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REGIOSELECTIVE OXIDATION OF CARBOHYDRATE TRIOLS: FACILE SYNTHESIS OF 2,3-*O*-ISOPROPYLIDENE-β-D-*threo*-HEXO-2,4-DIULOPYRANOSE AND 1,2-*O*-ISOPROPYLIDENE-β-D-*threo*-HEXO-2,5-DIULOPYRANOSE

LAETITIA DEN DRIJVER,
Chemistry, AEC, P.O. Box 256, Pretoria, 0001 (South Africa)

CEDRIC W. HOLZAPFEL*, JOHANNES M. KOEKEMOER, GERT J. KRUGER, AND MARTHA S. VAN DYK
Department of Chemistry, Rand Afrikaans University, Box 524, Johannesburg, 2000 (South Africa)
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ABSTRACT

Stannylation of 2,3-*O*-isopropylidene-β-D-fructopyranose with dibutyltin oxide followed by brominolysis afforded 2,3-*O*-isopropylidene-β-D-*threo*-hexo-2,4-diulopyranose, which was characterised as its oxime. Brominolysis of the *O*-dibutylstannylene derivative of 1,2-*O*-isoropylidene-β-D-fructopyranose furnished 1,2-*O*-isopropylidene-β-D-*threo*-hexo-2,5-diulopyranose, which was characterised as the corresponding *O*-methyloxime diacetate.

INTRODUCTION

Alduloses and diuloses are the main products when aqueous solutions of sugars are gamma-irradiated in the presence of oxygen[1–3]. As part of a study[4] of the preservation of Kent mangoes by radiation, the mutagenicity and cytotoxicity of the possible radiolysis products of D-fructose, the major sugar component of the fruit[5], were investigated. However, the products of radiolysis were formed in low yields and the study therefore required the synthesis of several new compounds, including D-*threo*-hexo-2,4-diulose. Heyns *et al.*[6] synthesised a potential precursor of this 2,4-diulose, namely the hydrated form **4** of 2,3-*O*-isopropylidene-β-D-*threo*-hexo-2,4-diulopyranose (**5**), by the catalytic oxidation of 2,3-*O*-isopropylidene-β-D-fructopyranose[7] (**1**). The compound was, however, obtained in yields of 3% or less. We now report an efficient synthesis of **5** (which could not be converted into the hydrate for which Heyns *et al.*[6] proposed the structure **4**) and the conversion of 1,2-*O*-isopropylidene-β-D-fructopyranose (**10**) into 1,2-*O*-isopropylidene-β-D-*threo*-hexo-2,5-diulopyranose (**12**).

*To whom correspondence should be addressed.

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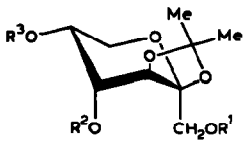
RESULTS AND DISCUSSION

The efficient synthesis of carbohydrate-derived hydroxyketones by the brominolysis reaction in weakly polar solvents of the *O*-dibutylstannylene derivatives of protected carbohydrates having two or three free hydroxyl groups has been reported[8–10]. In stannylene derivatives containing axial and equatorial stannylene oxygens, the former can be regioselectively oxidised, and this has been rationalised in terms of a cyclic mechanism for the oxidation. The result has also been ascribed[8,9] to the deactivation of the equatorial oxygen of one monomeric unit by co-ordination to the tin atom of the other, resulting in the formation of dimers in weakly polar solvents, Therefore, it appeared likely that brominolysis of 4,5-*O*-dibutylstannyl-2,3-*O*-isopropylidene-β-D-fructopyranose (**2**) would result in regioselective oxidation at position 4, assuming that **2** adopts the same preferred conformation[11] as 1,4,5-tri-*O*-acetyl-2,3-*O*-isopropylidene-β-D-fructopyranose (**3**), *i.e.*, with AcO-4 axial.

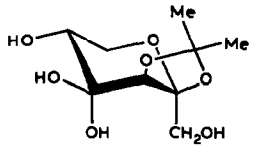
The triol **1** was converted into the corresponding stannylene derivative **2** by treatment with 1 mol of dibutyltin oxide in boiling benzene with azeotropic removal of water for 12 h. Brominolysis was carried out in benzene in the presence of 4 Å molecular sieves at room temperature. Chromatography allowed isolation of the main product (56%), the only other components being **1** and organotin by-products. The crystalline oxidation product was not identical (m.p. and $[\alpha]_D$) with the compound, formulated[6] as **4**, and could not be converted into such a hydrate on treatment with water under acidic or basic conditions. The molecular composition of this new compound was consistent with structure **5**, but it had no i.r. absorbtion for carbonyl. Although the compound showed only one spot in t.l.c., its ^{1}H-n.m.r. spectrum contained the signals for two compounds, present in the ratio 3:2. The f.a.b.-mass spectrum (in glycerol) revealed one compound to be the monomer (*m/z* 219 for $[M + H]^+$) and the other to be dimeric (*m/z* 437 for $[M + H]^+$). On the basis of this information, the ^{1}H-n.m.r. spectrum in $(CD_3)_2SO$ could be interpreted in terms of an equilibrium mixture of the hemiacetal **6** and the symmetrical dimer **7**. The major compound had resonances at δ 6.4 (d, $J_{5,OH}$ 4 Hz, HO-5, exchangeable with D_2O), 4.25 (s, H-3), and 1.13 and 1.26 (CMe_2). The minor component had resonances at δ 4.9 (t, *J* 5 Hz, HO-1), 3.9 (s, H-3), and 1.37 (CMe_2). Other carbohydrate α-ketols, *e.g.*, methyl L-*threo*-pentopyranosid-4-ulose[10], also exist as equilibrium mixtures of the monomeric and dimeric forms.

Acetylation of **5** furnished an approximately equimolar mixture (f.a.b.-mass spectrum) of the di- and tetra-acetates of **6** and **7**, respectively, which could not be readily fractionated. The only pure compound that could be obtained after chromatography was the diacetate **8**, the ^{1}H-n.m.r. spectrum ($CDCl_3$) of which contained resonances at δ 5.3 (dd, *J* 7.5 and 5 Hz, H-5), 4.80 (s, H-3), and 4.2 (dd, J_{AB} 12 Hz, H-1,1′).

Reduction of **5** with borohydride occurred slowly and furnished a complex mixture of products. However, reduction with $LiAlH_4$ or $LiBH_4$ proceeded



1 $R^1 = R^2 = R^3 = H$
2 $R^1 = H, R^2, R^3 = SnBu_2$
3 $R^1 = R^2 = R^3 = Ac$



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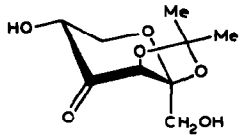

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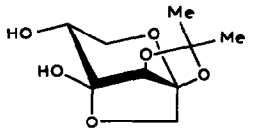

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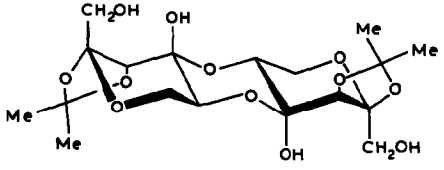

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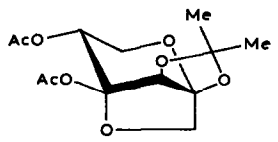
smoothly to give a 1:2 mixture, which was acetylated. Only the minor component could then be isolated pure by chromatography and identified as 1,4,5-tri-*O*-acetyl-2,3-*O*-isopropylidene-β-D-fructopyranose (**3**). The major product was probably the 4-β-epimer of **3** since the ^{1}H-n.m.r. spectrum of the mixture of acetates contained signals at δ 5.22 (dd, $J_{3,4}$ 2.5, $J_{4,5}$ 8 Hz) and 4.65 (dt, $J_{4,5} = J_{4,6} = 8$, $J_{5,6}$ 1.5 Hz) which could be ascribed to H-4,5 of this epimer. Thus, brominolysis of **2** did not result in isomerisation or skeletal rearrangement, and confirmed the structure **5**. In addition, it clearly demonstrated the different chemical behaviour of **5**, compared to that of the compound formulated[6] as **4**. The structure of the latter compound, the ^{1}H-n.m.r. spectrum of which could not be interpreted, and which decomposed on acetylation, was based entirely on the ^{1}H-n.m.r. spectrum of the material obtained on borohydride reduction followed by acetylation. However, interpretation of the proposed structure, *i.e.*, 1,4,5-tri-*O*-acetyl-2,3-*O*-isopropylidene-β-D-tagatopyranose, required the assumption, without any rationalisation, of a boat conformation $B_{0,4}$ somewhat skewed towards $^3S_0$.

The possibility must be considered now that the minor product of catalytic oxidation of **1** may not be formulated correctly. However, the structure **5** was verified by the X-ray structure determination of its oxime **9** (see Experimental).

Fig. 1 shows a stereoscopic view of the oxime **9**. From Fig. 1 and the puckering parameters (Φ = 147.4°, θ = 102°, and Q = 0.64), it is evident that the pyranoid ring has a conformation close to a skew or twisted boat ($^3S_0$). Inspection of Dreiding models indicates that, in this mobile conformation, unfavourable 1,3-diaxial interactions present in the alternative rigid chair conformations are avoided.



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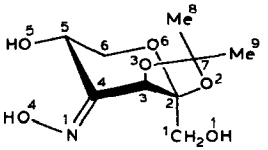

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Attempts to improve the yield of **5** by using chloroform as reaction solvent gave lower yields, and the addition of tetrabutylammonium bromide (which generally accelerates[12] the rates of alkylation and acylation of stannylenes) resulted in a decreased rate of oxidation and a lower yield (22%) of **5**. The stannylene derivative was resistant to oxidation in methanol or *N,N*-dimethylformamide. In the absence of molecular sieves, the reaction became sluggish after the addition of ~50% of the stoichiometric amount of bromine, and **5** was formed in an inferior yield (~25%). The addition of 1 equiv. of tributyltin methoxide[9] as a scavenger for hydrogen bromide slightly increased the yield, but the introduction of more organotin compound, which is always difficult to remove, complicated the isolation procedure. Related oxidation methods[13–16] were applied to **1**. The compound (in benzene) was successively treated with 0.5 or 1 equiv. of hexabutylstannoxane and bromine or *N*-bromosuccinimide. However, brominolysis was slow and furnished a mixture of compounds which was not investigated further.

The brominolysis of an appropriate stannylene derivative was also applied in the synthesis of 1,2-*O*-isopropylidene-β-D-*threo*-hexo-2,5-diulopyranose (**12**). The conversion of 1,2-*O*-isopropylidene-β-D-fructopyranose (**10**) into **12** using this

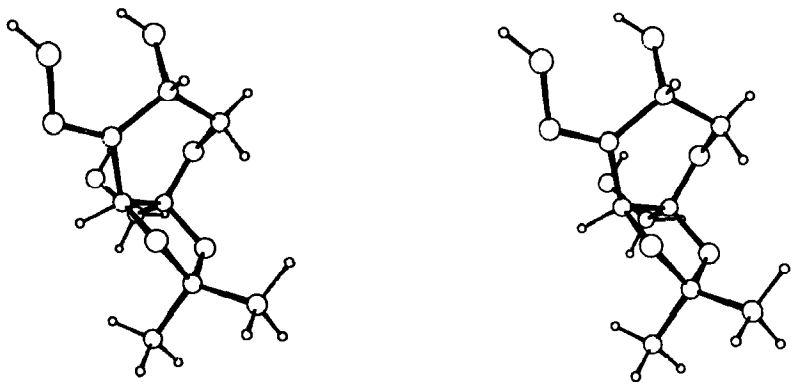
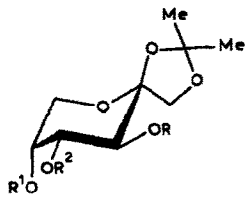
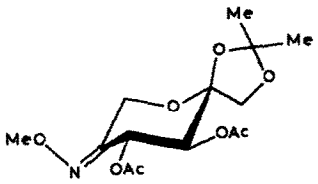


Fig. 1. A stereoscopic drawing of a molecule of the oxime **9**.

method was suggested by the regioselective stannylation[17] of HO-4,5 of **10** and the cyclic mechanism proposed[10] for the brominolysis reaction. Treatment of **10** with 1 mol of dibutyltin oxide in boiling benzene, with azeotropic removal of water, for 12 h gave the stannylene derivative **11**. Brominolysis of **11** in benzene in the presence of 4 Å molecular sieves at room temperature gave (t.l.c.) a 3:1 mixture of products of which the major (**12**) was isolated (48%) by chromatography. Compound **12** had i.r. absorption for carbonyl at 1725 cm^{-1}, consistent with its formulation as a non-hydrated monomer. The crystalline compound was homogeneous in t.l.c. in several solvent systems, but its ^{1}H-n.m.r. spectrum (the methyl resonances in particular) was consistent with an ~4:1 mixture. The f.a.b.-mass spectrum of **12** in glycerol showed strong $[M + H]^+$ and $[2M + H]^+$ ions with *m/z* 219 and 437, respectively, suggesting an equilibrium between monomeric (**12**) and dimeric (**13**) forms. A similar equilibrium was found for the structurally related methyl L-*threo*-pento-pyranosid-4-ulose[10]. The hydroxyketone **12** was characterised as its methyloxime diacetate **14**, the ^{1}H-n.m.r. spectrum of which contained resonances at δ 1.46 and 1.50 (CMe_2), 2.10 (2 AcO), 3.85 (MeON), 5.27 ($J_{3,4}$ 9 Hz, H-3), and 5.8 ($J_{3,4}$ 9.0, $J_{4,6}$ 1.5 Hz, H-4).



10 R = H, R^1 = R^2 = H
11 R = H, R^1, R^2 = $SnBu_2$



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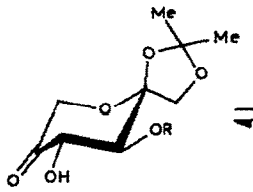

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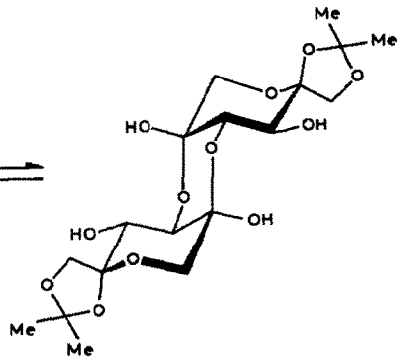

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Compounds **5** and **12** were hydrolysed[18] with refluxing aqueous 80% acetic acid and 0.5M hydrochloric acid in 1:1 acetonitrile–water for 48 h at room temperature, respectively, and characterised[18] as the acetylated di-*O*-benzyloxime derivatives.

The results described above provide additional evidence that the regioselective reaction of carbohydrate triols can be achieved by brominolysis of their stannylene derivatives and that, in stannylene derivatives containing axial and equatorial stannylene oxygens, the former can be regioselectively oxidised. However, brominolysis can be achieved only in non-polar solutions, which suggests that only the dimeric (or polymeric) forms of the stannylenes are attacked by bromine. It is possible that the dimers (or polymers) with penta-coordinated tin[19] readily add bromine, thus expanding[20] the coordination number of the tin atoms to 6.

EXPERIMENTAL

Melting points were determined with a Kofler hot-stage apparatus and are uncorrected. I.r. spectra (in chloroform) and optical rotations were recorded with a Perkin–Elmer 237 spectrophotometer and a Perkin–Elmer 141 polarimeter, respectively. Unless otherwise stated, ^{1}H-n.m.r. spectra were recorded with a Bruker WP-80 instrument for solutions in $CDCl_3$ (internal Me_4Si). The e.i.- and f.a.b.-mass spectra were determined with a Varian MAT-212/55-188 mass spectrometer. Column chromatography was performed on Kieselgel 60 (Merck, 60–200 mesh), and silica gel 60 F_{254} (Merck, 0.25 mm) was used for t.l.c.

2,3-*O*-Isopropylidene-β-D-fructopyranose (**1**) was prepared by the selective hydrolysis[6,7] of 2,3:4,5-di-*O*-isopropylidene-β-D-fructopyranose[21], and 1,2-*O*-isopropylidene-β-D-fructopyranose (**10**) was prepared by the selective hydrolysis[22] of 1,2:4,5-di-*O*-isopropylidene-β-D-fructopyranose. Elemental analyses were provided by the Microanalytical Laboratories, CSIR, Pretoria (South Africa).

2,3-O-Isopropylidene-β-D-threo-hexo-2,4-diulopyranose (**5**). — A mixture of **1** (426 mg, 2 mmol) and dibutyltin oxide (545 mg, 2.2 mmol) in benzene (15 mL) was heated under reflux for 12 h with azeotropic removal of water. Evaporation of the solvent gave the crude stannylene derivative which was used without further purification.

To a solution of the stannylene derivative in benzene (8 mL) were added freshly dried 4 Å molecular sieves (1 g), and the mixture was vigorously stirred at room temperature under nitrogen while a solution of bromine (320 mg, 2 mmol) in dry 1,2-dimethoxyethane (4 mL) was added dropwise during 30 min. The mixture was then filtered, diluted with dichloromethane (20 mL), successively washed with aqueous sodium metabisulfite and water, dried (Na_2SO_4), and concentrated. T.l.c. (ethyl acetate) of the residue revealed a product and **1**. Column chromatography (ethyl acetate) and crystallisation from a large proportion of ether gave **5** (238 mg, 56%), m.p. 135–137°, $[\alpha]_D^{20}$ −47° (*c* 2, methanol); ν_{max} 3580 (sh) and 3350 (br) cm^{-1}. Mass spectrum (e.i.): *m/z* 203 (M^+ − Me).

Anal. Calc. for $C_9H_{14}O_6$: C, 49.53; H, 6.47. Found: C, 49.67; H, 6.31.

Acetylation of **5**. — Compound **5** (150 mg) was treated with acetic anhydride (2 mL) and dry pyridine (2 mL) under nitrogen for 12 h. Evaporation of the solvent and column chromatography (ethyl acetate–hexane, 1:3) of the residue furnished

the hemiacetal diacetate **8** (15 mg) followed by mixed fractions. Compound **8** was isolated as a colourless foam, $[\alpha]_D^{20}$ −35° (*c* 1.1, chloroform); ν_{max} 1743 cm^{-1} (acetate). ^{1}H-N.m.r. data: δ 1.43 and 1.53 (2 s, each 3 H, CMe_2), 2.12 and 2.2 (2 s, each 3 H, 2 AcO), 3.85 (dd, 2 H, J_{AB} 11.0 Hz, H-1,1'), 4.0 (m, 2 H, H-6,6'), 4.45 (s, 1 H, H-3), 5.32 (dd, 1 H, $J_{5,6}$ 7.5, $J_{5,6'}$ 5.0 Hz, H-5). Mass spectrum (e.i.): *m/z* 287 (M^+ − 15).

Anal. Calc. for $C_{13}H_{18}O_8$: C, 51.65; H, 6.00. Found: C, 51.48; H, 5.85.

Reduction of **5**. — To a stirred solution of **5** (109 mg, 0.5 mmol) in dry 1,2-dimethoxyethane (10 mL) under argon at 0° was added $LiAlH_4$ (24 mg, 0.65 mmol) in portions. The mixture was allowed to attain room temperature. T.l.c. (5:1 chloroform–methanol) showed that the reduction was complete after 1.5 h. The excess of reductant was decomposed with ethyl acetate, and the mixture was diluted with dichloromethane (15 mL), washed with dilute acetic acid and water, dried (Na_2SO_4), and concentrated. The residue (95 mg) was treated immediately with acetic anhydride (1.5 mL) and dry pyridine (1.5 mL) for 12 h at room temperature. The solvents were then evaporated and chromatography (ethyl acetate–hexane, 1:4, then 1:3) of the light-yellow residue furnished 1,4,5-tri-*O*-acetyl-2,3-*O*-isopropylidene-β-D-fructopyranose (**3**, 16 mg) followed by mixed fractions. Compound **3** had m.p. and mixture m.p. 56–58°, and its ^{1}H-n.m.r. and mass spectra were identical with those of an authentic sample.

2,3-O-Isopropylidene-β-D-threo-hexo-2,4-diulopyranose oxime (**9**) *and its X-ray structure determination.* — A solution of **5** (436 mg, 2 mmol) in pyridine (5 mL) was stirred with hydroxylamine hydrochloride (145 mg, 2.1 mmol) under N_2 for 48 h and then concentrated to dryness. A solution of the residue in chloroform (25 mL) was washed with water, dried (Na_2SO_4), and concentrated to yield **9** (396 mg, 85%). Recrystallisation from ether–hexane gave material with m.p. 169–171°, $[\alpha]_D^{20}$ −70° (*c* 2.3, methanol); ν_{max} 3550 (sh), 3400 (sh), 3300 (br) cm^{-1}. Mass spectrum (e.i.): *m/z* 218 (M^+ − 15). ^{1}H-N.m.r. data [$(CD_3)_2SO$]: δ 1.3 and 1.4 (2 s, each 3 H, CMe_2), 3.3 (t, 1 H, *J* 6 Hz, exchangeable with D_2O, HO-1), 3.45 (d, 2 H, *J* 6 Hz, changed to s on addition of D_2O, H-1,1'), 4.45 (s, 1 H, H-3), 3.5 (bs, 1 H, exchangeable with D_2O, NOH), 4.63 (d, 1 H, *J* 4.5 Hz, exchangeable with D_2O, HO-5), 4.35 (dd, 1 H, $J_{5,6}$ 2.2, $J_{5,6'}$ 1 Hz, H-5), 4.0 (dd, 1 H, $J_{6,6'}$ 12.45, $J_{5,6}$ 2.5 Hz, H-6), 3.65 (dd, 1 H, $J_{6,6'}$ 12.45, $J_{5,6'}$ 1 Hz, H-6').

Anal. Calc. for $C_9H_{15}NO_6$: C, 46.35; H, 6.48; N, 6.01. Found: C, 46.20; H, 6.57; N, 5.85.

Single crystals of **9** were obtained from ether–hexane. The crystal data are summarised in Table I. Independent intensities were measured on a Philips PW1100 diffractometer, using graphite-monochromated CuK_α radiation (λ-1, 5418 Å). The $\omega - 2\theta$ scanning technique was employed, and the intensities were corrected for Lorentz and polarization effects.

The structure was solved by direct methods (MULTAN[23]) and refined by the full-matrix, least-squares method (SHELX-76[24]) with anisotropic temperature factors for the non-hydrogen atoms and isotropic ones for the hydrogen atoms. All

TABLE I

CRYSTAL DATA FOR OXIME **9**

Molecular formula	$C_9H_{15}NO_6$
Molecular weight	233.22
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Cell constants	
a (Å)	11.934(8)
b (Å)	11.848(8)
c (Å)	7.572(5)
Volume (Å^3)	1070.64
Z	4
Calculated density (g/cm^3)	1.447
Crystal dimension (mm)	0.3 × 0.2 × 0.1
Total number of reflections measured	1126
Number of observable reflections used ($I>0$)	1108
R-value (R; R_w)	0.038; 0.045
Weighting factor (overall)	$1/\sigma_F^2$
θ_{max} (°)	67

hydrogen atoms were refined in positions found from difference maps, except for those in the isopropylidene group and the one in the oxime moiety. The methyl hydrogens in the isopropylidene group were included in calculated positions with C–H bond distances constrained to 1.08 Å, and were refined as rigid groups free to rotate (Tables I and II). The crystallographic numbers used in Table II are indicated in structure **9**. The hydrogen atom in the oxime group was fixed in a calculated position assuming intermolecular hydrogen-bonding with HO-1 of an adjacent molecule.

The final fractional coordinates and equivalent isotropic temperature factors for the non-hydrogen atoms are listed in Table II, and a stereoscopic view of the molecule is shown in Fig. 1. (ORTEP)*.

*1,2-O-Isopropylidene-β-*D-threo-*hexo-2,5-diulopyranose* (**12**). — A mixture of **10** (545 mg, 2 mmol) and dibutyltin oxide (697 mg, 2.2 mmol) in benzene (15 mL) was heated under reflux for 12 h with azeotropic removal of water. The mixture was allowed to cool to room temperature, freshly dried 4 Å molecular sieves (1 g) were added, and the mixture was vigorously stirred at room temperature while a solution of bromine (320 mg, 2 mmol) in dry 1,2-dimethoxyethane (4 mL) was added dropwise during 30 min. The mixture was filtered and the solvent removed *in vacuo*. T.l.c. (ethyl acetate) of the residue revealed, in addition to **10**, one product. Column chromatography (ethyl acetate) furnished **12** (325 mg, 61%),

*Tables of F_o–F_c values, anisotropic temperature-factors of non-hydrogen atoms, coordinates and isotropic temperature factors of hydrogen atoms, and bond lengths and bond angles between all the atoms except the hydrogen atoms that are in calculated positions have been deposited with and can be obtained from, Elsevier Science Publishers B.V., BBA Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/346/*Carbohydr. Res.*, 155 (1986) 141–150.

TABLE II

FRACTIONAL COORDINATES ($\times 10^4$) AND EQUIVALENT ISOTROPIC TEMPERATURE FACTORS[a] ($Å^2 \times 10^3$) FOR THE NON-HYDROGEN ATOMS OF **9**[b]

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
C-1	1462(3)	1913(3)	7282(5)	35(1)
C-2	2417(2)	1752(2)	5990(4)	29(1)
C-3	3294(2)	2721(2)	5934(4)	27(1)
C-4	3253(2)	3409(2)	4267(4)	28(1)
C-5	3057(3)	2803(3)	2535(4)	32(1)
C-6	2700(3)	1597(3)	2895(4)	33(1)
C-7	4168(3)	1097(2)	6925(4)	32(1)
C-8	4296(3)	1309(3)	8881(4)	45(2)
C-9	4952(3)	195(3)	6241(5)	43(2)
O-1	848(2)	2913(2)	6962(3)	36(1)
O-2	3040(2)	788(2)	6489(3)	35(1)
O-3	4348(1)	2126(2)	5948(3)	31(1)
O-4	3492(2)	4973(2)	2754(3)	42(1)
O-5	2191(2)	3307(2)	1502(3)	43(1)
O-6	1913(2)	1560(2)	4334(3)	33(1)
N-1	3469(2)	4458(2)	4431(3)	34(1)

[a]Defined as the geometric mean of the diagonal elements of the diagonalised matrix of U_{ij}. [b]Standard deviations are given in parenthesis.

m.p. 174–176° (from ethyl acetate–chloroform), $[\alpha]_D^{20}$ −65° (*c* 1.6, methanol); ν_{max} 3576 (sh), 3345 (br), and 1725 cm^{-1}. Mass spectrum (e.i.): *m/z* 203 ($M^+ - 15$).

Anal. Calc. for $C_9H_{14}O_6$: C, 49.53; H, 6.47. Found: C, 49.35; H, 6.58.

*3,4-Di-*O*-acetyl-1,2-*O*-isopropylidene-β-*D*-*threo*-hexo-2,5-diulopyranose* O*-methyloxime* (**14**). — A solution of **12** (218 mg, 1 mmol) in pyridine (3 mL) was treated with *O*-methylhydroxylamine hydrochloride (90 mg, 1.1 mmol) at room temperature for 24 h. T.l.c. (5:1 chloroform–methanol) then revealed one main product. Acetic anhydride (3 mL) was added to the mixture and, after 12 h, the solvents were removed *in vacuo*. Column chromatography (ethyl acetate–hexane, 1:3) of the residue furnished **14** (269 mg, 81%), isolated as a colourless oil, $[\alpha]_D^{20}$ −73° (*c* 3.5, chloroform); ν_{max} 1743 cm^{-1}. Mass spectrum (e.i.): *m/z* 316 ($M^+ - 15$). ^{1}H-N.m.r. data: δ 1.45 and 1.50 (2 s, each 3 H, CMe_2), 3.95 (dd, 2 H, J_{AB} 11 Hz, H-1,1′), 5.31 (d, 1 H, *J* 9 Hz, H-3), 2.10 (s, 6 H, 2 AcO), 5.76 (dt, 1 H, $J_{3,4}$ 9, $J_{4,6} = J_{4,6'} = 1.5$ Hz, H-4), 3.85 (s, 3 H, NOMe), 4.62 and 4.15 (dd, 2 H, $J_{6,6'}$ 15, $J_{4,6} = J_{4,6'} = 1.5$ Hz, H-6,6′).

Anal. Calc. for $C_{14}H_{22}NO_8$: C, 50.75; H, 6.39; N, 4.25. Found: C, 50.56; H, 6.54; N, 4.10.

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