Carbohydrate Research, 78 (1980) 257–265

BROMINE OXIDATION OF 1,2-*O*-ISOPROPYLIDENE-α-D-GLUCOFURANOSE AND SUCROSE

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(Received April 3rd, 1979; accepted for publication, May 16th, 1979)

ABSTRACT

Sucrose and 1,2-*O*-isopropylidene-α-D-glucofuranose (**1**) were oxidised with bromine in aqueous solution at pH 7 and room temperature. The resulting keto derivatives were converted into their more-stable *O*-methyloximes, which were characterised by spectroscopic and chromatographic methods. Oxidation of **1** occurred at C-3 and C-5, with a preference for C-5. In the sucrose derivatives isolated after oxidation, those having a keto group in the glucopyranosyl moiety preponderated. The axial fructofuranosyl aglycon protects position 3 in the glucopyranosyl group and oxidation occurs only at C-2 and C-4. Small amounts of sucrose oxidised at C-3 in the fructofuranosyl moiety were also found.

INTRODUCTION

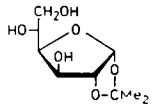
Studies of the bromine oxidation of glycopyranosides[1,2] have shown that hydroxyl, methoxyl, and glycosyl groups in *syn*-diaxial relation to an axial hydrogen obstruct oxidation of the alcohol in this position. Thus, the aglycon of the α anomer of a D-glucopyranoside in the $^4C_1$ conformation protects position 3, the axial HO-4 in D-galactopyranosides protects position 2, and the axial HO-2 in D-mannopyranosides protects position 4 from oxidation.

The work reported herein was undertaken to ascertain if similar effects prevail in furanosides.

RESULTS

On oxidation of 1,2-*O*-isopropylidene-α-D-glucofuranose (**1**) or sucrose (**4**) in aqueous solution at pH 7 and room temperature with ~2 mol of bromine (0.1M) per mol of carbohydrate, the oxidant was consumed after 7 and 3 h, respectively. The rate of oxidation of **1** did not differ significantly from those of methyl D-glycopyranosides[1] and trehaloses[2], under the same conditions. However, sucrose (**4**) was oxidised at a higher rate.

In order to facilitate characterisation, the reaction mixtures were treated with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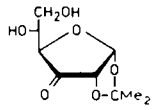
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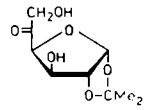
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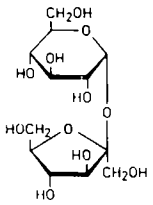
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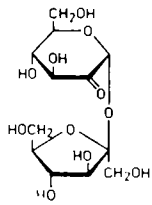
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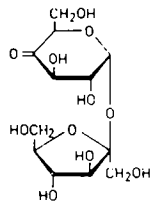
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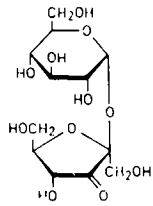
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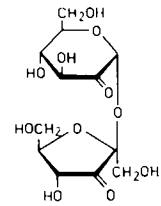
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methoxylamine hydrochloride, to convert the keto derivatives into their more-stable *O*-methyloximes[1]. Some of these derivatives were obtained as mixtures of *syn* and *anti* forms. As the *O*-methyloxime was used only for protection, no attempts were made to distinguish between these two forms, and in the following, in some cases, a *syn* and *anti* mixture will be regarded as consisting of one compound only. The *O*-methyloximes were separated by column chromatography and identified by ^{1}H- and ^{13}C-n.m.r. spectroscopy, and by g.l.c.–m.s. of their methyl derivatives. The yields of keto compounds were determined by g.l.c. of the trimethylsilylated *O*-methyloximes from oxidised **1**, and of the methylated *O*-methyloximes from oxidised **4** (some of the trimethylsilylated *O*-methyloximes from oxidised **4** did not separate on g.l.c.).

Bromine oxidation of **1** yielded the hexosuloses **2** (5%) and **3** (23%), and 28% of the starting material remained unchanged. The rest consisted of acidic components, probably formed *via* oxidative ring-cleavage[3]. No gluconic or glucuronic acid was found in the hydrolysate of oxidised **1**.

Compound **2** yielded allitol and glucitol after hydrolysis[1] and reduction. In the ^{1}H-n.m.r. spectrum of the *syn* and *anti* *O*-methyloximes of **2**, the signals for H-2 and H-4 appeared as doublets of doublets (long-range coupling[4] between H-2 and H-4) at lower field than the signals for H-2 and H-4 in **1** (Table I). In the ^{13}C-n.m.r. spectra of the *syn* and *anti* forms of methoximated **2**, the signal for C-3 appeared at a frequency expected for an oxime carbon[5] (Table II). Thus, **2** was identified as 1,2-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ulose.

Compound **3** yielded glucitol, iditol, and idosan after hydrolysis[1] and reduction. The *syn* and *anti* *O*-methyloximes of **3** separated on column chromatography. In the ^{1}H-n.m.r. spectrum of one form, the signals for H-4, H-6a, and H-6b appeared as doublets at a lower field than those for H-4, H-6a, and H-6b in **1**. In the ^{1}H-n.m.r. spectrum of the other form, the signal for H-4 appeared as a doublet, and H-6a and H-6b, owing to a fortuitous shift-coincidence, gave a singlet. In the ^{13}C-n.m.r. spectrum of methoximated **3**, the signal for C-5 appeared at a frequency expected

TABLE I

^{1}H-N.M.R. SPECTRAL DATA[a]

Group	*Proton*	O-*Methyloxime of* **2**		**3**		**5**	**6**	**7**		**8**	
		Chemical shift (δ)									
	CH_3	1.38	1.38	1.31	1.31						
	CH_3	1.44	1.39	1.47	1.45						
	$-N\text{-}OCH_3$	3.91	3.90	3.85	3.88	3.93	3.93	3.93	3.91	3.96	3.94
Glucose residue	H-1	5.96	5.99	5.96	5.95	6.45	5.65	5.52	5.47	6.53	6.51
	H-2	5.17	5.03	4.53	4.49	—	3.93			—	—
	H-3	-	—	4.34	4.43	4.60	4.33			4.48	
	H-4	4.81	5.12	4.92	5.22	3.57	—				
	H-5	~ 3.85	4.04	—			5.19	3.50-4.30		3.50-4.25	
	H-6a	3.62	3.48	4.29	4.22	3.80–4.30	3.69				
	H-6b	3.63	3.48	4.47	4.22		4.05				
Fructofuranosyl group	H-1a					3.57	3.73				
	H-1b					3.72	3.73				
	H-3							-	—	- -	—
	H-4							4.93	4.76	5.03	4.88
	H-5					3.80–4.30	3.70–4.30				
	H-6a							3.50-4.30		3.50-4.25	
	H-6b										
	Coupling constant (Hz)										
Glucose residue		$J_{1,2}$ 4.4	4.6	$J_{1,2}$ 3.7	3.6	$J_{3,4}$ 9.6	$J_{1,2}$ 1.8	$J_{1,2}$ 3.3	3.3	$J_{3,4}$ 8.8	8.8
		$J_{2,4}$ 1.5	1.7	$J_{2,3}$ 0	0	$J_{4,5}$ 9.6	$J_{2,3}$ 4.5				
		$J_{4,5}$ 2.7	1.9	$J_{3,4}$ 3.0	3.0		$J_{5,6a}$ 7.9				
		$J_{5,6a}$ 5.4	6.6	$J_{6a,6b}$ - 15.0	—		$J_{5,6b}$ 3.1				
		$J_{5,6b}$ 7.3	6.6				$J_{6a,6b}$ - 12.6				
Fructofuranosyl group						$J_{1a,1b}$ - 12.8	$J_{1a,1b}$ —	$J_{4,5}$ 7.0	8.4	$J_{4,5}$ 6.5	8.1

[a] **2** and **3** in CD_3OD; **5**–**8** in D_2O.

TABLE II

^{13}C-N.M.R. SPECTRAL DATA[a]

Parent compound	O, O, C	CH_3 CH_3	OCH_3, =N	*Glucose residue*						*Fructofuranosyl group*					
				C-1	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*
1	113.4	26.5 26.1		105.5	85.3	74.5	80.6	69.3	64.4						
	115.1	27.3	63.4	105.6	75.9	159.1	79.9	74.1	62.0						
2[b]	115.4	27.6 27.5	63.3	105.3	79.3[c]	159.7	80.6[c]	72.9	62.3						
	113.7	26.7 26.2	62.8	105.0	85.5	75.9	80.2	157.4	56.7						
3[b]	113.7	26.7 26.1	62.8	105.1	85.2	75.3	79.2	157.7	60.8						
4				93.1	72.1	73.5[c]	70.2	73.4[c]	63.4[d]	62.3	104.6	77.4	75.0	82.3	61.1[d]
5[b]			62.9	84.7	154.7	71.3	72.8	73.6	63.6[c]	61.5	105.7	76.4	74.9	82.7	61.0[c]
6[b]			63.1	89.5	71.9	70.5	153.6	72.7	62.6[c]	61.9	105.2	77.3	74.3	82.5	60.9[c]
7[b]			63.4	92.9	71.8	73.7[c]	69.8	72.9[c]	61.8[d]	65.7[d]	103.8	161.0	68.2	84.2	60.2[d]

[a]In p.p.m. downfield from tetramethylsilane. In D_2O. [b]*Syn* and/or *anti* *O*-methyloximes. [c,d]Mutual assignment uncertain.

for an oxime carbon[5] (Table II). Thus, **3** was identified as 1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranos-5-ulose.

On treatment of the *O*-methyloximes of **2** and **3** with acid under mild conditions[11], the carbonyl compounds were regenerated with simultaneous hydrolysis of the isopropylidene group. Therefore, a direct comparison with data previously reported for **2** and **3** could not be made[6].

Bromine oxidation of sucrose (**4**) yielded the uloses **5**–**8** in yields of 21, 14, 1, and 4%, respectively. The remainder was starting material (10%) and acidic components, probably generated *via* oxidative ring-cleavage[3], as oxidation at C-1 or C-6 was not observed.

Compound **5** yielded glucitol and mannitol after reduction, hydrolysis, and reduction. In the ^{1}H-n.m.r. spectrum of methoximated **5**, signals from the hexopyranosidulose residue almost coincided with those of methoximated methyl α-D-*arabino*-hexopyranosidulose[1] (Table I), and in the ^{13}C-n.m.r. spectrum, the signal for C-2 of the hexopyranosidulose group appeared at a frequency expected for an oxime carbon[5] (Table II). Thus, **5** was identified as β-D-fructofuranosyl α-D-*arabino*-hexopyranosidulose.

Compound **6** yielded galactitol, glucitol, and mannitol after reduction, hydrolysis, and reduction. In the ^{1}H-n.m.r. spectrum of methoximated **6**, signals from the hexopyranosidulose residue almost coincided with those of the methoximated methyl α-D-*xylo*-hexopyranosid-4-ulose[1] (Table I), and in the ^{13}C-n.m.r. spectrum, the signal for C-4 of the hexopyranosidulose group appeared at a frequency expected for an oxime carbon[5] (Table II). Thus, **6** was identified as β-D-fructofuranosyl α-D-*xylo*-hexopyranosid-4-ulose.

In the sugar analysis of reduced, hydrolysed, and reduced **7**, allitol, glucitol, and mannitol and/or altritol were detected. In the ^{1}H-n.m.r. spectrum of methoximated **7**, the signal ascribable to H-4 of the hexofuranosid-diulose residue appeared as a doublet at lower field than the corresponding signal in **4** (Table I), and in the ^{13}C-n.m.r. spectrum, the signal for C-3 appeared at a frequency expected for an oxime carbon[5] (Table II). Thus, **7** was identified as α-D-glucopyranosyl β-D-*erythro*-hexo-2,5-furanosid-2,3-diulose.

In the ^{1}H-n.m.r. spectrum of methoximated **8**, signals from the hexopyranosidulose residue almost coincided with those in the spectrum of methoximated **5**, and those from the hexofuranosid-diulose residue almost coincided with the corresponding signals for **7**. Hence, **8** was identified as α-D-*arabino*-hexopyranosylulose β-D-*erythro*-hexo-2,5-furanosid-2,3-diulose. As the yield of **8** was low, and about equal amounts of the *syn* and *anti* forms were obtained, the ^{13}C-n.m.r. spectrum was obscure, and provided no further information on the structure of **8**.

Assignments of the signals in the ^{13}C-n.m.r. spectra from **1** and **4** and methoximated **2**, **3**, and **5**–**7** were made by selective decoupling of the protons[5]. In previous studies, assignment of some signals in the ^{13}C-n.m.r. spectrum of sucrose (**4**) were uncertain[7,8]. Our assignments were made by selective decoupling, with reference to the 300-MHz, ^{1}H-n.m.r. spectrum for sucrose[9].

On oxidation followed by methoximation, the signals for the oxidised carbons were shifted strongly downfield, those for adjacent carbons generally upfield, and those for carbons in β-position relative to the methoxime group sometimes downfield. The remaining carbons were not significantly affected.

DISCUSSION

It has been proposed that the rate-determining step in the bromine oxidation of a secondary alcohol is the removal of the secondary hydrogen with its electron pair[10]. In 1,2-*O*-isopropylidene-α-D-glucofuranose, H-3 is *endo* in the bicyclic system and therefore less susceptible to attack by bromine than the relatively unhindered hydrogen at the exocyclic C-5. It was also observed that oxidation occurred preferentially at C-5.

In the glucopyranosyl unit of sucrose, oxidation occurs only at C-2 and C-4. In accordance with earlier findings, C-3 is obviously hindered from oxidation by the axially oriented fructofuranosyl unit at C-1. The glucopyranosyl unit of sucrose appeared to be oxidised to a greater extent than the fructofuranosyl unit. In the fructofuranosyl residue, all of the ring hydrogens are in a 1,2-*cis* relationship to hydroxyl or hydroxymethyl groups and probably more hindered than H-2 and H-4 in the glucopyranosyl moiety. This situation could explain the relative resistance of the fructofuranosyl unit. When this unit is oxidised, oxidation occurs only at C-3. Position 4 is hindered from oxidation not only by the substituents at C-3 and C-5, but also by the pseudoaxial glucopyranosyl residue at C-2. However, there is also a possibility that when a keto group is introduced in the fructofuranosyl moiety, further oxidation to ring-cleavage acids, or degradation in some other way, occurs. The above results imply that, when keto groups are introduced in both rings, in addition to **8**, α-D-*xylo*-hexopyranosyl-4-ulose β-D-*erythro*-hexo-2,5-furanosid-2,3-diulose should also be obtained. This compound was either not formed in sufficient quantities for detection, or decomposed before analysis.

Compounds **2** and **3** have previously been prepared[6] by chromic oxidation of **1**. The hepta-acetate of **6** has been synthesised[11] by oxidation (ruthenium tetraoxide or dimethyl sulphoxide–acetic anhydride) of the hepta-acetate of **4**, having HO-4 in the glucosyl unit unprotected. β-D-Fructofuranosyl α-D-*ribo*-hexosid-3-ulose, obtained by the fermentation of sucrose with *Agrobacterium tumefaciens*[11], has been used as starting material for the preparation of C-3 tritium-labelled sucrose by reduction with sodium borotritide[12]. Glucose, tritiated on C-3, has been obtained from the labelled sucrose by enzymic hydrolysis. These compounds are of interest for biochemical studies. By analogous methods, sucrose, glucose, or fructose, labelled in other positions, may be prepared from **5**, **6**, or **7**.

EXPERIMENTAL

General methods. - Melting points are corrected. Solutions were concentrated

at reduced pressure below 40°. Optical rotations were measured with a Perkin–Elmer 141 polarimeter, ^{1}H-n.m.r. spectra were recorded with a Varian HA-100D spectrometer and ^{13}C-n.m.r. spectra with a Jeol FX 90Q Fourier Transform n.m.r. spectrometer. G.l.c. was performed with a Packard 427 instrument, fitted with a flame-ionisation detector. Low- and high-resolution mass spectra were recorded on Varian MAT CH7 and AEI MS 902 instruments, respectively. The mass spectra of *syn* and *anti* forms of the methylated *O*-methyloximes showed only minor differences, and data are given only for the preponderant geometric isomer. For quantitative analysis, g.l.c. separations were performed on a capillary glass-column (25 m × 0.3 mm) containing OV-101, at (*a*) 100–275° (4°/min) for the trimethylsilylated *O*-methyloximes from oxidized **1**, and (*b*) 175–280° (2°/min) for the methylated *O*-methyloximes from oxidised sucrose. Detector responses were determined only for **1** (0.52), **4** (0.80), and the *O*-methyloximes of **2** (0.33), **5** (0.45), and **8** (0.22). The responses were determined by reference to trimethylsilylated *myo*-inositol and methylated cyclohexyl α-D-glucopyranoside, respectively. The responses of isomers were assumed to be equal. Peak areas were measured with an Autolab minigrator. The organic acids obtained by oxidation were analysed by paper electrophoresis on Whatman No. 1 paper with 0.5M sodium acetate buffer (pH 4.5) at 25°, and detection with *p*-anisidine hydrochloride and silver nitrate–sodium hydroxide.

Oxidation of 1,2-O-isopropylidene-α-D-glucofuranose (**1**). To a solution of bromine (4 g) in water (250 ml) was added a solution of **1** (2.5 g) in water (50 ml). The mixture was kept at room temperature and pH 7.0. When the oxidant had been consumed (after 7 h), the pH was adjusted to 5.0, and the mixture was concentrated to 100 ml and added to a solution of methoxylamine hydrochloride (2 g) in water (30 ml) at pH 4.0. After 2.5 h, the pH was adjusted to 7.0 and the volume to 250 ml. *myo*-Inositol (5 mg) was added to a 10-ml sample, the mixture was concentrated to dryness, and portions of the residue were (*a*) trimethylsilylated and analysed by g.l.c., and (*b*) methylated as described below and analysed by g.l.c.–m.s. The remainder of the residue was extracted with chloroform (5 × 50 ml). The combined extracts were concentrated, and the residue was eluted from a column of silica gel 60 (Merck, 230–400 mesh) with chloroform–ethanol (10:1), to give the following compounds.

The *O*-methyloxime (53 mg) of 1,2-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ulose (**2**), m.p. 98–113° (*syn,anti* mixture), $[\alpha]_{578}^{20}$ +206° (*c* 0.4, ethanol).

Anal. Calc. for $C_{10}H_{17}NO_6$: C, 48.6; H, 6.9; N, 5.7. Found: C, 48.7; H, 6.8; N, 5.3.

Mass spectrum of the methylated derivative: *inter alia*, *m/e* 73 (100%), 84 (17), 85 (18), 88 (90), 89 (98), 90 (16), 100 (23), 126 (17), 128 (22), 129 (31), 131 (48), 186 (13), 187 (18), 260 (5) and 275 (2, M^+).

By sugar analysis[13] of the hydrolysed[1] and reduced ($NaBH_4$) *O*-methyloxime of **2**, allitol and glucitol (73:27) were detected.

The *O*-methyloxime (525 mg) of 1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranos-5-ulose (**3**) had (*a*) m.p. 60–64°, $[\alpha]_{578}^{20}$ 121° (*c* 0.4 ethanol); (*b*) $[\alpha]_{578}^{20}$ 38° (*c* 0.4 ethanol) (*syn,anti* mixture).

Anal. Found: C, 48.7; H, 6.9; N, 5.4.

Mass spectrum of methylated derivative: *inter alia*, *m/e* 85 (100%), 86 (21), 87 (67), 100 (16), 113 (23), 115 (29), 125 (12), 126 (10), 129 (11), 132 (17), 158 (13), 173 (12), 214 (2), 216 (2), 217 (2), 230 (2), 245 (2), and 275 (2, M^+).

By sugar analysis[13] of the hydrolysed[1] and reduced ($NaBH_4$) *O*-methyloxime of **3**, iditol, idosan, and glucitol (27:29:44) were detected.

Oxidation of sucrose (**4**). — Sucrose (3 g) was oxidised, as described above, with bromine (3.2 g) in water (200 ml), and the products were methoximated. The volume was adjusted to 250 ml. To a 10-ml sample was added cyclohexyl α-D-glucopyranoside (5 mg). The mixture was concentrated to dryness, and to a solution of the residue in *N*,*N*-dimethylformamide (2 ml) was added sodium hydride (30 mg), and the mixture was treated in an ultrasonic bath for 30 min. The mixture was cooled (0°) and methyl iodide (2 ml) was added. After treatment in the ultrasonic bath (30 min), water (50 ml) was added and the mixture was extracted with chloroform (50 ml). The extract was washed with water and concentrated, and a portion of the residue was analysed by g.l.c. and g.l.c.–m.s. The remainder was eluted from a column of silica gel 5 (Riedel de Haën, 230–400 mesh) with chloroform–pyridine–ethanol (10:4:1). The fractions were then eluted from columns of silica gel 60 (Merck, 230–400 mesh) with acetonitrile–ethanol–water (10:1:1). The following compounds were obtained.

O-Methyloxime (39 mg) of β-D-fructofuranosyl α-D-*arabino*-hexopyranosidulose (**5**), syrup, $[\alpha]_{578}^{20}$ +37° (*c* 0.8, ethanol).

Calc. for $C_{20}H_{37}NO_{11}$: Mol. wt., 467.237. Found: Mol. wt., 467.235.

Mass spectrum of methylated derivative: *inter alia*, *m/e* 45 (100%), 71 (64), 72 (76), 73 (23), 75 (62), 85 (10), 87 (47), 88 (34), 89 (17), 95 (10), 101 (66), 111 (41), 113 (13), 114 (11), 115 (21), 116 (24), 127 (14), 141 (19), 145 (44), 155 (27), 187 (34), 200 (6), 218 (20), 219 (13), 232 (19), 235 (6), and 467 (1, M^+).

By sugar analysis[13] of the hydrolysed[1], reduced ($NaBH_4$), hydrolysed, and reduced *O*-methyloxime of **5**, glucitol and mannitol (72:28) were detected.

The *O*-methyloxime (62 mg) of β-D-fructofuranosyl α-D-*xylo*-hexopyranosid-4-ulose (**6**), syrup, $[\alpha]_{578}^{20}$ +46° (*c* 0.9, ethanol).

Anal. Found: Mol. wt., 467.233.

Mass spectrum of the methylated derivative: *inter alia*, *m/e* 45 (100%), 71 (37), 72 (41), 73 (14), 75 (61), 84 (16), 87 (26), 88 (17), 89 (24), 101 (40), 111 (35), 116 (14), 117 (13), 127 (11), 141 (12), 145 (19), 155 (15), 187 (43), 200 (21), 218 (13), 219 (21), 232 (5), 235 (3), 422 (0.5), and 467 (0.2, M^+).

By sugar analysis[13] of the hydrolysed[1], reduced ($NaBH_4$), hydrolysed, and reduced *O*-methyloxime of **6**, galactitol, glucitol, and mannitol (13:64:23) were detected.

The *O*-methyloxime (24 mg) of α-D-glucopyranosyl β-D-*erythro*-hexo-2,5-furanosid-2,3-diulose (**7**), syrup, $[\alpha]_{578}^{20}$ +33° (*c* 0.7, ethanol).

Anal. Found: Mol. wt., 467.234.

Mass spectrum of the methylated derivative: *inter alia*, *m/e* 45 (100%), 70 (12),

71 (100), 72 (23), 75 (66), 88 (18), 96 (16), 101 (63), 102 (22), 111 (29), 115 (10), 187 (21), 219 (3), 231 (17), and 232 (22).

By sugar analysis[13] of the hydrolysed[1], reduced ($NaBH_4$), hydrolysed, and reduced *O*-methyloxime of **7**, allitol, glucitol, and mannitol and/or altritol (4:76:20) were detected.

The bis(*O*-methyloxime) (19 mg) of α-D-*arabino*-hexopyranosylulose β-D-*erythro*-hexo-2,5-furanosid-2,3-diulose (**8**), syrup, $[\alpha]_{578}^{20}$ +16° (*c* 0.9 ethanol).

Anal. Calc. for $C_{20}H_{36}N_2O_{11}$: Mol. wt., 480.232. Found: Mol. wt., 480.229.

Mass spectrum of the methylated derivative: *inter alia*, peaks at *m/e* 45 (100%), 71 (58), 72 (13), 73 (13), 75 (47), 96 (12), 101 (29), 102 (11), 130 (11), 140 (11), 200 (9), 231 (10), 232 (37), 233 (4), 277 (1), and 480 (1, M^+).

ACKNOWLEDGMENTS

We thank Docent Kjell Olsson for valuable discussion, Mrs. Maria Elena Riquelme for skilled technical assistance, Mr. Suresh Gohil for recording the mass spectra, and Docent Nigel Marsden for help on linguistics.

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