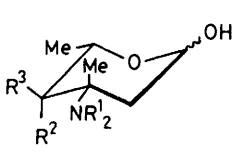
Branched-chain Sugars. Part 11.[1] An Approach to the Synthesis of D-Evernitrose *via* the Addition of Iodine Azide to a *C*-Methylene Sugar[2]

By **John S. Brimacombe,* May S. Saeed,** and **Timothy J. R. Weakley,** Chemistry Department, The University, Dundee DD1 4HN

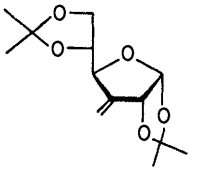
Methyl 3-acetamido-2,3,6-trideoxy-3-*C*,4-*O*-dimethyl-α-D-*arabino*-hexopyranoside (16), a known precursor of D-evernitrose, has been synthesised *via* the addition of iodine azide to methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-*C*-methylene-α-D-*erythro*-hexopyranoside (6). One of the adducts isolated from this reaction was assigned the structure methyl 3-azido-4,6-*O*-benzylidene-2,3-dideoxy-3-*C*-(iodomethyl)-α-D-*arabino*-hexopyranoside (9) by analogy and from the fact that ring-closure and *N*-acetylation gave the spiro-*N*-acetylaziridine (11), whose structure was secured by *X*-ray crystallography. The corresponding spiro-aziridine (10) was transformed into (16) in five steps.

In Part 10,[1] we described an approach to the synthesis of the antibiotic sugars L-evernitrose (1) [3,4] and L-vancosamine (2) [5] based on the cyclisation of periodate-oxidised methyl α-L-rhamnopyranoside with nitroethane.[6] Be-



(1) R^1 = O; R^2 = H; R^3 = OMe

(2) R^1 = H; R^2 = OH; R^3 = H



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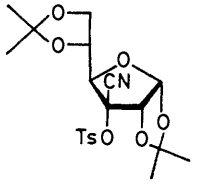

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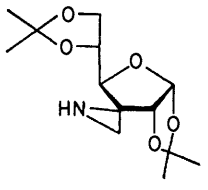
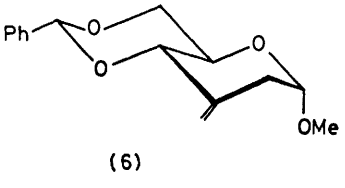
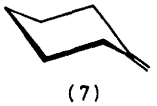


(5)



(6)



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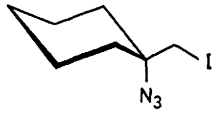
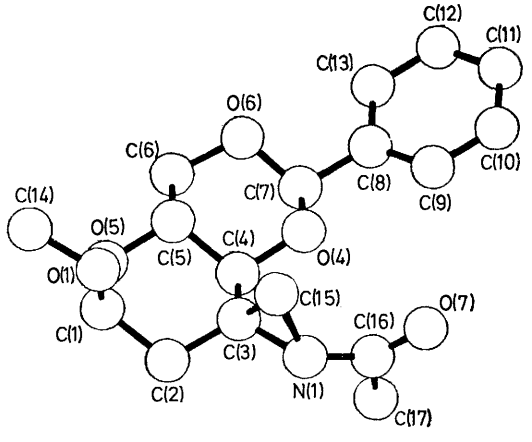


(8)

sides this more traditional approach, a Me–C–NH_2 branch can be introduced into sugars *via* the addition of mercuric azide to an appropriately protected *C*-methylene sugar [7] [*e.g.* (3)] and *via* sulphonylated cyanohydrins [8] [*e.g.* (4)], which are smoothly transformed into the corresponding spiro-aziridine [*e.g.* (5)] on reduction. The latter approach to methyl-branched amino-sugars, which was introduced by Bourgeois,[8] has been used in recent syntheses of D- and L-evernitrose [9,10] and a derivative of L-vancosamine.[11] Our own studies on the synthesis of these antibiotic sugars led us to examine the reaction of methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-*C*-methylene-α-D-*erythro*-hexopyranoside (6) with mercuric azide [12] in hot aqueous tetrahydrofuran, but, to our dismay, there was no discernible reaction. However, we were consoled by the knowledge [13] that iodine azide adds regioselectively to methylenecyclohexane (7) to give 1-azido-1-(iodomethyl)cyclohexane (8), which can be transformed quantitatively into a synthetically useful spiro-aziridine.[14] An analogous sequence of reactions on the *C*-methylene sugar (6) could yield two spiro-aziridines, depending on the stereoselectivity of pseudo-halogen addition.

RESULTS AND DISCUSSION

T.l.c. showed that, at least, three products were formed when iodine azide [15] was allowed to react with the unsaturated sugar (6) in acetonitrile, but only one of them could be obtained in a pure form following preparative chromatography on deactivated alumina. This crystalline adduct, which was obtained in 24% yield, underwent ring-closure to the spiro-aziridine (10) on treatment with lithium aluminium hydride in ether at 0 °C. Acetylation of (10) gave the *N*-acetate (11), whose stereochemistry at C-3 was established by single-crystal *X*-ray crystallographic analysis (see Experimental section). The stereoview shown in the Figure reveals that the nitrogen atom of the aziridine ring has

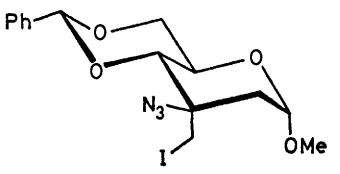


Stereoview of the spiro-*N*-acetylaziridine (11)

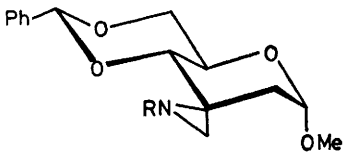
an equatorial orientation, with the pyranose ring assuming the $^4C_1$ conformation, establishing that (11) possesses the D-*arabino*-configuration. This stereochemical information was vital if a structural correlation was subsequently to be made with L-evernitrose, whose branch-point configuration was by no means secure.[4] Indeed, the structure of L-evernitrose was revised and firmly established [3] as 2,3,6-trideoxy-3-*C*,4-*O*-dimethyl-3-nitro-L-*arabino*-hexose (1) prior to the completion of this work. Fortunately, the spiro-aziridine (10) has the same absolute configuration as D-(1).

Analogy [*i.e.* (7) ⟶ (8)] [13,15] suggests that the original adduct has the structure (9), although its regioisomer would also furnish the spiro-aziridine (10) on ring-closure. Since the structure (9) rests on analogy and the other adducts were not identified, we are not in a position to comment meaningfully on the regio- and stereo-selectivities of the addition of iodine azide to (6).

The spiro-aziridine (10) was converted into methyl 3-acetamido-2,3,6-trideoxy-3-*C*,4-*O*-dimethyl-α-D-*arabino*-hexopyranoside (16) as follows. High-pressure hydrogenolysis over Raney nickel gave, after *N*-acetylation of the resulting amino sugar (12), methyl 3-acetamido-4,6-*O*-

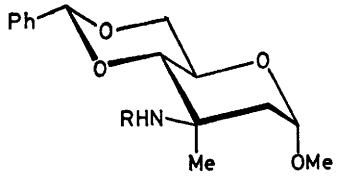


(9)



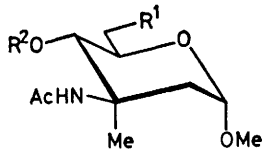
(10) R = H

(11) R = Ac



(12) R = H

(13) R = Ac



(14) R^1 = Br; R^2 = PhCO

(15) R^1 = R^2 = H

(16) R^1 = H; R^2 = Me

TABLE 1

Final atomic parameters for (11). E.s.d. values (in parentheses) refer to the least significant digits

Atom	*x/a*	*y/b*	*z/c*
C(1)	0.334 4(5)	0.141 6(6)	0.300 8(3)
C(2)	0.214 8(5)	0.038 5(6)	0.294 3(3)
C(3)	0.080 0(5)	0.118 1(4)	0.301 4(3)
C(4)	0.080 6(4)	0.207 9(5)	0.371 1(2)
C(5)	0.201 2(5)	0.311 8(5)	0.366 4(3)
C(6)	0.201 7(5)	0.403 7(6)	0.435 9(3)
C(7)	−0.037 8(5)	0.374 3(5)	0.444 3(2)
C(8)	−0.169 8(5)	0.453 7(5)	0.450 9(2)
C(9)	−0.285 6(5)	0.411 4(6)	0.411 6(3)
C(10)	−0.407 0(6)	0.486 0(8)	0.419 2(4)
C(11)	−0.414 8(7)	0.604 0(7)	0.464 0(4)
C(12)	−0.299 7(7)	0.647 2(6)	0.503 7(4)
C(13)	−0.176 1(6)	0.572 6(5)	0.497 9(3)
C(14)	0.466 8(6)	0.299 0(7)	0.224 0(4)
C(15)	0.009 3(5)	0.166 5(5)	0.233 1(3)
C(16)	−0.168 6(5)	0.042 2(5)	0.312 5(3)
C(17)	−0.172 7(6)	−0.040 5(7)	0.383 3(3)
N	−0.042 6(4)	0.042 3(4)	0.276 4(2)
O(1)	0.341 0(3)	0.217 9(4)	0.233 9(2)
O(4)	−0.042 9(3)	0.288 9(3)	0.378 6(2)
O(5)	0.325 9(3)	0.232 0(4)	0.364 3(2)
O(6)	0.068 9(4)	0.473 5(4)	0.440 8(2)
O(7)	−0.268 4(4)	0.095 8(5)	0.283 8(2)

TABLE 2

Interatomic distances and angles in (11)

(*a*) Distances (Å)

C(1)–C(2)	1.521(7)	C(7)–O(6)	1.399(6)
C(1)–O(1)	1.392(6)	C(7)–C(8)	1.494(7)
C(1)–O(5)	1.415(6)	C(8)–C(9)	1.388(7)
C(2)–C(3)	1.519(7)	C(8)–C(13)	1.395(7)
C(3)–C(4)	1.499(6)	C(9)–C(10)	1.384(8)
C(3)–C(15)	1.472(7)	C(10)–C(11)	1.367(10)
C(3)–N	1.485(6)	C(11)–C(12)	1.389(10)
C(4)–C(5)	1.532(6)	C(12)–C(13)	1.400(9)
C(4)–O(4)	1.432(5)	C(14)–O(1)	1.456(7)
C(5)–C(6)	1.507(7)	C(15)–N	1.485(6)
C(5)–O(5)	1.430(6)	C(16)–N	1.389(6)
C(6)–O(6)	1.455(6)	C(16)–C(17)	1.480(8)
C(7)–O(4)	1.419(5)	C(16)–O(7)	1.210(6)

(*b*) Angles (°)

C(2)–C(1)–O(1)	107.3(4)	C(7)–C(8)–C(9)	121.4(4)
C(2)–C(1)–O(5)	113.4(4)	C(7)–C(8)–C(13)	118.9(4)
O(1)–C(1)–O(5)	112.3(4)	C(9)–C(8)–C(13)	119.7(5)
C(1)–C(2)–C(3)	110.3(4)	C(8)–C(9)–C(10)	120.4(5)
C(2)–C(3)–C(4)	110.0(4)	C(9)–C(10)–C(11)	120.9(6)
C(2)–C(3)–C(15)	119.3(4)	C(10)–C(11)–C(12)	119.2(6)
C(2)–C(3)–N	116.5(4)	C(11)–C(12)–C(13)	121.1(6)
C(4)–C(3)–C(15)	120.9(4)	C(8)–C(13)–C(12)	118.8(5)
C(4)–C(3)–N	121.9(4)	C(3)–C(15)–N	59.3(3)
C(15)–C(3)–N	60.8(3)	C(17)–C(16)–N	114.7(4)
C(3)–C(4)–C(5)	108.4(4)	C(17)–C(16)–O(7)	123.8(5)
C(3)–C(4)–O(4)	111.8(3)	N–C(16)–O(7)	121.1(5)
C(5)–C(4)–O(4)	108.4(4)	C(3)–N–C(15)	59.9(3)
C(4)–C(5)–O(5)	108.9(4)	C(3)–N–C(16)	125.8(4)
C(6)–C(5)–O(5)	108.6(4)	C(15)–N–C(16)	122.9(4)
C(5)–C(6)–O(6)	107.7(4)	C(1)–O(1)–C(14)	114.3(4)
C(8)–C(7)–O(4)	108.4(3)	C(4)–O(4)–C(7)	110.3(3)
C(8)–C(7)–O(6)	108.4(4)	C(1)–O(5)–C(5)	112.6(3)
O(4)–C(7)–O(6)	111.4(3)	C(6)–O(6)–C(7)	111.6(4)

benzylidene-2,3-dideoxy-3-*C*-methyl-α-D-*arabino*-hexopyranoside (13), which was readily identified from its ^{1}H n.m.r. spectrum. This compound was converted smoothly into the 6-bromo-4-benzoate (14) when allowed to react with *N*-bromosuccinimide [16] in refluxing carbon tetrachloride in the presence of barium carbonate. High-pressure hydrogenation over Raney nickel, with concomitant debenzoylation, transformed (14) into methyl 3-acetamido-2,3,6-trideoxy-3-*C*-methyl-α-D-*arabino*-hexopyranoside (15), which gave (16) on careful methylation.[17] The ^{1}H n.m.r. spectra of (15) and (16) were indistinguishable from those of the respective L-enantiomers, which a related study [1] had made available. Another synthesis of (16), which converges with our synthesis in its later stages, has been reported recently by Yoshimura *et al.*,[9] who also transformed this compound into D-evernitrose. Thus, the foregoing route formally constitutes a synthesis of D-evernitrose.

Finally, we draw attention to the fact that the configuration at the branch-point in such methyl-branched amino sugars as (12) can now be determined, with reasonable assurance, using ^{13}C n.m.r. spectroscopy.[11]

EXPERIMENTAL

The experimental procedures are those used in Part 10.[1]

Methyl 3-*Azido*-4,6-O-*benzylidene*-2,3-*dideoxy*-3-C-(*iodomethyl*)-α-D-arabino-*hexopyranoside* (9).—A solution of iodine chloride (1.04 g) in dry acetonitrile (9 ml) was added over 10 min to a stirred and cooled (−10 °C) suspension of sodium azide (0.84 g) in dry acetonitrile (9 ml). The mixture was stirred for 10 min, during which time it turned reddish brown, before a solution of the alkene (6) (prepared essentially as described for the L-enantiomer [18]) (0.75 g) in dry acetonitrile (5 ml) was added. It was then allowed to warm to room temperature and stirred overnight, after which it was poured into water. The aqueous solution was extracted with ether, and the ethereal extract was washed with aqueous sodium hydrogen sulphite and dried ($MgSO_4$). Removal of the solvent and chromatography of the residue on deactivated alumina (eluant benzene) gave, as the first component eluted, the *iodoazide* (9) (0.3 g, 24%), m.p. 88—91 °C; $[\alpha]_D$ +45° (*c* 1 in $CHCl_3$); $\nu_{max.}$ 2 100 cm^{-1} (N_3) (Found: C, 42.2; H, 4.1; N, 9.7. $C_{15}H_{18}IN_3O_4$ requires C, 41.8; H, 4.2; N, 9.7%); δ($CDCl_3$): 7.38 (5 H, m, *Ph*CH), 5.67 (1 H, s, PhC*H*), 4.76 (1 H, d, $J_{1,2} \leqslant 1$, $J_{1,2'}$ 4 Hz, H-1), 3.36 (3 H, s, OMe), 2.46 (1 H, q, J_{gem} 14 Hz, H-2), and 1.67 (1 H, m, H-2′).

Spiro-[(1-*acetylaziridine*)-2,3′-(*methyl* 4,6-O-*benzylidene*-2,-3-*dideoxy*-α-D-arabino-*hexopyranoside*)] (11).—A solution of the iodoazide (9) (1.3 g) in ether (3 ml) was added gradually over 25 min to a stirred and cooled (0 °C) suspension of lithium aluminium hydride (0.3 g) in ether (10 ml). On completion of the addition, the reaction mixture was allowed to warm to room temperature and stirring was continued overnight. The excess of reagent was destroyed by the addition of wet ethyl acetate to the cooled (0 °C) solution, followed by a 10% solution of sodium hydroxide (2 ml). The ether layer was decanted, the residual solids were washed with ether (3 × 50 ml), and the combined ethereal layers were washed with water (2 × 30 ml) and dried ($MgSO_4$). Removal of the solvents gave the crude spiro-aziridine (10) (0.7 g).

A solution of (10) (0.7 g) in pyridine (1 ml) containing acetic anhydride (1 ml) was set aside overnight, after which work-up of the reaction mixture in the usual way and chromatography on silica gel [eluant ether–toluene (6 : 2 v/v)] gave the *spiro*-N-*acetylaziridine* (11) (0.5 g, 52%), m.p. 114—115 °C (from light petroleum); $[\alpha]_D$ +48° (*c* 1 in $CHCl_3$); $\nu_{max.}$ 1 690 cm^{-1} (*N*Ac) (Found: C, 63.9; H, 6.8; N, 4.45. $C_{17}H_{21}NO_5$ requires C, 63.9; H, 6.6; N, 4.4%); δ($CDCl_3$) 7.37 (5 H, m, *Ph*CH), 5.57 (1 H, s, PhC*H*), 4.84 (1 H, d, $J_{1,2}$ 4 Hz, H-1), 4.40—3.68 (4 H, H-4–6′), 3.36 (3 H, s, OMe), 2.71 and 2.24 (2 H, s, CH_2), 2.55 (1 H, q, J_{gem} 14 Hz, H-2), 2.03 (3 H, s, *N*Ac), and 1.62 (1 H, d, H-2′).

Methyl 3-*Acetamido*-4,6-O-*benzylidene*-2,3-*dideoxy*-3-C-*methyl*-α-D-arabino-*hexopyranoside* (13).—The spiro-aziridine (10) (0.7 g) in methanol (40 ml) was hydrogenated over Raney nickel [19] (*ca.* 1.5 g) at 20 atm and room temperature for 16 h. The residue obtained on removal of the catalyst and solvent was extracted with chloroform (3 × 30 ml) and the combined extracts were dried and evaporated to leave a syrup (0.47 g) containing the amino-sugar (12).

Acetylation of (12) in pyridine (2 ml) and acetic anhydride (1 ml) for 2 h at room temperature gave, after the usual work-up and chromatography on silica gel [eluant ether–toluene (6 : 2 v/v)], the *acetamido-sugar* (13) (0.33 g, 41%), $[\alpha]_D$ +28° (*c* 1 in $CHCl_3$); $\nu_{max.}$ 1 650 and 1 540 cm^{-1} (NHAc); δ($CDCl_3$) 7.42 (5 H, m, *Ph*CH), 5.58 (1 H, s, PhC*H*), 4.74 (1 H, br d, $J_{1,2}$ 4, $J_{1,2'} \leqslant 1$ Hz, H-1), 4.38—3.58 (4 H, H-4—H-6′), 3.32 (3 H, s, OMe), 2.68 (1 H, q, J_{gem} 14 Hz, H-2), 2.33 (1 H, d, H-2′), 1.88 (3 H, s, *N*Ac), and 1.55 (3 H, s, 3-Me).

Methyl 3-*Acetamido*-4-O-*benzoyl*-6-*bromo*-2,3,6-*trideoxy*-3-C-*methyl*-α-D-arabino-*hexopyranoside* (14).—A solution of the acetal (13) (0.3 g) in dry carbon tetrachloride (18 ml) containing *N*-bromosuccinimide (0.18 g) and barium carbonate (0.2 g) was heated under reflux for 4.5 h; t.l.c. [carbon tetrachloride–acetone–ether (7 : 3 : 1 v/v/v)] then showed that one major and two minor products had been formed. The reaction mixture was filtered, the filtrate was concentrated, and the residue was extracted with methylene chloride, which was washed with aqueous sodium hydrogen sulphite and aqueous sodium hydrogen carbonate, and dried ($MgSO_4$). Removal of the solvent and chromatography of the residue on silica gel [eluant ethyl acetate–light petroleum (1 : 1 v/v)] gave the bromobenzoate (14) (0.32 g, 86%), $[\alpha]_D$ +78° (*c* 1 in $CHCl_3$); $\nu_{max.}$ 1 720 (C=O) and 1 650 and 1 535 cm^{-1} (NHAc), as a syrup that did not crystallise; δ($CDCl_3$) 7.88 (5 H, m, $PhCO_2$), 6.23 (1 H, br s, NH), 5.47 (1 H, d, $J_{4,5}$ 10 Hz, H-4), 4.88 (1 H, m, H-1), 4.20 (1 H, m, H-5), 3.55 (2 H, m, H-6 and H-6′), 3.43 (3 H, s, OMe), 2.60 (2 H, m, H-2 and H-2′), 1.86 (3 H, s, *N*Ac), and 1.66 (3 H, s, 3-Me). The ^{1}H n.m.r. spectrum of (14) was identical to that reported for the material [m.p. 71—72 °C; $[\alpha]_D$ +81° (*c* 1 in $CHCl_3$)] prepared by Yoshimura *et al.*[9]

Methyl 3-*Acetamido*-2,3,6-*trideoxy*-3-C-*methyl*-α-D-arabino-*hexopyranoside* (15).—The bromo-compound (14) (0.3 g) in methanol (100 ml) containing triethylamine (0.1 g) was hydrogenated over Raney nickel [19] (*ca.* 1 g) at 20 atm and room temperature for 18 h. The residue obtained after removal of the catalyst and solvent was extracted with chloroform (2 × 50 ml), and the combined extracts were dried ($MgSO_4$) and concentrated; t.l.c. [methylene chloride–acetone–benzene (2 : 1 : 1 v/v/v)] then revealed the p,esence of four products. Chromatography on silica gel [eluant first methylene chloride–acetone–benzene (2 : 1 : 1 v/v/v) and then acetone] gave the *trideoxy-sugar* (15) (60 mg,

37%), $[\alpha]_D$ +96 ± 3° (*c* 1 in $CHCl_3$), as the last component eluted from the column. The ^1H n.m.r. spectrum of (15) was indistinguishable from that of its L-enantiomer having $[\alpha]_D$ −104° (*c* 0.7 in $CHCl_3$).[1]

Methyl 3-Acetamido-2,3,6-trideoxy-3-C,4-O-dimethyl-α-D-arabino-hexopyranoside (16).—Methylation of the alcohol (15) (as described [1] for the L-enantiomer) yielded the *methylated derivative* (16) (83%), m.p. 136—138 °C; $[\alpha]_D$ +72° (*c* 1 in $CHCl_3$) (Found: C, 56.9; H, 8.9; N, 6.2. $C_{11}H_{21}NO_4$ requires C, 57.1; H, 9.15; N, 6.05%), whose ^1H n.m.r. spectrum was indistinguishable from those of the compound [m.p. 136—138 °C; $[\alpha]_D$ +73° (*c* 1 in $CHCl_3$)] prepared by Yoshimura *et al.*[9] and its L-enantiomer [1] [m.p. 136—138 °C; $[\alpha]_D$ −71° (*c* 0.85 in $CHCl_3$)]. The conversion of (16) into D-evernitrose has already been described.[9]

Crystal Structure Determination of (11)

Crystal Data.—$C_{17}H_{21}NO_5$, *M* 319.4. Orthorhombic, space group $P2_12_12_1$, a = 9.770(5), b = 9.375(6), c = 17.810(9) Å, U = 1 631.3 Å^3, D_c = 1.30 g cm^{-3}, Z = 4, $F(000)$ = 680. CuK_α radiation, λ = 1.541 8 Å, μ = 7.1 cm^{-1}.

Data Collection and Structure Analysis.—The crystals were elongated prisms with prominent {011} faces. Data were collected from two crystals mounted along the *a* and *b* directions, respectively. Equi-inclination multi-film Weissenberg photographs of reciprocal lattice levels 0—7 *kl* and *h*0—5*l* were scanned by using a microdensitometer (S.R.C. Service, Daresbury Laboratory) and 993 reflections were classified as statistically significant.

The molecule could not be unambiguously distinguished by *E* maps obtained using the observed reflections only, so that 1 103 unobserved reflections with $|F| = 0.25|F_o|_{min.}$ were added to the data set. When sufficient multi-solution reflections to give 512 phase combinations were used to generate *E* maps, the one of highest figure-of-merit contained a recognisable molecule; this was confirmed by a Fourier synthesis phased by atoms at the positions of the thirteen strongest peaks. Subsequent refinement using only the observed reflections, first by Fourier syntheses and then by several rounds of full-matrix least-squares, was straightforward. A difference synthesis calculated when *R* had fallen to 0.07 showed peaks of similar magnitude to the stronger ' noise ' peaks close to the positions expected for twelve of the twenty-one hydrogen atoms. All hydrogen atoms were included at calculated positions in the last cycles of refinement in which all non-hydrogen atoms were refined anisotropically (a total of 214 variables) using a weighting scheme of the form $w = 1/(1 + 0.0041\ F^2)$. Refinement converged to *R* 0.048.

Calculations were carried out on the University of Dundee DEC 10 computer using the SHELX 76 program.[20] Observed and calculated structure factors together with the anisotropic thermal parameters are deposited as Supplementary Publication No. SUP 22809 (8 pp).*

The numbering system used (see Figure) is such that the carbon and oxygen atoms of the parent hexose are numbered according to normal carbohydrate convention, while the remaining atoms are numbered arbitrarily.

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* For details of the Supplementary Publications scheme see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1979, Index issue.

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