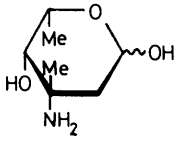
Branched-chain Sugars. Part 9.[1] Characterisation of the Stereoisomeric Methyl 3-Deoxy-3-*C*-methyl-3-nitropentopyranosides resulting from the Condensation of Nitroethane with L'-Methoxydiglycolaldehyde and the *X*-Ray Crystal Structure of Methyl 2,4-Di-*O*-acetyl-3-deoxy-3-*C*-methyl-3-nitro-β-D-xylopyranoside

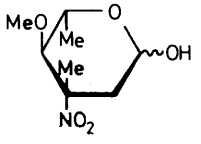
By **Mohammed M. Abuaan, John S. Brimacombe,* and John N. Low,** Chemistry Department, The University, Dundee DD1 4HN

Base-catalysed cyclisation of the ' dialdehyde ' (7) (obtained on periodate oxidation of methyl β-D-xylopyranoside) with nitroethane gave, after acetylation, a mixture containing five of the eight possible methyl 2,4-di-*O*-acetyl-3-deoxy-3-*C*-methyl-3-nitropentopyranosides. The solvolytic behaviour of the corresponding methyl 3-acetamido-3-deoxy-2,4-di-*O*-methanesulphonyl-3-*C*-methylpentopyranosides [*e.g.* (17) and (22)] and interconversions between the stereoisomers, by way of the monosulphonates (24) and (25), revealed that four of the stereoisomers formed in the nitroethane condensation possess α-L-*lyxo*, α-L-*xylo*, β-D-*xylo*, and α-L-*arabino* configurations. The crystal structure of methyl 2,4-di-*O*-acetyl-3-deoxy-3-*C*-methyl-3-nitro-β-D-xylopyranoside (8) is reported.

THE recent discovery of two unusual branched-chain sugars, 3-amino-2,3,6-trideoxy-3-*C*-methyl-L-*lyxo*-hexose (vancosamine) (1)[2] and 2,3,6-trideoxy-3-*C*,4-*O*-dimethyl-3-nitro-L-*arabino*-hexose (evernitrose) (2),[3,4] as components of vancomycin [5] and some everninomicins,[3,6] respectively, has focused attention on the synthesis of these and related branched-chain sugars. Several successful syntheses of branched-chain amino- and nitro-sugar derivatives have been reported[7-11]



(1)



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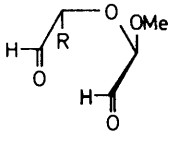
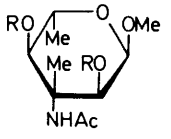


(3) R = Me
(7) R = H

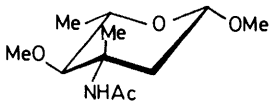
already. One obvious approach to the synthesis of 3-*C*-methyl-3-nitroaldopyranosides involves the base-catalysed cyclisation of a sugar ' dialdehyde ' [*e.g.* (3)] with nitroethane. In contrast to cyclisations with nitromethane, which have found extensive use in the synthesis of amino-sugars,[8a] there are comparatively few examples of analogous cyclisations of sugar ' dialdehydes ' with nitroethane.[8] One of the reasons for this is undoubtedly the difficulty encountered in assigning the configuration at the branch-point of the stereoisomeric products that are formed.

Lichtenthaler *et al.*[8b,12] have used an empirical ^{1}H n.m.r. method to assign the configuration at the branch-point in such derivatives as (4), which are readily derived from 3-*C*-methyl-3-nitro-sugars, based on the chemical shift of the methyl protons of the acetamido-group. These signals were found to fall within one of two reasonably well-defined ranges, depending on whether the 3-acetamido-group is equatorially or axially disposed on a chair conformation of the pyranose ring. Although this spectroscopic method seems to give reliable results when applied to a group of closely related derivatives, such as examined by Lichtenthaler *et al.*,[8b,12] recent experience has revealed that there are pitfalls in its use. For example, the 3-acetamido-group of the evernitrose-derived β-glycoside (5) was originally assigned [3] an axial orientation on the basis of its chemical shift, whereas a recent crystallographic study [4] has established that it is, as shown, equatorially disposed. While the use of ^{13}C n.m.r. methods holds considerable promise for assigning the configuration at the tertiary centre of branched-chain sugars, chemical methods seem to be the most reliable of those in current use.

Both methanesulphonyloxy-groups in *e.g.* (6) are solvolysed under mild conditions (usually in refluxing, wet 2-methoxyethanol) since they are *trans*-disposed to the neighbouring acetamido-group, which participates in their displacement.[13] The mechanism of such solvolyses is well understood and results in inversion of configuration at the reacting centre(s). On the other hand, vicinal sulphonyloxy-groups that are *cis*-related to an acetamido-group do not undergo solvolysis under analogous conditions because the acetamido-group is



(4) R = Ac
(6) R = SO_2Me



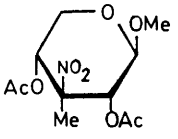
(5)

unable to assist in their displacement. Solvolytic experiments have been used by us [7] and others [8b,14] to establish the relative configurations of the substituents at C-2, C-3, and C-4 in branched-chain nitro-sugars, following their conversion into appropriate sulphonylated derivatives. This information, coupled with that afforded by ^{1}H n.m.r. spectroscopy and a knowledge of the compound's ancestry, usually suffices to establish the absolute configuration. A previous attempt [7] to use solvolytic procedures to establish the configurations of branched-chain nitro-sugars resulting from cyclisation of the ' dialdehyde ' (3) with nitroethane

was beset by difficulties, notably that of isolating the pure stereoisomers. As noted by Baer [8a,15] with related ' dialdehydes ', some of the products appeared to be formed following epimerisation of (3) at the carbon atom bearing the methyl group under the basic conditions of the reaction, thus raising the number of possible stereoisomers to sixteen. Epimerisation at the acetal carbon atom is also possible, although it appears to occur less frequently, if at all. In order to circumvent complications caused by epimerisation and to test our procedures as thoroughly as possible, we have examined the cyclisation of L'-methoxydiglycolaldehyde (7) (obtained by periodate oxidation of methyl β-D-xylopyranoside) with nitroethane. Since three new asymmetric centres are created in this reaction, it is possible to produce eight stereoisomers, each of which will possess either a β-D- or an α-L-configuration.

RESULTS AND DISCUSSION

The base-catalysed reaction between the ' dialdehyde ' (7) and nitroethane gave, after acetylation, five of the eight possible methyl 2,4-di-*O*-acetyl-3-deoxy-3-*C*-methyl-3-nitropentopyranosides. Preparative chromatography on silica gel afforded a fraction containing stereoisomers *A*, *B*, and *C*, followed by fractions containing the crystalline stereoisomers *D* (32%) and *E* (6%). Fractional crystallisation from ether–light petroleum yielded stereoisomer *A* (6.7%) and a small amount (2%) of stereoisomer *B*. Stereoisomer *C* (≤35%) could not be obtained crystalline, but it furnished a crystalline methyl 3-acetamido-2,4-di-*O*-acetyl-3-deoxy-3-*C*-methylpentopyranoside following catalytic hydrogenation of the mother-liquor and acetylation of the resulting amine.



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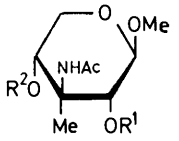
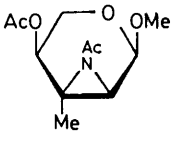


(9) $R^1 = R^2 = H$
(10) $R^1 = R^2 = Ac$
(11) $R^1 = R^2 = SO_2Me$
(24) R^1 = H; $R^2 = SO_2C_6H_4Me$-*p*



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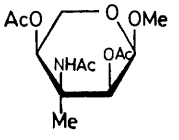


(13)

Stereoisomer *D* [m.p. 97—98 °C, $[\alpha]_D$ −56° (*c* 1.3, $CHCl_3$)], one of the principal products, was identified as methyl 2,4-di-*O*-acetyl-3-deoxy-3-*C*-methyl-3-nitro-β-D-xylopyranoside (8) on the basis of the following evidence. Its ^1H n.m.r. spectrum showed that both H-4 ($J_{4,5}$ 4.4, $J_{4,5'}$ 8.8 Hz) and H-2 ($J_{1,2}$ 6.2 Hz) were strongly coupled to H-5' and H-1, respectively, signifying that the pyranose ring adopts predominantly a $^4C_1$ conformation with the 2- and 4-acetoxy-groups and the 1-methoxy-group in equatorial orientations. Hydrogenation of (8) over Raney nickel, with accompanying de-esterification, and *N*-acetylation of the product gave the diol (9), which was further characterised as the di-*O*-acetate (10) and the bis(methanesulphonate) (11). Solvolysis of (11) in refluxing, wet 2-methoxyethanol gave, after acetylation, the *N*-acetylepimine derivative (12) rather than the triacetate (13). The ^1H n.m.r. spectrum of (12) contains three-proton singlets at δ 2.16 and 2.13, ascribed to the *N*- and *O*-acetyl groups, and, at lowest field (δ 5.03), a

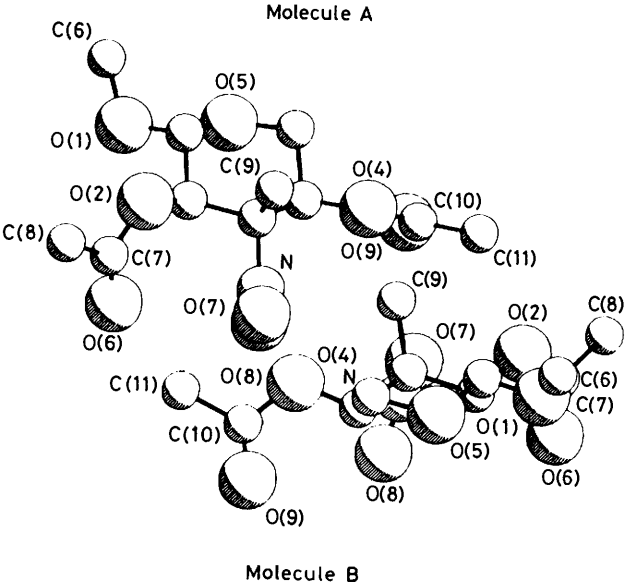
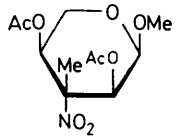


FIGURE A stereoview of methyl 2,4-di-*O*-acetyl-3-deoxy-3-*C*-methyl-3-nitro-β-D-xylopyranoside (8), and the numbering scheme for the pendant atoms

triplet (*J* 7.5 Hz) that could be ascribed to H-4. Other features of the ^1H n.m.r. spectrum (see Experimental section) are regarded as being compatible more with structure (12) than an alternative oxazoline structure. Of significance is the fact that both methanesulphonyloxy-groups were displaced on solvolysis of (11); hence, they must be *trans*-related to the 3-acetamido-group. This information, coupled with the ^1H n.m.r. evidence, indicates that compounds (8)—(11) have the β-D-*xylo* configuration. A single-crystal structure determination on the branched-chain nitro-sugar (8) confirmed this assignment, thereby dispelling any uncertainties occasioned by the unexpected course of solvolysis of the bis(methanesulphonate) (11). A stereoview of the two molecules of (8) in the asymmetric unit is shown in the Figure, while details of the structure analysis are included in the Experimental section.

An analogous procedure was used in identifying stereoisomer *C* as methyl 2,4-di-*O*-acetyl-3-deoxy-3-*C*-methyl-3-nitro-α-L-xylopyranoside (14). As noted earlier, this stereoisomer was readily converted into a crystalline triacetate (15), which, on de-*O*-acetylation and methanesulphonylation of the resulting diol (16), gave the

bis(methanesulphonate) (17). Solvolysis of (17) in refluxing, wet 2-methoxyethanol resulted in the displacement of both sulphonyloxy-groups giving, after acetylation of the resulting diol, methyl 3-acetamido-2,4-di-*O*-acetyl-3-deoxy-3-*C*-methyl-β-D-ribopyranoside (18). The identity of (18) follows from its mode of formation and the fact that it was readily distinguishable (m.p.,



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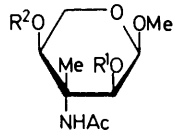
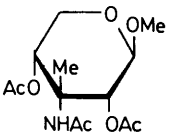


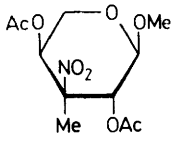
(15) $R^1 = R^2 = Ac$
(16) $R^1 = R^2 = H$
(17) $R^1 = R^2 = SO_2Me$
(25) $R^1 = SO_2C_6H_4Me\text{-}p$; $R^2 = H$
(26) $R^1 = R^2 = SO_2C_6H_4Me\text{-}p$



(18)

$[\alpha]_D$, and ^1H n.m.r. spectroscopy) from the isomeric triacetate (15). This evidence established the *trans-trans*-relationship of the nitrogen- and oxygen-containing substituents at C-2—C-4 in compounds (14)—(17), which can therefore be assigned the α-L-*xylo* configuration. The spin-couplings of the ring-protons (see Experimental section) are compatible with this assignment and indicate that compounds (14)—(17) favour a $^1C_4$ conformation in solution.

The spin-couplings ($J_{1,2}$ 7.5 and $J_{4,5}$ 1.9, $J_{4,5'}$ 2.5 Hz) of the ring-protons in the ^1H n.m.r. spectrum of stereoisomer *E* [m.p. 167—168 °C, $[\alpha]_D$ +33° (*c* 1.4, $CHCl_3$)] indicated that the molecule preferentially adopts the $^4C_1$ conformation with the 4-acetoxy-group in an axial orientation and the 2-acetoxy- and 1-methoxy-groups in equatorial orientations. Thus, depending on the configuration at the branch-point, this stereoisomer possesses either the α-L-*lyxo* or α-L-*arabino* configuration. A decision in favour of the α-L-*arabino* configuration (19) for stereoisomer *E* was reached following solvolysis of the bis(methanesulphonate) (22), which was prepared from the diol (20). The crystalline monomethane-



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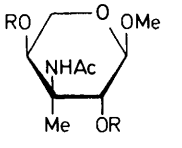
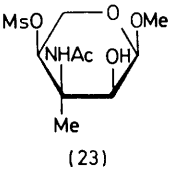


(20) R = H
(21) R = Ac
(22) $R = SO_2Me$



(23)

sulphonate obtained on solvolysis of (22) was identified as methyl 3-acetamido-3-deoxy-4-*O*-methanesulphonyl-3-*C*-methyl-α-L-ribopyranoside (23) from its ^1H n.m.r. spectrum, which revealed H-4 as a quartet ($J_{4,5}$ 3.4, $J_{4,5'}$ 8 Hz) at δ 4.76; this signal is easily recognised since it appears at a lower field than the other signals in the spectrum, owing to the deshielding effect of the geminal methanesulphonyloxy-group. Since the 2-methanesulphonyloxy-group undergoes solvolysis, it must be *trans*-related to the 3-acetamido-group, while the 4-methanesulphonyloxy-group, which resists solvolysis, is *cis*-related as depicted in (22).

Having established the β-D-*xylo* configuration (8) for stereoisomer *D* and its derivatives, it was possible to show that stereoisomer *E* has the α-L-*arabino* configuration in another way. Equimolar toluene-*p*-sulphonylation of the diol (9) in the presence of a phase-transfer catalyst [16] gave the 4-toluene-*p*-sulphonate (24), whose structure was indicated by the appearance of H-4 as a low-field quartet ($J_{4,5}$ 5.6, $J_{4,5'}$ 9.8 Hz) at δ 5.52 in the ^1H n.m.r. spectrum. Solvolysis of (24) in refluxing, wet 2-methoxyethanol gave the α-L-*arabino* diol (20), which yielded (21) on acetylation. The acetylated derivative (21) was indistinguishable from that obtained from stereoisomer *E* (19).

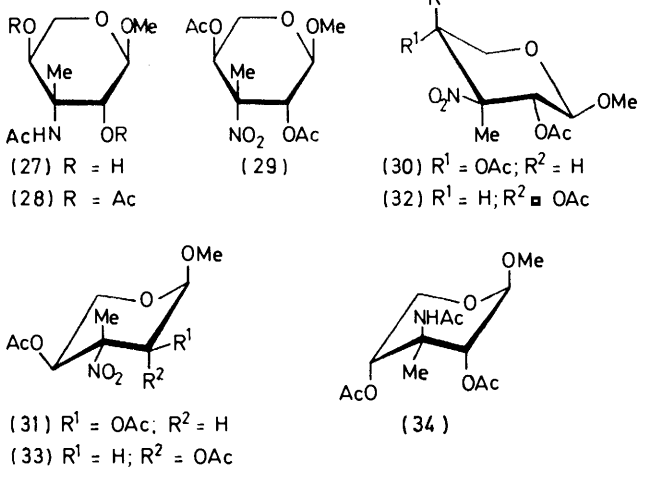
Advantage was also taken of the α-L-*xylo* configuration assigned to the diol (16) in establishing the configuration of stereoisomer *A* [m.p. 129—130 °C, $[\alpha]_D$ −25° (*c* 1, $CHCl_3$)]. Toluene-*p*-sulphonylation of (16) in the presence of a phase-transfer catalyst [16] afforded a mixture of the mono-toluene-*p*-sulphonate (25) and the bis(toluene-*p*-sulphonate) (26), which was readily separated by chromatography on silica gel. The 2-toluene-*p*-sulphonate (25) was identified by ^1H n.m.r. spectroscopy [H-2 appeared as a low-field doublet ($J_{1,2}$ *ca.* 4 Hz) at δ 5.40] and by comparison with the ^1H n.m.r. spectrum of the bis(toluene-*p*-sulphonate) (26). Solvolysis of the 2-toluene-*p*-sulphonate (25) gave the diol (27), which was characterised as the acetylated derivative (28), whose mode of synthesis requires it to have the α-L-*lyxo* configuration. Since stereoisomer *A* gave (28) on catalytic reduction and acetylation, it must be methyl 2,4-di-*O*-acetyl-3-deoxy-3-*C*-methyl-3-nitro-α-L-lyxopyranoside (29).

Because only a small amount of stereoisomer *B* [m.p. 132—133 °C, $[\alpha]_D$ −199° (*c* 1, $CHCl_3$)] was available, its structure has not been secured, although a single-crystal structure analysis is in progress.*

The spin-coupling patterns of the ring-protons indicate that the branched-chain nitro-sugars (8), (14), (19), and (29) strongly favour the conformations (30)—(33), respectively, having the 3-nitro-group equatorially disposed. The preference of the nitro-group for an equatorial orientation is most strikingly demonstrated by comparing the β-D-*xylo* isomer (8), which adopts the $^4C_1$ conformation (30), with the corresponding 3-acetamido-derivative (10) ($J_{1,2}$ 3, $J_{4,5}$ 2.2, and $J_{4,5'}$ 2.8 Hz), which clearly favours the alternative $^1C_4$ conformation (34). The simplifying assumption that the 3-nitro-group in stereoisomer *B* is equatorially orientated would rule out the β-D-*lyxo* configuration, which should display a large $J_{4,5ax}$ coupling in the $^4C_1$ conformation, although the ring-proton couplings, all of which are small, do not readily distinguish among the remaining possibilities.

* This indicates that stereoisomer B is methyl 2,4-di-*O*-acetyl-3-deoxy-3-*C*-methyl-3-nitro-β-D-arabinopyranoside.

In view of the interplay of kinetic and thermodynamic factors in nitroalkane condensations, it would not be wise to attempt too rigorous a stereochemical generalisation on the formation of the methyl 3-deoxy-3-*C*-methyl-3-*C*-nitropentopyranosides from the ' dialdehyde ' (7), even though kinetic control is likely to prevail under the conditions employed. However, meaningful interpretation of the results would require knowledge of the primary adduct formed (*i.e.* which of the two aldehydic carbon atoms is attacked first) and of the conformation it adopts prior to ring-closure. It suffices to note that the condensation is endowed with a marked stereoselectivity



(27) R = H
(28) R = Ac
(29)
(30) R^1 = OAc; R^2 = H
(32) R^1 = H; R^2 = OAc
(31) R^1 = OAc; R^2 = H
(33) R^1 = H; R^2 = OAc
(34)

that favours the formation of the α-L- and β-D-*xylo* isomers. Unlike analogous nitromethane condensations in which the configuration of the 3-nitro-group is determined by kinetically controlled protonation of the *aci*-nitro salts during neutralisation,[17] the configuration at the branch-point in the products of nitroethane condensations is determined in the cyclisation step. Comparing the size of the nitro and methyl groups, the preference of the bulkier nitro-group for an equatorial orientation in the reconstituted pyranose ring is understandable.

EXPERIMENTAL

T.l.c. was performed on Kieselgel G, and spots were detected with vanillin–sulphuric acid.[18] I.r. spectra were recorded for Nujol mulls or films with a Perkin-Elmer Infracord spectrophotometer. ^{1}H N.m.r. spectra were measured with a Brucker Spectrospin (90 MHz) spectrometer and were analysed as previously described.[19] A Perkin-Elmer Model 141 polarimeter and 1-dm tubes were used for the measurement of specific rotations. Light petroleum refers to the fraction of b.p. 60—80 °C.

Preparation of the Methyl 2,4-*Di*-O-*acetyl*-3-*deoxy*-3-C-*methyl*-3-*nitropentopyranosides*.—Methyl β-D-xylopyranoside [19] (51.5 g) was added over 20 min, with swirling, to a cooled (5 °C) solution of sodium metaperiodate (185.2 g) in water (1.3 l), and, on completion of addition, the oxidation was allowed to proceed at room temperature for 35 min, whereafter formic acid produced during the reaction was neutralised by the gradual addition of a solution of 1M sodium hydrogencarbonate. Care was taken to ensure that the reaction mixture did not become alkaline. The oxidation was complete after 2 h, during which time a total of 283 ml of 1M sodium hydrogencarbonate was added. The solids that precipitated during the oxidation were filtered off and the solution of ' dialdehyde ' (7) was reduced in volume (bath temperature *ca.* 45 °C), with occasional filtration, to 300 ml. Ethanol (600 ml) was then added and solids were filtered off and washed with ice-cold ethanol (100 ml). The combined filtrate and washings were set aside overnight at 0 °C, filtered, and concentrated to a syrup, which was dissolved in hot ethanol (500 ml). This solution was set aside overnight before any solids were removed by filtration.

To the swirled ethanolic solution of ' dialdehyde ' (7) was added nitroethane (84 ml) followed by an ethanolic solution of sodium ethoxide [375 ml; containing sodium (8 g)]. After 4 h at room temperature, the reaction mixture was neutralised (solid carbon dioxide), filtered, and solid material on the filter was washed with ethanol (100 ml). The combined filtrate and washings were concentrated and the resulting syrup was dissolved in absolute ethanol (500 ml). This solution was set aside overnight and any inorganic material that precipitated was removed prior to concentration of the solution. The residue in dry pyridine (300 ml) was treated with acetic anhydride (150 ml) for 1 h at 0 °C and afterwards at room temperature for 24 h. Most of the solvents were removed under reduced pressure (bath temperature ≤35 °C) and the residue was taken up in chloroform (600 ml), which was washed in turn with dilute hydrochloric acid, saturated sodium hydrogencarbonate solution, and water, dried ($MgSO_4$), and concentrated to a syrup (89 g).

Chromatography of a portion (16 g) of this syrup on silica gel [carbon tetrachloride–acetone–ether (7 : 1 : 1)] gave first a fraction (6.9 g) containing three components, which was dissolved in ether–light petroleum (1 : 1, 6 ml) and left in the refrigerator for 24 h. The solution deposited *methyl* 2,4-*di*-O-*acetyl*-3-*deoxy*-3-C-*methyl*-3-*nitro*-α-L-*lyxopyranoside* (29) (1.1 g, 6.7%), m.p. 129—130 °C (after two recrystallisations from ether–light petroleum); $[\alpha]_D$ −25° (*c* 1, $CHCl_3$) (Found: C, 45.3; H, 5.7; N, 4.6. $C_{11}H_{17}NO_8$ requires C, 45.3; H, 5.8; N, 4.8%); δ ($CDCl_3$) 5.92 (1 H, q, $J_{4.5}$ 6.2, $J_{4.5'}$ 9.7 Hz, H-4), 5.33 (1 H, d, $J_{1,2}$ 1.5 Hz, H-2), 4.74 (1 H, d, H-1), 3.92 (1 H, q, J_{gem} 10 Hz, H-5), 3.51 (1 H, t, H-5'), 3.42 (3 H, s, OMe), 2.11 and 2.04 (6 H, each s, 2 × OAc), and 1.89 (3 H, s, CMe). The mother-liquors were concentrated and the syrupy residue was thinned with ether–light petroleum (1 : 3, 6 ml). On cooling (0—4 °C), this solution deposited crystals of an unidentified *methyl* 2,4-*di*-O-*acetyl*-3-*deoxy*-3-C-*methyl*-3-*nitropentopyranoside* (stereoisomer *B*) (0.32 g, 1.95%), m.p. 132—133 °C; $[\alpha]_D$ −199° (*c* 1, $CHCl_3$) (Found: C, 45.6; H, 5.9; N, 4.9%); δ ($CDCl_3$) 5.86 (1 H, d, $J_{1.2}$ 4 Hz, H-2), 5.28 (1 H, narrow m, H-4), 5.05 (1 H, d, H-1), 3.90 (2 H, m, H-5 and H-5'), 3.40 (3 H, s, OMe), 2.16 and 2.06 (6 H, each s, 2 × OAc), and 1.94 (3 H, s, CMe). The mother-liquor (*ca.* 5.2 g), which was enriched in methyl 2,4-di-*O*-acetyl-3-deoxy-3-*C*-methyl-3-nitro-α-L-xylopyranoside (14), was concentrated and treated as described in the next experiment. Subtraction of the signals for stereoisomers (29) and *B* from the ^{1}H n.m.r. spectrum of the mother-liquor gave the following data for (14); δ ($CDCl_3$) 5.56 (1 H, q, $J_{4.5}$ 6, $J_{4.5'}$ 11 Hz, H-4), 5.49 (1 H, d, $J_{1,2}$ 4 Hz, H-2), 5.00 (1 H, d, H-1), 3.41 (3 H, s, OMe), 2.10 and 2.06 (6 H, each s, 2 × OAc), and 1.89 (3 H, s, CMe).

Continued elution gave *methyl* 2,4-*di*-O-*acetyl*-3-*deoxy*-3-C-*methyl*-3-*nitro*-β-D-*xylopyranoside* (8) (5.2 g, 31.6%), m.p. 97—98 °C (from ether–light petroleum), $[\alpha]_D$ −56° (*c* 1.3, $CHCl_3$) (Found: C, 45.2; H, 5.6; N, 4.9%); δ ($CDCl_3$) 5.65 (1 H, q, $J_{4.5}$ 4.4, $J_{4.5'}$ 8.8 Hz, H-4), 5.53 (1 H, d, $J_{1.2}$ 6.2 Hz, H-2), 4.47 (1 H, d, H-1), 4.20 (1 H, q, J_{gem} 12.6 Hz, H-5), 3.48 (1 H, q, H-5′), 3.44 (3 H, s, OMe), 2.12 and 2.09 (6 H, each s, 2 × OAc), and 1.72 (3 H, s, CMe) followed by *methyl* 2,4-*di*-O-*acetyl*-3-*deoxy*-3-C-*methyl*-3-*nitro*-α-L-*arabinopyranoside* (19) (1.01 g, 6.1%), m.p. 167—168 °C (from ether); $[\alpha]_D$ +33° (*c* 1.4, $CHCl_3$) (Found: C, 45.4; H, 6.1; N, 4.7%); δ ($CDCl_3$) 5.88 (1 H, d, $J_{1.2}$ 7.5 Hz, H-2), 5.29 (1 H, narrow q, $J_{4.5}$ 1.9, $J_{4.5'}$ 2.5 Hz, H-4), 4.33 (1 H, d, H-1), 4.20 (1 H, q, J_{gem} 13.6 Hz, H-5), 3.79 (1 H, q, H-5′), 3.50 (3 H, s, OMe), 2.13 and 2.07 (6 H, each s, 2 × OAc), and 1.80 (3 H, s, CMe).

Methyl 3-*Acetamido*-2,4-*di*-O-*acetyl*-3-*deoxy*-3-C-*methyl*-α-L-*xylopyranoside* (15).—A solution of the mother-liquor (5.2 g) from the previous experiment in methanol (150 ml) containing 2% palladium–charcoal (2 g) was hydrogenated at 30 atm for 48 h, whereafter it was filtered and concentrated. The residue (3 g) in dry pyridine (100 ml) was treated with acetic anhydride (3 ml) for 24 h at room temperature. Work-up in the usual manner and chromatography on silica gel [elution with light petroleum–acetone–ether–ethanol (8 : 4 : 1 : 1)] gave the *triacetate* (15) (1.84 g), m.p. 197—198 °C (from ether–light petroleum); $[\alpha]_D$ −104° (*c* 1, $CHCl_3$) (Found: C, 51.4; H, 7.2; N, 4.5. $C_{13}H_{21}NO_7$ requires C, 51.5; H, 6.9; N, 4.6%); δ ($CDCl_3$) 5.91 (1 H, q, $J_{4.5}$ *ca.* 6, $J_{4.5'}$ *ca.* 9.5 Hz, H-4), 5.82 (1 H, d, $J_{1.2}$ 4 Hz, H-2), 4.89 (1 H, d, H-1), 3.64 (2 H, m, H-5 and H-5′), 3.36 (3 H, s, OMe), 2.11 and 2.05 (6 H, each s, 2 × OAc), 1.86 (3 H, s, NAc), and 1.45 (3 H, s, CMe).

Methyl 3-*Acetamido*-3-*deoxy*-3-C-*methyl*-β-D-*xylopyranoside* (9).—A solution of the nitroglycoside (8) (3.06 g) in dry methanol (100 ml) containing Raney nickel [20] (5 g) was hydrogenated at 30 atm and room temperature for 24 h. Removal of the catalyst and solvent gave a syrup (1.44 g), which was dissolved in dry methanol (300 ml) and treated with acetic anhydride (4 ml) for 20 h at room temperature. Removal of the solvents, followed by addition and distillation of toluene from the residue, gave a syrup that crystallised on trituration with chloroform. Recrystallisation from light petroleum gave the *diol* (9) (1.6 g, 70%), m.p. 145—147 °C; $[\alpha]_D$ −31° (*c* 1.2, MeOH); $\nu_{max.}$ 3 400 (OH) and 1 645 and 1 550 cm^{-1} (NHAc) (Found: C, 48.9; H, 7.9; N, 6.2. $C_9H_{17}NO_5$ requires C, 49.3; H, 7.8; N, 6.4%).

Methyl 3-*Acetamido*-2,4-*di*-O-*acetyl*-3-*deoxy*-3-C-*methyl*-β-D-*xylopyranoside* (10).—A solution of the diol (9) (0.31 g) in dry pyridine (10 ml) was treated with acetic anhydride (1 ml) for 20 h at room temperature, whereupon work-up in the usual way gave the *triacetate* (10) (0.32 g, 75%), m.p. 158—159 °C (from chloroform–light petroleum); $[\alpha]_D$ −33° (*c* 0.4, MeOH) (Found: C, 51.3; H, 6.8; N, 4.6. $C_{13}H_{21}NO_7$ requires C, 51.5; H, 6.9; N, 4.6%); δ ($CDCl_3$) 5.47 (1 H, narrow q, $J_{4.5}$ 2.2, $J_{4.5'}$ 2.8 Hz, H-4), 4.77 (1 H, d, $J_{1.2}$ *ca.* 3 Hz, H-2), 4.62 (1 H, d, H-1), 4.07 (1 H, q, J_{gem} 12.9 Hz, H-5), 3.69 (1 H, q, H-5′), 3.48 (3 H, s, OMe), 2.17 and 2.14 (6 H, each s, 2 × OAc), 1.96 (3 H, s, NAc), and 1.49 (3 H, s, CMe).

Methyl 3-*Acetamido*-3-*deoxy*-2,4-*di*-O-*methanesulphonyl*-3-C-*methyl*-β-D-*xylopyranoside* (11).—To a cooled (0 °C) solution of the diol (9) (1 g) in dry pyridine (30 ml) was added methanesulphonyl chloride (2 ml) over 1 h. On complete addition, the solution was set aside overnight at room temperature and then worked-up in the usual way to give the bis(methanesulphonate) (11) (1.3 g, 76%), m.p. 150—151 °C (from chloroform–ether); $[\alpha]_D$ −54° (*c* 0.9, $CHCl_3$) (Found: C, 35.15; H, 5.6; N, 3.6; S, 17.4. $C_{11}H_{21}NO_9S_2$ requires C, 35.2; H, 5.6; N, 3.7; S, 17.1%); δ ($CDCl_3$) 5.88 (1 H, q, $J_{4.5}$ 5.2, $J_{4.5'}$ 9.6 Hz, H-4), 5.22 (1 H, d, $J_{1.2}$ 7.6 Hz, H-2), 4.44 (1 H, d, H-1), 4.21 (1 H, q, J_{gem} 12 Hz, H-5), 3.56 (1 H, q, H-5′), 3.52 (3 H, s, OMe), 3.08 and 3.03 (6 H, each s, 2 × OSO_2Me), 1.98 (3 H, s, NAc), and 1.34 (3 H, s, CMe).

Methyl 3-*Acetamido*-3-*deoxy*-2,4-*di*-O-*methanesulphonyl*-3-C-*methyl*-α-L-*xylopyranoside* (17).—To a solution of the triacetate (15) (1.49 g) in dry methanol (15 ml) was added a methanolic solution of sodium methoxide (7 ml, containing 0.14 g of sodium) and the solution was set aside overnight at room temperature. Neutralisation (solid carbon dioxide), filtration, and evaporation gave a residue, which was extracted with chloroform (2 × 25 ml). The dried ($MgSO_4$) chloroform extract was evaporated and methanesulphonyl chloride (2 ml) was added over 1 h to a solution of the residue (1.07 g) in dry, cold (0 °C) pyridine (30 ml). The solution was kept for 24 h at room temperature, and the solvents were then removed under reduced pressure and methylene chloride (100 ml) was added to the residue. Work-up of the organic extract in the usual way gave the *bis*(*methanesulphonate*) (17) (1.47 g, 80%), m.p. 178—179 °C (from chloroform–ether); $[\alpha]_D$ −80° (*c* 0.8, MeOH) (Found: C, 35.2; H, 5.8; N, 3.9; S, 16.8. $C_{11}H_{21}NO_9S_2$ requires C, 35.2; H, 5.6; N, 3.7; S, 17.1%); δ ([$^2H_6$]DMSO) 5.61 (1 H, q, $J_{4.5}$ *ca.* 6, $J_{4.5'}$ *ca.* 10 Hz, H-4), 5.51 (1 H, d, $J_{1.2}$ 4 Hz, H-2), 4.93 (1 H, d, H-1), 3.70 (2 H, m, H-5 and H-5′), 3.34 (3 H, s, OMe), 3.15 (6 H, s, 2 × OSO_2Me), 1.82 (3 H, s, NAc), and 1.24 (3 H, s, CMe).

Methyl 3-*Acetamido*-2,4-*di*-O-*acetyl*-3-*deoxy*-3-C-*methyl*-α-L-*arabinopyranoside* (21).—A solution of the nitroglycoside (19) (2.32 g) in methanol (100 ml) containing Raney nickel [20] (5 g) was hydrogenated at 30 atm and room temperature for 48 h, whereupon it was filtered and concentrated. A solution of the residue (1.26 g) in dry methanol (100 ml) was treated with acetic anhydride (3 ml) overnight at room temperature and, after a conventional work-up, gave syrupy methyl 3-acetamido-3-deoxy-3-*C*-methyl-α-L-arabinopyranoside (20) (1.13 g). A solution of the diol (20) (0.41 g) in dry pyridine (10 ml) was acetylated with acetic anhydride (2 ml), as previously described, to give the *triacetate* (21) (0.48 g, 85%), m.p. 104—105 °C (from ether–light petroleum); $[\alpha]_D$ +40.5° (*c* 1.4, $CHCl_3$) (Found: C, 51.5; H, 6.7; N, 4.9. $C_{13}H_{21}NO_7$ requires C, 51.5; H, 6.9; N, 4.6%); δ ($CDCl_3$) 5.44 (1 H, q, $J_{4.5}$ 4.7, $J_{4.5'}$ 2.3 Hz, H-4), 5.07 (1 H, d, $J_{1.2}$ 6 Hz, H-2), 4.50 (1 H, d, H-1), 3.99 and 3.71 (2 H, each q, J_{gem} 13 Hz, H-5 and H-5′), 3.48 (3 H, s, OMe), 2.16 and 2.11 (6 H, each s, 2 × OAc), 1.91 (3 H, s, NAc), and 1.58 (3 H, s, CMe).

Methyl 3-*Acetamido*-3-*deoxy*-2,4-*di*-O-*methanesulphonyl*-3-C-*methyl*-α-L-*arabinopyranoside* (22).—To a cold (0 °C) solution of the diol (20) (1.13 g; obtained as described in the previous experiment) in dry pyridine (30 ml) was added methanesulphonyl chloride (2 ml) over 1 h; the solution was set aside overnight and worked-up in the usual way to give the *bis*(*methanesulphonate*) (22) (1.49 g, 68%), m.p. 191—192 °C (from chloroform–ether); $[\alpha]_D$ +64° (*c* 0.6, $CHCl_3$) (Found: C, 35.7; H, 5.9; N, 4.0; S, 17.1. $C_{11}H_{21}NO_9S_2$ requires C, 35.2; H, 5.6; N, 3.7; S, 17.1%); δ ($CDCl_3$) 3.57 (3 H, s, OMe), 3.18 and 3.06 (6 H, each s, 2 × OSO_2Me), 1.96 (3 H, s, NAc), and 1.68 (3 H, s, CMe).

Methyl 3-Acetamido-3-deoxy-3-C-methyl-2-O-toluene-p-sulphonyl-α-L-xylopyranoside (25) *and the Corresponding 2,4-Bis(toluene-p-sulphonate)* (26).—To a solution of the triacetate (15) (0.79 g) in dry methanol (10 ml) was added a methanolic solution of sodium methoxide (5 ml, containing 0.18 g of sodium), and the solution was left overnight before it was neutralised (solid carbon dioxide) and concentrated. Extraction of the residue with chloroform (2 × 25 ml), filtration of the combined extracts, and removal of the solvent gave chromatographically pure methyl 3-acetamido-3-deoxy-3-*C*-methyl-α-L-xylopyranoside (16) (0.48 g, 84%); $\nu_{max.}$ (film) 3 400 cm^{-1} (OH). To a solution of the diol (16) (0.48 g) in 5% sodium hydroxide solution (5 ml) was added tetrabutylammonium hydrogensulphate (0.15 g) and a solution of toluene-*p*-sulphonyl chloride (0.6 g) in methylene chloride (20 ml). The two-phase system was stirred vigorously at room temperature for 2 h; two new components were then detected in the organic layer by t.l.c. [benzene–acetone (7 : 5)]. The separated organic layer was washed with water (3 × 5 ml), dried ($MgSO_4$), and concentrated. Chromatography of the residue on silica gel [elution with benzene–acetone (7 : 5)] gave first the *bis(toluene-p-sulphonate)* (26) (0.15 g, 13%), m.p. 175—176 °C (from ether); $[\alpha]_D$ −61° (*c* 0.9, $CHCl_3$) (Found: C, 52.6; H, 5.7; N, 2.6; S, 11.9. $C_{23}H_{29}NO_9S_2$ requires C, 52.3; H, 5.5; N, 2.7; S, 12.2%); δ ([$^2H_6$]acetone) 7.62 (8 H, m, 2 × C_6H_4), 5.59 (1 H, q, $J_{4.5}$ *ca.* 6, $J_{4.5'}$ *ca.* 10 Hz, H-4), 5.48 (1 H, d, $J_{1,2}$ 4.5 Hz, H-2), 4.53 (1 H, d, H-1), 3.51 (2 H, m, H-5 and H-5′), 3.23 (3 H, s, OMe), 2.44 (6 H, s, 2 × Ar-*Me*), 1.30 (3 H, s, NAc), and 1.24 (3 H, s, CMe). Continued elution furnished the *2-toluene-p-sulphonate* (25) (78 mg), m.p. 164—165 °C (from ether); $[\alpha]_D$ −26° (*c* 0.75, $CNCl_3$) (Found: C, 51.6; H, 5.9; N, 3.5; S, 8.4. $C_{16}H_{23}NO_7S$ requires C, 51.4; H, 6.2; N, 3.8; S, 8.6%); δ ([$^2H_6$]acetone) 7.65 (4 H, m, C_6H_4), 5.40 (1 H, d, $J_{1/2}$ 4 Hz, H-2), 4.52 (1 H, d, H-1), 3.23 (3 H, s, OMe), 2.44 (3 H, s, Ar-*Me*), 1.59 (3 H, s, NAc), and 1.23 (3 H, s, CMe).

Methyl 3-Acetamido-3-deoxy-3-C-methyl-4-O-toluene-p-sulphonyl-β-D-xylopyranoside (24).—A two-phase system consisting of the diol (9) (0.37 g), tetrabutylammonium hydrogensulphate (0.115 g), and toluene-*p*-sulphonyl chloride (0.46 g) dispersed between dichloromethane (20 ml) and a 5% solution of sodium hydroxide (2 ml) was stirred vigorously for 2 h at room temperature. Work-up as described in the previous experiment gave the *4-toluene-p-sulphonate* (24) (0.175 g, 28%), m.p. 129—130 °C; $[\alpha]_D$ −27.5° (*c* 0.8, $CHCl_3$) (Found: C, 51.1; H, 6.2; N, 3.6; S, 8.8. $C_{16}H_{23}NO_7S$ requires C, 51.4; H, 6.2; N, 3.8; S, 8.6%); δ ([$^2H_6$]acetone) 7.64 (4 H, m, C_6H_4), 5.52 (1 H, q, $J_{4,5}$ *ca.* 5.6, $J_{4,5'}$ *ca.* 9.8 Hz, H-4), 4.38 (1 H, d, $J_{1,2}$ 7 Hz, H-1), 3.85 (1 H, q, J_{gem} 11.8 Hz, H-5), 3.54 (1 H, q, H-5′), 3.38 (3 H, s, OMe), 2.47 (3 H, s, Ar-*Me*), 1.55 (3 H, s, NAc), and 1.21 (3 H, s, CMe).

Methyl 3-Acetamido-2,4-di-O-acetyl-3-deoxy-3-C-methyl-α-L-lyxopyranoside (28).—A solution of the nitroglycoside (29) (0.19 g) in methanol (50 ml) containing 2% palladium–charcoal (1 g) was hydrogenated at 30 atm and room temperature for 24 h, whereafter the catalyst and solvent were removed. A solution of the residue in pyridine (20 ml) was treated overnight with acetic anhydride (2 ml), whereupon work-up in the usual manner, chromatography on silica gel [elution with carbon tetrachloride–acetone–ether–ethanol (7 : 1 : 1 : 1)], and trituration with ether gave the *triacetate* (28) (0.18 g, 91%), which was recrystallised from light petroleum, m.p. 141—142 °C; $[\alpha]_D$ +9° (*c* 1.1, $CHCl_3$) (Found: C, 51.4; H, 7.2; N, 4.9. $C_{13}H_{21}NO_7$ requires C, 51.5; H, 6.9; N, 4.6%); δ ($CDCl_3$) 5.55 (1 H, q, $J_{4.5}$ 4.5, $J_{4,5'}$ 6.1 Hz, H-4), 5.33 (1 H, d, $J_{1,2}$ 4.8 Hz, H-2), 4.56 (1 H, d, H-1), 4.00—3.60 (2 H, m, J_{gem} 12.2 Hz, H-5 and H-5′), 3.43 (3 H, s, OMe), 2.14 and 2.12 (6 H, each s, 2 × OAc), 1.94 (3 H, s, NAc), and 1.52 (3 H, s, CMe).

Solvolytic Experiments.—(a) *The solvolysis of methyl 3-acetamido-3-deoxy-2,4-di-O-methanesulphonyl-3-C-methyl-β-D-xylopyranoside* (11). A solution of the bis(methanesulphonate) (11) (0.4 g) in wet 95% 2-methoxyethanol (30 ml) containing sodium acetate (0.3 g) was heated under gentle reflux for 16 h, whereafter the solution was filtered and concentrated. The residue in dry pyridine (10 ml) was treated overnight at room temperature with acetic anhydride (3 ml), and the solution was then processed in the usual way. Chromatography of the residue on silica gel [elution with carbon tetrachloride–acetone–ether–ethanol (7 : 1 : 1 : 1)] gave syrupy *methyl N,4-O-diacetyl-2,3-epimino-2,3-dideoxy-3-C-methyl-α-L-ribopyranoside* (12) (0.12 g, 46%); $[\alpha]_D$ −49° (*c* 0.7, $CHCl_3$); δ ($CDCl_3$) 5.03 (1 H, t, $J_{4,5} = J_{4,5'} \approx 7.5$ Hz, H-4), 4.89 (1 H, d, $J_{1,2}$ 4 Hz, H-1), 3.57 (2 H, m, H-5 and H-5′), 3.43 (3 H, s, OMe), 2.96 (1 H,d, H-2), 2.16 and 2.13 (6 H, each s, NAc and OAc), and 1.40 (3 H, s, CMe).

(b) *The solvolysis of methyl 3-acetamido-3-deoxy-2,4-di-O-methanesulphonyl-3-C-methyl-α-L-xylopyranoside* (17). A solution of the bis(methanesulphonate) (17) (0.7 g) in wet 95% 2-methoxyethanol (25 ml) containing sodium acetate (0.62 g) was heated under gentle reflux for 24 h, whereafter processing and chromatography, as described in (a), gave *methyl 3-acetamido-2,4-di-O-acetyl-3-deoxy-3-C-methyl-β-D-ribopyranoside* (18) (0.19 g, 34%), m.p. 105—106 °C (from ether); $[\alpha]_D$ −78° (*c* 0.7, $CHCl_3$) (Found: C, 51.2; H, 6.8; N, 4.4. $C_{13}H_{21}NO_7$ requires C, 51.5; H, 6.9; N, 4.6%); δ ($CDCl_3$) 5.13 and 5.00 (2 H, br s and narrow m, H-2 and H-4), 4.74 (1 H, br s, H-1), 4.05 and 3.76 (2 H, each q, $J_{4.5} = J_{4.5'} \approx 2$, and J_{gem} 13 Hz, H-5 and H-5′), 3.42 (3 H, s, OMe), 2.18 and 2.14 (6 H, each s, 2 × OAc), 1.91 (3 H, s, NAc), and 1.75 (3 H, s, CMe).

(c) *The solvolysis of methyl 3-acetamido-3-deoxy-2,4-di-O-methanesulphonyl-3-C-methyl-α-L-arabinopyranoside* (22). A solution of the bis(methanesulphonate) (22) (0.45 g) in wet 95% 2-methoxyethanol (25 ml) containing sodium acetate (0.36 g) was heated under gentle reflux for 16 h, after which the solids were filtered off and the solvent was removed. Chromatography of the residue on silica gel [elution as in (a)] gave a syrup that crystallised on trituration with chloroform. Recrystallisation from ether gave *methyl 3-acetamido-3-deoxy-4-O-methanesulphonyl-3-C-methyl-α-L-ribopyranoside* (23) (0.19 g, 53%), m.p. 159—161 °C; $[\alpha]_D$ −30° (*c* 1, $CHCl_3$) (Found: C, 40.4; H, 6.6; N, 4.7; S, 10.6. $C_{10}H_{19}NO_7S$ requires C, 40.4; H, 6.4; N, 4.7; S, 10.8%); δ ($CDCl_3$) 4.76 (1 H, q, $J_{4,5}$ 3.4, $J_{4,5'}$ 8 Hz, H-4), 4.62 (1 H, d, $J_{1,2}$ *ca.* 2.5 Hz, H-1), 4.04 and 3.73 (2 H, each q, J_{gem} 12.4 Hz, H-5 and H-5′), 3.49 (3 H, s, OMe), 3.09 (3 H, s, OSO_2Me), 2.01 (3 H, s, NAc), and 1.66 (3 H, s, CMe).

(d) *The solvolysis of methyl 3-acetamido-3-deoxy-3-C-methyl-4-O-toluene-p-sulphonyl-β-D-xylopyranoside* (24). A solution of the 4-toluene-*p*-sulphonate (24) (0.11 g) in wet 95% 2-methoxyethanol (13 ml) containing sodium acetate (87 mg) was heated under gentle reflux for 2 h, whereafter it was processed as in (a). The resulting diol (20) was acetylated (as previously described) to give the *triacetate* (21), m.p. 106—107 °C (from ether–hexane); $[\alpha]_D$ +40.5° (*c* 0.6, $CHCl_3$), whose i.r. and n.m.r. spectra were indistinguishable

from those of the material previously obtained from the 3-*C*-methyl-3-nitroglycoside (19).

(e) *The solvolysis of methyl* 3-*acetamido*-3-*deoxy*-3-C-*methyl*-2-O-*toluene*-p-*sulphonyl*-α-L-*xylopyranoside* (25). A solution of the 2-toluene-*p*-sulphonate (25) (69 mg) in wet 95% 2-methoxyethanol (10 ml) containing sodium acetate (51 mg) was solvolysed as in (a) and the resulting diol (27) was acetylated (as previously described) to give the *triacetate* (28) (18 mg, 32%), m.p. 143—144 °C (from ether–hexane); $[\alpha]_D$ +10° (*c* 0.245, $CHCl_3$). The i.r. and n.m.r. spectra of (28) were indistinguishable from those of the material previously obtained from the 3-*C*-methyl-3-nitroglycoside (29).

TABLE 1

Final atomic parameters for compound (8); the estimated standard deviations (in parentheses) refer to the least significant digits

Atom Molecule A	*x*/*a*	*y*/*b*	*z*/*c*
C(1)	0.422 7(8)	0.489 2(5)	0.427 9(15)
C(2)	0.483 1(8)	0.439 5(5)	0.476 0(13)
C(3)	0.437 3(7)	0.397 4(4)	0.593 2(13)
C(4)	0.395 4(8)	0.433 6(5)	0.722 3(15)
C(5)	0.333 9(8)	0.482 5(6)	0.659 0(18)
C(6)	0.421 8(9)	0.572 4(6)	0.253 5(19)
C(7)	0.588 2(8)	0.386 9(6)	0.312 2(15)
C(8)	0.594 3(10)	0.359 3(7)	0.147 5(18)
C(9)	0.374 4(8)	0.355 2(5)	0.513 2(16)
C(10)	0.327 1(9)	0.406 4(6)	0.973 4(16)
C(11)	0.278 8(10)	0.361 1(7)	1.058 6(18)
N	0.507 9(7)	0.361 9(4)	0.672 9(14)
O(1)	0.474 1(5)	0.530 5(3)	0.343 9(10)
O(2)	0.504 8(5)	0.409 4(3)	0.332 3(9)
O(4)	0.342 9(5)	0.393 3(3)	0.818 5(9)
O(5)	0.388 9(6)	0.520 2(3)	0.560 2(10)
O(6)	0.643 1(5)	0.388 4(5)	0.410 8(11)
O(7)	0.517 0(7)	0.309 8(4)	0.634 7(14)
O(8)	0.557 1(6)	0.385 6(5)	0.767 7(12)
O(9)	0.353 3(8)	0.453 1(5)	1.025 7(12)
Molecule B			
C(1)	0.341 8(8)	0.069 9(5)	0.848 6(16)
C(2)	0.383 1(7)	0.119 7(5)	0.942 2(15)
C(3)	0.425 0(7)	0.165 3(5)	0.828 4(15)
C(4)	0.491 7(7)	0.130 1(5)	0.726 6(14)
C(5)	0.448 1(9)	0.076 8(5)	0.646 3(16)
C(6)	0.251 1(12)	−0.013 8(7)	0.876 2(23)
C(7)	0.319 6(9)	0.162 3(7)	1.176 3(17)
C(8)	0.246 8(10)	0.196 7(7)	1.253 3(19)
C(9)	0.360 5(9)	0.200 9(5)	0.732 3(16)
C(10)	0.608 1(9)	0.164 4(6)	0.552 8(14)
C(11)	0.631 3(10)	0.209 6(6)	0.426 1(16)
N	0.479 1(9)	0.209 0(5)	0.927 4(15)
O(1)	0.304 8(6)	0.030 2(4)	0.950 1(11)
O(2)	0.311 7(5)	0.149 7(4)	1.024 9(10)
O(4)	0.522 5(5)	0.170 7(3)	0.606 0(10)
O(5)	0.408 2(5)	0.040 1(4)	0.763 8(10)
O(6)	0.386 6(8)	0.148 9(6)	1.246 7(13)
O(7)	0.440 8(8)	0.253 6(5)	0.967 4(16)
O(8)	0.552 6(7)	0.196 1(5)	0.971 2(15)
O(9)	0.658 3(6)	0.126 2(5)	0.602 0(12)

Crystal Structure Determination of Methyl 2,4-*Di*-O-*acetyl*-3-*deoxy*-3-C-*methyl*-3-*nitro*-β-D-*xylopyranoside* (8).—*Crystal data*. $C_{11}H_{17}NO_8$, M = 291.133. Orthorhombic, a = 15.054(10), b = 22.536(15), c = 8.432(8) Å, U = 2 860.61 Å^3, Z = 8, D_c = 1.419 g cm^{-3}, space group $P2_12_12_1$, Cu-K_α radiation, λ = 1.542 8 Å, μ = 9.07 cm^{-1}.

Crystallographic measurements and structure analysis. Initial unit-cell dimensions and information on the space group were obtained from Weissenberg photographs taken with Mo-K_α radiation (λ = 0.710 7 Å) for the layers 0—6 of crystals mounted about the *a*, *b*, and *c* axes. The raw intensity data were obtained at the S.R.C. microdensitometer service. About 60 low-angle reflections were remeasured on a Hilger and Watts linear diffractometer (Mo-K_α radiation). Of the reflections measured, 1 373 were considered to be statistically significant and were used in the structure analysis and refinement. Reduction of the data and subsequent computing were carried out on the University of Dundee DEC-10 computer using the SHEL-X 76 program.[21] No absorption corrections were applied.

The structure was solved using multisolution tangent refinement for 435 reflections with $E > 1.3$. An *E*-map calculated using the set of phases having the lowest residual and highest figure-of-merit revealed 24 of the 40 non-hydrogen atoms of the two molecules (labelled A and B) in the asymmetric unit. The positions of the other 16 non-hydrogen atoms were obtained from a Fourier map after structure-factor calculations based on the original 24 atoms.

TABLE 2

Interatomic distances (Å) and angles (°) in compound (8) (estimated standard deviations in parentheses)

(*a*) Interatomic distances	Molecule A	Molecule B
C(1)–C(2)	1.498(16)	1.506(17)
C(2)–C(3)	1.534(15)	1.542(17)
C(3)–C(4)	1.501(16)	1.540(16)
C(4)–C(5)	1.536(18)	1.527(17)
C(1)–O(5)	1.412(15)	1.400(15)
C(5)–O(5)	1.450(16)	1.424(15)
C(1)–O(1)	1.403(14)	1.358(16)
C(6)–O(1)	1.445(16)	1.423(20)
C(2)–O(2)	1.426(13)	1.450(14)
C(7)–O(2)	1.364(14)	1.313(17)
C(7)–C(8)	1.524(20)	1.492(21)
C(7)–O(6)	1.173(15)	1.208(18)
C(4)–O(4)	1.451(15)	1.444(14)
C(10)–O(4)	1.361(15)	1.371(16)
C(10)–C(11)	1.444(20)	1.517(19)
C(10)–O(9)	1.207(17)	1.219(16)
C(3)–C(9)	1.501(16)	1.498(17)
C(3)–N	1.490(15)	1.525(16)
N–O(7)	1.224(14)	1.207(16)
N–O(8)	1.214(15)	1.202(17)
(*b*) Bond angles		
C(1)–C(2)–C(3)	111.4(9)	109.9(10)
C(2)–C(3)–C(4)	108.7(9)	105.7(9)
C(3)–C(4)–C(5)	113.1(10)	111.9(9)
C(4)–C(5)–O(5)	106.0(10)	109.3(10)
C(5)–O(5)–C(1)	111.7(9)	112.3(9)
O(5)–C(1)–C(2)	112.0(10)	109.2(11)
O(1)–C(1)–O(5)	105.6(8)	107.4(10)
O(1)–C(1)–C(2)	107.4(9)	109.3(11)
C(6)–O(1)–C(1)	113.6(9)	114.6(11)
O(2)–C(2)–C(1)	105.3(9)	107.1(9)
O(2)–C(2)–C(3)	110.9(9)	106.9(9)
C(7)–O(2)–C(2)	119.5(9)	120.1(9)
O(2)–C(7)–C(8)	108.7(10)	117.9(12)
O(6)–C(7)–C(8)	128.0(12)	122.0(14)
O(6)–C(7)–O(2)	123.3(11)	120.0(13)
O(4)–C(4)–C(3)	107.1(9)	106.1(8)
O(4)–C(4)–C(5)	108.4(10)	108.9(10)
C(10)–O(4)–C(4)	119.7(9)	117.8(9)
O(4)–C(10)–C(11)	114.3(11)	112.2(11)
O(9)–C(10)–C(11)	126.8(13)	124.8(12)
O(9)–C(10)–O(4)	118.9(12)	123.1(11)
C(2)–C(3)–C(9)	112.7(10)	115.4(10)
C(4)–C(3)–C(9)	113.9(10)	113.3(10)
N–C(3)–C(2)	107.6(9)	107.9(10)
N–C(3)–C(4)	105.3(9)	106.9(9)
N–C(3)–C(9)	108.3(9)	107.3(9)
O(7)–N–C(3)	118.4(10)	115.8(12)
O(8)–N–O(7)	121.9(11)	123.6(13)
O(8)–N–C(3)	119.7(10)	120.3(11)

Positional and isotropic thermal parameters were refined by three rounds of full-matrix least-squares to R 0.116. Unit weights were used throughout. Some of the hydrogen atoms were revealed on a difference-Fourier map ($|F_o - F_c|$), but it was decided to include all hydrogen atoms at positions calculated by the SHEL-X 76 program. All non-hydrogen atoms were given anisotropic temperature factors, while hydrogen atoms were given isotropic temperature factors approximately 1.5 times that of their parent non-hydrogen atom. Positional parameters for all atoms were then adjusted by several further rounds of least-squares calculations. The refinement converged at R 0.068.

Final atomic parameters for (8) are given in Table 1, and interatomic distances and angles in Table 2. Observed and calculated structure factors, the thermal parameters, and the torsion angles are available as Supplementary Publication No. SUP 22705 (11 pp.).* A stereoview of the two molecules A and B in the asymmetric unit is shown in the Figure. The carbon atoms in the pyranose ring and O(1)—O(5) of (8) are numbered using the normal carbohydrate convention, while other atoms are numbered arbitrarily.

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