}$ 7 Hz, 5-Me) {lit.,[4] m.p. 137·5—138°, $[\alpha]_D$ −133° (*c* 1·44 in $CHCl_3$)}.

The mother liquors in the refrigerator later deposited crystals of a compound (A) (13·1 g), m.p. 109—110°, $[\alpha]_D$ −59° (*c* 1 in $CHCl_3$) (Found: C, 47·4; H, 6·3; N, 4·7%) having the same mobility as the nitro-glycoside (2) on t.l.c. After (A) had been filtered off, the filtrate was concentrated to a syrup that was chromatographed on silica gel (elution with light petroleum–acetone, 9 : 1) to give a mixture of compounds (2) and (A), followed by a compound (B) (3·5 g), m.p. 136—137° (from light petroleum–ether), $[\alpha]_D$ −74° (*c* 1 in $CHCl_3$) (Found: C, 47·6; H, 6·3; N, 4·2%). Continued elution afforded a compound (C) (3 g), m.p. 122—123° (from ether–light petroleum), $[\alpha]_D$ +19° (*c* 1 in $CHCl_3$) (Found; C, 47·0; H, 6·3; N, 4·8%). The structures of these compounds are under investigation; cursory examination of their n.m.r. spectra suggests that only (C) is a single compound, whereas the others may be either molecular-addition complexes similar to those isolated in other work [6] or mixtures of stereoisomers.

Methyl 3-*Acetamido*-3,6-*dideoxy*-3-C-*methyl*-α-L-*glucopyranoside* (6).—A solution of the branched-chain nitro-glycoside (2) (4·2 g) in methanol (100 ml) containing Raney nickel [17] (5 g) was hydrogenated at 30 atm for 24 h. Filtration and evaporation left a chromatographically pure syrup (2·1 g, 75%), presumed to be methyl 3-amino-3,6-dideoxy-3-*C*-methyl-α-L-glucopyranoside. A solution of the amino-sugar (2·1 g) in methanol (300 ml) was treated with acetic anhydride (4 ml) for 48 h at room temperature. Removal of the solvents and decolourization (charcoal) afforded the *acetamido-derivative* (6) (2·3 g, 90%), m.p. 144—145° (from ether–ethanol), $[\alpha]_D$ −118° (*c* 0·5 in $CHCl_3$) (Found: C, 51·1; H, 8·2; N, 5·9. $C_{10}H_{19}NO_5$ requires C, 51·5; H, 8·2; N, 6·0%), τ 5·35 (1H, d, $J_{1,2}$ 4·5 Hz, H-1), 6·60 (3H, s, OMe), 8·00 (3H, s, NAc), 8·66 (3H, s, 3-Me), and 8·70 (3H, d, $J_{5,6}$ 6 Hz, 5-Me).

[14] H. H. Baer and S.-H. Lee Ching, *Canad. J. Chem.*, 1973, **51**, 1812.
[15] 'Chromatography,' E. Merck AG, Darmstadt, 2nd edn., p. 30.
[16] W. T. Haskins, R. M. Hann, and C. S. Hudson, *J. Amer. Chem. Soc.*, 1946, **68**, 628.
[17] S. Nishimura, *Bull. Chem. Soc. Japan*, 1959, **32**, 61.

Methyl 3-*Acetamido*-3,6-*dideoxy*-3-C-*methyl*-2,4-*bis*-O-*methylsulphonyl*-α-L-*glucopyranoside* (7).—A cold (0°) solution of the diol (6) (1 g) in dry pyridine (30 ml) was treated gradually with methanesulphonyl chloride (2 ml), then kept at ambient temperature for 24 h. Work-up in the usual manner gave the *bismethanesulphonate* (7) (1·2 g, 65%), m.p. 161—162° (from methanol), $[\alpha]_D$ −102° (*c* 0·5 in $CHCl_3$) (Found: C, 36·7; H, 5·6; N, 3·6; S, 15·8. $C_{12}H_{23}NO_9S_2$ requires C, 37·0; H, 5·9; N, 3·6; S, 16·4%), τ 6·61 (3H, s, OMe), 6·94 and 6·98 (each 3H, s, 2 × OMs), 8·03 (3H, s, NAc), 8·60 (3H, s, 3-Me), and 8·66 (3H, d, $J_{5,6}$ 6 Hz, 5-Me).

Methyl 3-*Acetamido*-2,4-*di*-O-*acetyl*-3,6-*dideoxy*-3-C-*methyl*-α-L-*talopyranoside* (8).—A solution of the dimesylate (7) (0·5 g) in moist 95% 2-methoxyethanol (30 ml) containing sodium acetate (0·32 g) was heated under gentle reflux for 48 h, then filtered. The solvents were removed and the residue in pyridine (10 ml) was treated with acetic anhydride (8 ml) for 6 h at room temperature. Work-up in the usual way gave the *acetylated talopyranoside* (8) (0·16 g, 38%), m.p. 170—171° (from ether–light petroleum), $[\alpha]_D$ −24° (*c* 0·125 in $CHCl_3$) (Found: C, 53·1; H, 7·2; N, 4·35. $C_{14}H_{23}NO_7$ requires C, 53·0; H, 7·25; N, 4·4%), τ 4·80br (1H, s, H-4), 5·03br (1H, s, H-2), 5·23br (1H, s, H-1), 5·79 (1H, q, $J_{5,6}$ 7 Hz, H-5), 6·60 (3H, s, OMe), 7·78 and 7·90 (each 3H, s, 2 × OAc), 8·13 (3H, s, NAc), 8·24 (3H, s, 3-Me), and 8·82 (3H, d, $J_{5,6}$ 7 Hz, 5-Me).

1,2,4-*Tri*-O-*acetyl*-3,6-*dideoxy*-3-C-*methyl*-3-*nitro*-α-L-*glucopyranose* (10).—The nitro-glycoside (2) (4·4 g) in 2M-hydrochloric acid (90 ml) was heated under reflux for 16 h, cooled, and neutralized with barium carbonate. The filtered solution was concentrated, the residue was dissolved in methanol, and insoluble material was filtered off. Removal of the solvent gave a thick syrup that was acetylated in pyridine (50 ml) and acetic anhydride (40 ml) for 6 h at room temperature. Work-up in the usual manner yielded the *nitro-acetate* (10) (3·9 g, 75%), m.p. 125—126° (from ether–light petroleum), $[\alpha]_D$ −26° (*c* 0·5 in $CHCl_3$) (Found: C, 47·2; H, 5·6; N, 3·9. $C_{13}H_{19}NO_9$ requires C, 46·85; H, 5·7; N, 4·2%), τ 4·21 (2H, s, H-1 and H-2), 4·45 (1H, d, $J_{4,5}$ 10 Hz, H-4), 6·20 (1H, m, H-5), 7·83—7·93 (9H, 3 peaks, 3 × OAc), 8·17 (3H, s, 3-Me), and 8·72 (3H, d, $J_{5,6}$ 7 Hz, 5-Me).

3-*Acetamido*-1,2,4-*tri*-O-*acetyl*-3,6-*dideoxy*-3-C-*methyl*-α-L-*glucopyranose* (9).—(a) *From the acetamido-glycoside* (6). The glycoside (6) (7 g) in 4M-hydrochloric acid (100 ml) was heated under reflux for 36 h, cooled, and was neutralized with barium carbonate. The filtered solution was concentrated to a thick syrup that was dissolved in methanol (200 ml) and insoluble material was filtered off. This process was repeated to ensure that essentially all inorganic material had been removed. Finally, the residual syrup was acetylated in pyridine (70 ml) and acetic anhydride (50 ml) for 12 h at room temperature. Work-up in the accepted manner gave the *tetra-acetate* (9) (3·3 g, 30%), m.p. 239—240° (from ether), $[\alpha]_D$ −21° (*c* 0·5 in $CHCl_3$) (Found: C, 52·1; H, 6·7; N, 3·8. $C_{15}H_{23}NO_8$ requires C, 52·2; H, 6·7; N, 4·1%), τ 7·90—7·93 (9H, 2 peaks, 3 × OAc), 8·17 (3H, s, NAc), 8·53 (3H, s, 3-Me), and 8·78 (3H, d, $J_{5,6}$ 6 Hz, 5-Me).

(b) *From the nitro-triacetate* (10). A solution of the nitro-compound (10) (3·85 g) in methanol (100 ml) containing 2% palladium–charcoal (2 g) was hydrogenated for 24 h at ambient temperature and 30 atm. The catalyst was filtered off, the solvent was removed, and the residue in pyridine (60 ml) was treated with acetic anhydride (50 ml) for 12 h at room temperature. Work-up gave the product (9) (3 g, 75%), m.p. 239—240° (from ether–light petroleum), $[\alpha]_D$ −21° (*c* 0·5 in $CHCl_3$), which was indistinguishable (mixed m.p., i.r. and n.m.r. spectroscopy) from that described in (a).

3-*Acetamido*-4-O-*acetyl*-3,6-*dideoxy*-3-C-*methyl*-L-*glucal* (12).—To a solution of the tetra-acetate (9) (1·35 g) in glacial acetic acid (1·5 ml) and acetic anhydride (1·5 ml) at 0° was added a 30% solution of hydrogen bromide in acetic acid (10 ml). The solution of the acetobromo-derivative (11) was then set aside for 24 h, after which it was added to a solution prepared in the following way.

Sodium acetate trihydrate (14 g) was dissolved in 50% aqueous acetic acid (35 ml) in a 100 ml three-necked flask equipped with dropping funnel, stirrer, and thermometer. The solution was cooled to −10°, and zinc dust (10 g) and copper sulphate (1 g) in water (2·5 ml) were added with vigorous stirring. When the blue colour had disappeared and the evolution of hydrogen had commenced, the solution of the bromo-compound (already prepared) was added dropwise during 1 h while the internal temperature was maintained at −10 to −5°. Stirring was then continued for 24 h at −10°. Isolation of the product was carried out as rapidly as possible in the following way. The suspension was filtered while the solution was kept cold by addition of ice, and the insoluble material was washed with cold 50% aqueous acetic acid. The filtrate and washings were extracted with chloroform (3 × 50 ml) and the combined extracts were washed with cold water, potassium hydrogen carbonate solution, and water again, dried (Na_2SO_4), and evaporated to give a syrup. T.l.c. showed this to contain several components, including starting material. Chromatography on silica gel (elution with methylene chloride–acetone, 6 : 1) afforded the pure *glycal* (12) (0·425 g, 48%), m.p. 85—86° (from ether–light petroleum), $[\alpha]_D$ −9° (*c* 0·5 in $CHCl_3$) (Found: C, 58·0; H, 7·2; N, 5·9. $C_{11}H_{17}NO_4$ requires C, 58·1; H, 7·5; N, 6·2%), τ 3·75 (1H, d, $J_{1,2}$ *ca.* 6 Hz, H-1), 4·70 (1H, d, $J_{2,1}$ *ca.* 6 Hz, H-2), 4·86 (1H, d, $J_{4,5}$ 10 Hz, H-4), 5·95 (1H, m, H-5), 7·83 (3H, s, OAc), 8·11 (3H, s, NAc), 8·48 (3H, s, 3-Me), and 8·73 (3H, d, $J_{5,6}$ 6 Hz, 5-Me). The product rapidly decolourized a solution of bromine in carbon tetrachloride.

Methyl 3-*Acetamido*-4-O-*acetyl*-2,3,6-*trideoxy*-3-C-*methyl*-αβ-L-arabino-*hexopyranoside* (13).—A mixture of boron trifluoride–ether complex, methanol, and methylene chloride (1 : 1 : 3 v/v; 15 ml) was added to a solution of the glycal (12) (0·5 g) in methylene chloride (10 ml), and the solution was set aside at room temperature for 18 h; t.l.c. (methylene chloride–acetone, 6 : 1) then showed that all the starting material had reacted. After dilution with methylene chloride, the solution was washed with aqueous sodium hydrogen carbonate solution, dried (Na_2SO_4), and concentrated to give a syrupy mixture of the 2-deoxyglycosides (13) (0·55 g). Although the glycosides could not be separated by preparative t.l.c., the α : β anomeric ratio was estimated to be *ca.* 3 : 1 by integration over the methoxy-signals at τ 6·60 and 6·50, respectively. The spectrum of the α-anomer also showed τ 5·06 (1H, d, $J_{4,5}$ 10 Hz, H-4), 7·85 (3H, s, OAc), 8·13 (3H, s, NAc), 8·44 (3H, s, 3-Me), and 8·80 (3H, d, $J_{5,6}$ 6 Hz, 5-Me).

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