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CHEMISTRY OF GLYCOSYLAMINES. ISOPROPYLIDENE ACETALS OF *N*-ACETYL-α-D-GLUCOFURANOSYLAMINE

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ABSTRACT

The reaction of *N*-acetyl-α-D-glucofuranosylamine with 2,2-dimethoxypropane, catalyzed by *p*-toluenesulfonic acid, gave 1-acetamido-2,3:5,6-di-*O*-isopropylidene-1-*O*-methyl-D-glucitol (65.6%), 1-acetamido-2,3-*O*-isopropylidene-1-*O*-methyl-D-glucitol (3.7%), and *N*-acetyl-5,6-*O*-isopropylidene-α-D-glucofuranosylamine (3.2% yield). The structures of these compounds were determined by chemical and spectroscopic methods, and their relation to the pattern of n.m.r. resonances of the isopropylidene methyl groups is discussed.

INTRODUCTION

The ready synthesis of *N*-acylglycosylamines and their relative stability in acid medium[1], compared with that of the *N*-alkyl or -aryl analogs, suggest that these compounds may be potentially useful, synthetic intermediates in carbohydrate chemistry. However, selective blocking reactions, or substitution by reactive groups, have not been developed with these *N*-acyl compounds. Most of the studies on glycosylamines have centered on the nature of the *N*-substituents on C-1, and their rearrangements[1].

We started from *N*-acetyl-α-D-glucofuranosylamine (**1**) as a model compound; it was obtained in 53% yield by ammonolysis of penta-*O*-acetyl-β-D-glucopyranose with 5% aqueous ammonia[2]. Heating of **1** with 2,2-dimethoxypropane in the presence of a small proportion of *p*-toluenesulfonic acid at 60° afforded, after column chromatography, 1-acetamido-2,3:5,6-di-*O*-isopropylidene-1-*O*-methyl-D-glucitol (**2**; 65.6%), 1-acetamido-2,3-*O*-isopropylidene-1-*O*-methyl-D-glucitol (**3**; 3.7%), and *N*-acetyl-5,6-*O*-isopropylidene-α-D-glucofuranosylamine (**4**; 3.2% yield) (see Scheme 1).

RESULTS AND DISCUSSION

Studies[3] on the isopropylidenation of 2-acetamido-2-deoxy-D-glucose in $HCONMe_2$ had shown the formation of *N*,*O*-isopropylidene derivatives, a possibility that was not detected in our case. We used an excess of 2,2-dimethoxypropane as

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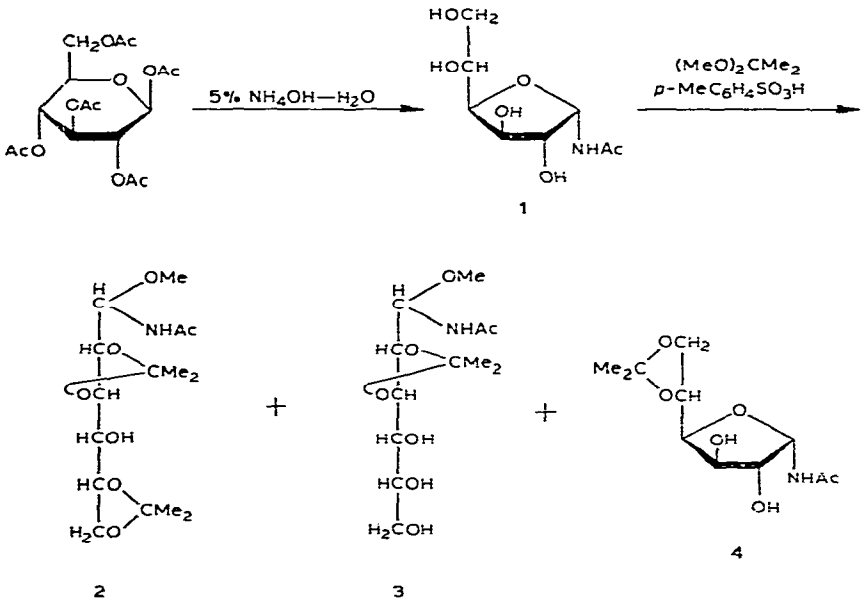


the solvent, as basic media (pyridine or $HCONMe_2$) partially isomerize **2** to a pyranoid structure. Ready opening of the furanoid ring explains the favored formation of the 2,3 : 5,6-di-*O*-isopropylidene derivative, which otherwise would be stereochemically precluded.

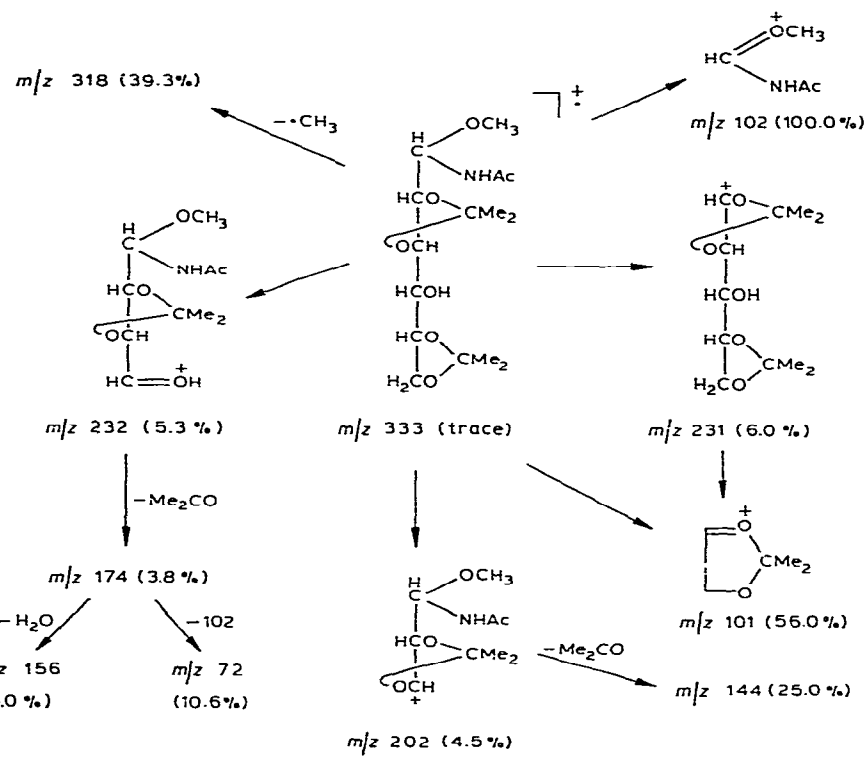
The isopropylidene groups in derivatives **2** and **3** showed extreme lability in acid media, being hydrolyzed at room temperature to compound **1** by very dilute acids. A number of attempts, under the most varied conditions, to hydrolyze **2** selectively to **3** in a preparative way were unsuccessful. Compound **2** is soluble in water, ethanol, ethyl ether, chloroform, or benzene, and the solutions are stable; it partially crystallizes, after several weeks, from ethyl ether–light petroleum, or by slow evaporation to dryness of its acetone solution. After purification by column chromatography, it crystallizes in part, but a substantial proportion remains as a syrup that possesses the same optical rotation and spectroscopic properties as the crystals. The configuration of C-1 is not yet known, but n.m.r. data suggest that the syrup, as well as the crystalline material, is a mixture of C-1 diastereoisomers.

*Structure of 1-acetamido-2,3 : 5,6-di-*O*-isopropylidene-1-*O*-methyl-*D*-glucitol* (**2**). — The i.r. spectrum showed the main groups present: amide carbonyl (1670, 1650 cm^{-1}), amide II (1560, 1530 cm^{-1}), and amide III (1250, 1220 cm^{-1}) bands; *gem*-dimethyl group (1380 cm^{-1}) and the dioxolane ring[4] as a broad band at 1170–1075 cm^{-1}. The n.m.r. spectra were recorded at 100 MHz for solutions in deuteriochloroform. A diffuse doublet at δ 6.18 that disappeared on adding deuterium oxide was assigned to the NH group ($J_{1,NH}$ 10 Hz); also, the "anomeric" proton at δ 5.21, which

appeared as a pair of doublets, collapsed to a doublet ($J_{1,2}$ 4 Hz). The remaining protons of the sugar chain (H-2 to H-6,6') appeared as a large multiplet at δ 3.90–4.25. The signal of the 4-hydroxyl group appeared, superimposed on that of the 1-methoxyl group, at δ 3.40, and the signal of the *N*-acetyl group resonated at δ 2.06. The peaks of these groups appeared to be partitioned, each into two signals of ~2:1 relative strength, suggesting a mixture of C-1 diastereoisomers in that ratio. The same appearances and proportions were observed in the spectra of both the crystalline and the syrupy **2**. At δ 1.43 and 1.36, there appeared the resonances of the isopropylidene-methyl groups; the structural implications will be discussed later.

The coupling of H-1 with NH showed that an isopropylidene bridge involving the acetamido group was not formed. When a nitrogen atom was involved in the dioxolane ring, the isopropylidene group resonated at lower field[3].

The pattern of substitution on the sugar chain was clarified by mass spectroscopy, as well as chemically. The important fragments in the rupture of compound **2** by electron impact at 70 eV are shown in Scheme 2. The proposed pathways agree with previous studies with isopropylidene derivatives, conducted, in some cases, with deuterated compounds[5]. The most important route is that involving cleavage of the C-1–C-2 bond. In this open-chain diacetal, the structurally significant peak at *m/z* 101, diagnostic for the presence of a 5,6-isopropylidene group, is supported by



Scheme 2

the peak at *m/z* 232, whose structure is, in turn, justified by the peaks at *m/z* 202, 144, 174, and 156. The location of the 2,3-*O*-isopropylidene group is shown unambiguously by these peaks.

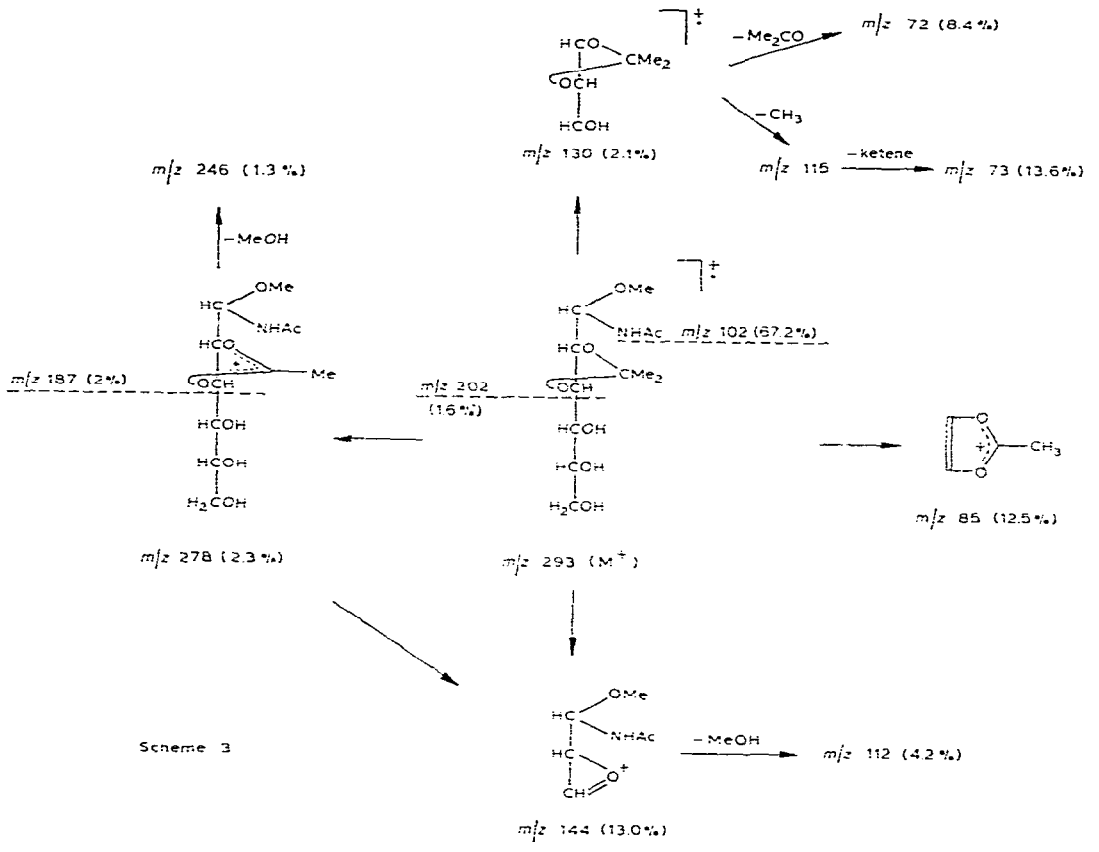
The presence of a free hydroxyl group on C-4 was confirmed by methylation of crystalline compound **2** with diazomethane–boron trifluoride in dichloromethane[6]. Complete methylation was not achieved, and a mixture of **2** with 1-acetamido-2,3:5,6-di-*O*-isopropylidene-1,4-di-*O*-methyl-D-glucitol and its *N*-methyl derivative was obtained. The mass spectrum of this mixture showed new peaks of high intensity, not present in the spectrum of pure **2**. Particularly relevant was the rupture of the C-3–C-4 bond to give the methylated fragment of *m/z* 145 (13.8%) comprising C-4 to C-6 of the methylated molecular ions. This fragment, by loss of an isopropylidene-methyl group, gave *m/z* 130 (42.7%), and the subsequent loss of ketene led to *m/z* 88 (42.3%). Alternatively, the losses of acetone or acetic acid gave *m/z* 87 (50.5%) or 85 (33.5%), respectively.

Hydrolysis of the methylated mixture afforded D-glucose and 4-*O*-methyl-D-glucose. The latter was isolated as a syrup by preparative chromatography on 3MM paper giving an optical rotation in agreement with that in the literature. Confirmation for this syrupy monomethyl derivative[7] was obtained through its transformation into 1,2,4,5,6-penta-*O*-acetyl-3-*O*-methyl-D-glucitol, and subsequent, mass-spectrometric identification by the characteristic peaks[7] at *m/z* 261, 198, 129, and 87.

*Structure of 1-acetamido-2,3-*O*-isopropylidene-1-*O*-methyl-*D*-glucitol* (**3**). — Compound **3** was isolated after chromatography of the crude syrup obtained in the synthesis on a column of silicic acid. It was eluted with 3:97 absolute ethanol–chloroform, and obtained pure in 3.7% yield. Periodate oxidation showed the liberation of formaldehyde, indicating a free C-5–C-6 diol system, but the quantitative results of the oxidation were erratic, probably owing to the ready hydrolysis of the isopropylidene substituent. The structure proposed for **3** appeared to be supported by the spectroscopic data; the i.r. spectrum showed the same peaks as for compound **2**, and the n.m.r. spectrum at 60 MHz of **3** in pyridine-d_5 equilibrated with deuterium oxide showed one isopropylidene peak at δ 1.42. The acetamido (δ 2.05) and the methoxyl (δ 3.35) signals appeared partitioned, showing a minor component at δ 2.12 and 4.00 respectively, attributable to a C-1 diastereoisomeric mixture. The seven protons of the sugar backbone appeared as three unresolvable multiplets. The mass spectrum showed structurally significant peaks at *m/z* 202, 187, 144, and 130, as shown in Scheme 3 (base peak, *m/z* 60).

Owing to the sensitivity of the isopropylidene groups to the slightest acidic conditions, it is uncertain whether compound **3** originated in the reaction, or was produced during the column chromatography on silicic acid. Likewise, the last fractions from the column, containing starting material (**1**) and an unresolved mixture of monoisopropylidene derivatives (comprising ~15% of the crude syrup from the synthesis), probably originated in that way.

Structure of N-*acetyl-5,6-*O*-isopropylidene-D-glucofuranosylamine* (**4**). — Compound **4** (3.2% yield) was eluted from the column with 47:3 absolute ethanol–

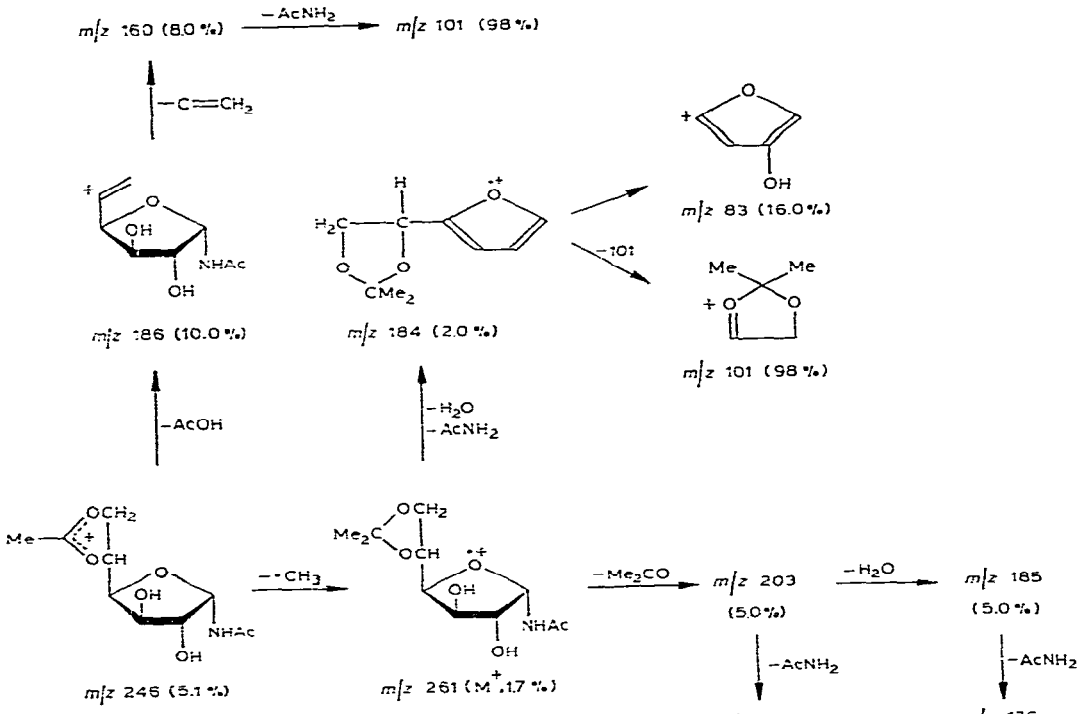


Scheme 3

chloroform. However, when a solution of the original syrup in benzene was kept for several weeks at room temperature, compound **4** crystallized in 4.6% yield. This direct crystallization was favored by pre-extraction of the syrup with light petroleum at room temperature (to eliminate some polymeric materials produced from 2,2-dimethoxypropane).

Periodate oxidation showed the uptake of one mol of periodate per mol, and did not give a positive chromotropic acid reaction for formaldehyde[8,9]. The i.r. spectrum showed the same bands as the aforedescribed compounds. The n.m.r. spectrum (60 MHz, D_2O) showed H-1 as a doublet (δ 5.41, $J_{1,2}$ 2 Hz); the six protons of the sugar chain (H-2–6,6′) appeared as a large multiplet (δ 3.90–4.40). A singlet (δ 2.03) and a doublet (δ 1.42 and 1.38) indicated the *N*-acetyl group and the isopropylidene-methyl groups, respectively. The mass spectrum of **4** confirmed the results obtained by periodate oxidation and n.m.r. spectroscopy. Scheme 4 shows the most probable pathways of rupture. The characteristic, dioxolane terminal-fragment (*m/z* 101) appeared with high intensity (98%), although some contribution from the furanoid ring is apparent.

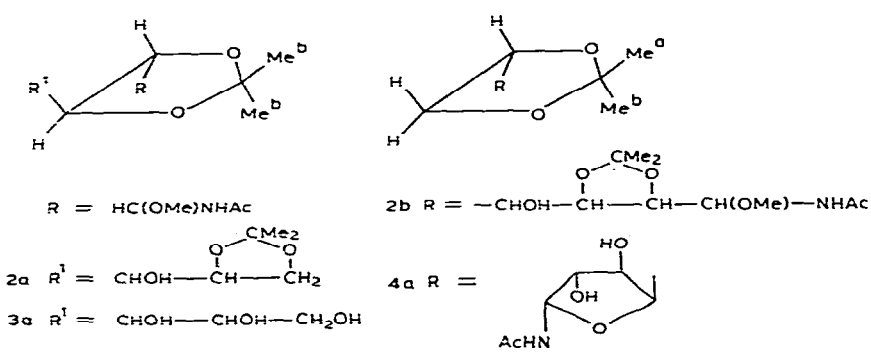
The compounds here described show the n.m.r. signals for the isopropylidene-



Scheme 4

methyl protons in agreement with the pattern of substitution already shown. Compounds **2** and **3** have the 2,3-*O*-isopropylidene group in the stereochemical arrangement depicted in **2a** and **3a**, respectively, which correspond to an α-T acetal (*threo*)[10], with both methyl groups *cis* to the *H*/*R* substituents, and are consequently designed as Me[b].

On the other hand, the 5,6-*O*-isopropylidene group in compounds **2** and **4** has the stereochemistry shown in **2b** and **4a**, respectively, which corresponds to an



α-terminal arrangement[10], with Me^a (*cis to H/H*) and Me^b groups, in the 1,3-dioxolane ring.

As the Me^b groups, owing to proximity to the *R* substituents, are usually more deshielded than Me^a groups, compound **2**, having one Me^a and three Me^b groups, should show a pattern of two signals of relative strength 1:3, and these appeared at δ 1.36 and 1.43, respectively. The latter signal had a slight shoulder on the high-field side, due to the different environments of the Me^b groups.

On the same basis, the two Me^b groups of compound **3** appeared as a single resonance at δ 1.42 (also having a slight shoulder) and compound **4** exhibited peaks of equal strength at δ 1.38 and 1.43, attributable to the protons of Me^a and Me^b respectively.

EXPERIMENTAL

General procedures. — Melting points (Kofler hot-stage) are uncorrected. Optical rotations were measured at 20–25° with a Perkin–Elmer 141 automatic polarimeter. T.l.c. was conducted on plates of Silica Gel G (Merck) with (*A*) water-saturated 2-butanone as the eluant. The spots were detected with (*1*) iodine vapor or (*2*) 5% sulfuric acid in ethanol, with subsequent heating at 140°. Paper chromatography was performed on Whatman No. 1 paper by the descending technique, with (*B*) 5:2:2 (v/v/v) 1-butanol–ethanol–water as the developing solvent, and detection of the spots with (*3*) silver nitrate–sodium methoxide[11], and (*4*) aniline hydrogenphthalate[12]. Column chromatography was conducted on silicic acid (Baker, 100 mesh). N.m.r. spectra were recorded with a Varian A-60 (60 MHz) or with a Varian XL-100 (100 MHz) spectrometer at 20–25°, with tetramethylsilane as the internal reference-standard. Mass spectra were recorded with a Varian-Mat CH-7 spectrometer commanded by a Varian-Mat data system 166 computer, at an ionizing potential of 70 eV; the temperature of the direct-insertion probe was 130°.

Synthesis of 1-acetamido-2,3:5,6-di-O-isopropylidene-1-O-methyl-D-glucitol (**2**). — A mixture of *N*-acetyl-α-D-glucofuranosylamine[2] (**1**; 5 g), 2,2-dimethoxypropane (37 mL), and *p*-toluenesulfonic acid (75 mg) was heated for 3 h in a water bath at 60°. The mixture was diluted with benzene (100 mL), and cooled to 0°. Deacidite FF resin (5 g) was added, the suspension was shaken until the solution was neutral, filtered, and the filtrate evaporated to dryness. The resulting crude syrup (6.63 g), mainly compound **2**, had $[\alpha]_D$ −22.0° (*c* 0.9; ethanol). Paper chromatography (solvent *B*, reagent *3*) showed a round, diffuse spot, R_F 0.88. T.l.c. (solvent *A*; reagents *1* and *2*) showed a principal spot at R_F 0.61 with a fading tail. By trituration with ethyl ether–petroleum ether (b.p. 60–80°), and after long standing, the syrup partially crystallized (0.90 g; 12% yield). Recrystallization from acetone–ethyl ether gave **2**, m.p. 121–124°, $[\alpha]_D$ −25.7° (*c* 1.2; ethanol). T.l.c. and paper chromatography showed one spot, R_F 0.61 and 0.88, respectively.

As direct crystallization gave a poor yield of compound **2**, an attempt was made

to improve it, and also to have a complete pattern of the reaction, through use of column chromatography.

Column chromatography on silicic acid. — The crude syrup (15.0 g) from a new preparation was chromatographed on a column (600 × 40 mm) of silica activated for 1 h at 110°. The following eluants were employed: benzene (fractions 1–28, 1076 mL), chloroform (fractions 29–45, 1190 mL), and solutions of increased concentrations of absolute ethanol in chloroform as follows: 1% (fractions 46–47, 490 mL), 3% (fractions 48–50, 460 mL), 6% (fractions 51–58, 1320 mL), and methanol (fraction 59, 400 mL). The fractions were combined on the basis of t.l.c. (solvent *A*, reagent *2*) as follows. Fractions 1–12 (254 mg) mainly consisted of a syrupy polymer formed from 2,2-dimethoxypropane.

Fractions 13–47 were compound **2**, obtained as a pure syrup (9.85 g; 65.6% yield), which, by dissolution in acetone or benzene, gave crystals (3.93 g), m.p. 125°, $[\alpha]_D$ −25.3° (*c* 1.2, ethanol); t.l.c., one spot, R_F 0.59. It was the same as the product that crystallized directly from the crude syrup, and had ν_{max}^{Nujol} 1670, 1650 (CO), 1560–1530 (C–N), 1380 (*gem*-dimethyl group), 1250, 1220 (N–H, C–N), and 1170–1075 cm^{-1} (dioxolane group); n.m.r. (100 MHz, $CDCl_3$): δ 6.18 (d, NH, $J_{1,NH}$ 10 Hz), 5.21 (dd, H-1, $J_{1,2}$ 4 Hz), 4.25–3.90 (m, 6 H, H-2–H-6,6'), 3.40 (4 H, methoxyl and hydroxyl groups), 2.06 (3 H, *N*-acetyl group), and 1.43 and 1.36 (9 and 3 H, isopropylidene groups); mass spectrum: see Scheme 2.

This crystalline solid was soluble in water, chloroform, and benzene; and insoluble in cold, but somewhat soluble in hot, light petroleum (b.p. 60–80°). On long standing in methanol solution, it partially loses the isopropylidene substituents.

Anal. Calc. for $C_{15}H_{27}NO_7$: C, 54.05; H, 8.10; N, 4.20. Found: C, 54.08; H, 8.29; N, 4.20.

The remaining, uncrystallizable syrup from this fraction showed optical rotation, R_F in t.l.c. and paper chromatography, and n.m.r. spectra identical to those of crystalline material.

Fractions 48–53: some of these fractions afforded compound **3** as a pure syrup (0.490 g; 3.7% yield), $[\alpha]_D$ −11.7° (*c* 1.4, ethanol). Paper chromatography (solvent *B*, reagent *3*) showed one spot, R_F 0.49; it had ν_{max}^{film} 3400, 3300 (NH), 3200, 3150 (HO), 1670, 1640 (CO), 1540, 1530(C–N), 1380, 1370, (*gem*-dimethyl group) 1260, 1220 (C–N, N–H), and 1145–1035 cm^{-1} (broad band, dioxolane group); n.m.r. (60 MHz, pyridine-d_5–D_2O): δ 5.77 (d, H-1, $J_{1,2}$ 4 Hz), 4.94–4.77 (m, 2 H), 4.35–4.10 (m, 4 H), 3.35 (3 H, methoxyl group), 2.05 (3 H, *N*-acetyl group), and 1.42 (6 H, isopropylidene group): mass spectrum: see Scheme 3.

Anal. Calc. for $C_{12}H_{23}NO_7$: C, 49.14; H, 7.84; N, 4.77. Found: C, 48.86; H, 8.31; N, 4.42.

Fractions 54 and 55: both fractions gave a crystalline residue (0.389 g, 3.2% yield) that, in t.l.c. (solvent *A*, reagent *2*), showed one spot, R_F 0.42. The solid was soluble in protic solvents and in acetone; insoluble in benzene and in light petroleum. Recrystallized from chloroform it had m.p. 154–158°, $[\alpha]_D$ −62.2° (*c* 0.9, ethanol); ν_{max}^{Nujol} 3350 (NH), 3200 (HO), 1670, 1640 (CO), 1550, 1525 (C–N, N–H), 1380 (*gem*-

dimethyl group), 1250, 1220 (C–N, N–H), and 1100–1035 cm^{-1} (broad, dioxolane ring); n.m.r. (60 MHz, D_2O): δ 5.41 (d, H-1, $J_{1,2}$ 2 Hz), 4.40–3.90 (m, 6 H, H-2–H-6,6'), 2.03 (3 H, *N*-acetyl group), and 1.43 and 1.38 (3 and 3 H, isopropylidene-methyl groups); mass spectrum: see Scheme 4.

Anal. Calc. for $C_{11}H_{19}NO_6$: C, 50.57; H, 7.27; N, 5.36. Found: C, 50.58; H, 7.51; N, 5.16.

Periodate oxidation. — A solution of compound **4** (3.0 mg) in 15mM sodium metaperiodate (3.42 mL) was kept at 25°. Samples (0.1 mL) were taken at intervals, and diluted with water to 25 mL; the periodate consumed was determined according to spectrometric methods[8]. The following values were obtained (moles, time in h): 0.33 (0.5), 0.57 (2), 0.68 (4), 0.89 (6), and 1.02 (24). No formaldehyde was detected with the chromotropic acid reagent[9].

Fractions 56–59: these fractions (1 g) were complex mixtures of di- and mono-isopropylidene derivatives with starting compound (**1**).

Methylation of compound **2**. — The crystalline product (200 mg) was dissolved in dichloromethane (37 mL), and a few drops of boron trifluoride etherate[6] and an ethereal solution of diazomethane[13] (30 mL, containing ~0.25 g of reactant) were added. The solution was kept for 4 h at room temperature, the suspension filtered, and the filtrate evaporated to a syrup. This was a mixture of methylated and unmethylated **2** which, in its mass spectrum, showed high-intensity fragments at *m/z* 158 (38.4%; rupture of C-4–C-5 of M^+, and subsequent loss of a Me group and ketene) and 145 (13.8%, rupture of C-3–C-4). The latter peak, in turn, gave, by the losses indicated in parentheses, *m/z* 130 (42.7%, CH_3), 88 (42.3%, CH_3 and ketene), 87 (50.5%, acetone), and 85 (33.5%, acetic acid), which agree with the 4-*O*-methyl derivative of **2**.

The syrup was dissolved in 0.5M sulfuric acid (25 mL) and the solution was heated for 3 h in a boiling-water bath. After neutralization of the acid with $BaCO_3$, the suspension was filtered, and the filtrate evaporated to dryness. In paper chromatography (solvent *B*, reagent *4*) the residue showed two spots, R_F 0.22 (glucose) and 0.33 (monomethylglucose). The methyl derivative was isolated, and purified, by preparative chromatography on Whatman No. 3MM paper as a syrup (40 mg), $[\alpha]_D$ +50.0° (*c* 1.0, water); lit.[14] $[\alpha]_D$ +53.0° (*c* 2.1, water).

The methylglucose was reduced with sodium borohydride in water during 3 h, the base neutralized with Dowex 50(H^+) resin, the suspension filtered, and the filtrate evaporated to dryness, with additions of methanol. The residue was dissolved in 1 : 1 acetic anhydride–pyridine (1 mL), and the solution kept for 24 h at room temperature, and evaporated to dryness. A syrup (12 mg) was obtained whose mass spectrum showed *m/z* 261 (0.8%), 189 (2.4%), 129 (7.9%), and 87 (10.9%), characteristic for a 4- or 3-*O*-methylhexitol[7].

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REFERENCES

1 H. PAULSEN AND K. W. PFLUGHAUPT, in W. PIGMAN AND D. HORTON (Eds.), *The Carbohydrates* 2nd edn., Vol. 1B, Academic Press, New York, 1980, pp. 881–927.
2 M. E. GELPI AND R. A. CADENAS, *Carbohydr. Res.*, 28 (1973) 147–149.
3 A. HASEGAWA AND H. G. FLETCHER, JR., *Carbohydr. Res.*, 29 (1973) 223–237.
4 R. S. TIPSON, H. S. ISBELL, AND F. E. STEWART, *J. Res. Natl. Bur. Stand.*, 62 (1959) 257–282.
5 D. C. DEJONGH AND K. BIEMANN, *J. Am. Chem. Soc.*, 86 (1964) 67–74; A. BUCHS, A. GLANGETAS, AND J. M. J. TRONCHET, *Org. Mass Spectrom.*, 10 (1975) 970–980; *Helv. Chim. Acta*, 57 (1974) 1332–1339; A. HASEGAWA AND M. KISO, *Carbohydr. Res.*, 63 (1978) 91–98.
6 I. O. MASTRONARDI, S. M. FLEMATTI, J. O. DEFARRARI, AND E. G. GROS, *Carbohydr. Res.*, 3 (1966) 177–183.
7 H. BJÖRNDAL, B. LINDBERG, AND S. SVENSSON, *Carbohydr. Res.*, 5 (1967) 433–440; H. BJÖRNDAL, B. LINDBERG, Å. PILOTTI, AND S. SVENSSON, *ibid.*, 15 (1970) 339–349.
8 R. D. GUTHRIE, *Methods Carbohydr. Chem.*, 1 (1962) 435–441.
9 J. C. SPECK, JR., *Methods Carbohydr. Chem.*, 1 (1962) 441–445.
10 N. BAGGETT, K. W. BUCK, A. B. FOSTER, R. JEFFERIS, B. H. REES, AND J. M. WEBBER, *J. Chem. Soc.*, (1965) 3382–3388.
11 R. A. CADENAS AND J. O. DEFERRARI, *Analyst*, 86 (1961) 132–134.
12 S. M. PARTRIDGE, *Nature*, 164 (1949) 443.
13 F. ARNDT, *Org. Synth., Coll. Vol.*, 2 (1963) 165–167.
14 J. MUNRO AND E. G. V. PERCIVAL, *J. Chem. Soc.*, (1935) 873–875.