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Note

Formation of 1,2-*O*-(1,2-ethanediyl)-β-D-mannopyranose in a neighboring-group participation reaction of 2-*O*-(2-hydroxyethyl)-D-mannose

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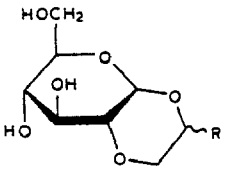
Bicyclic 1,2-*O*-(1-methyl-1,2-ethanediyl)-D-glucose acetals are formed[1,2] during the acid hydrolysis of *O*-(2-hydroxypropyl)cellulose, by an intramolecular reaction between 2-*O*-(2-hydroxypropyl) groups and the anomeric centre of the substituted aldoses liberated. The corresponding 1,2-*O*-(1,2-ethanediyl) acetals have been found[3,4] in hydrolysates of *O*-(2-hydroxyethyl) derivatives of cellulose and starch. Depending on such factors as the strength of the acid catalyst, and the solvent, these acetals may exist as mixtures of pyranose (**1**) and furanose (**2**) forms in equilibrium with the 2-substituted aldose (**3**). The *O*-(2-hydroxypropyl) derivatives (R = CH_3) also form[5,6] diastereoisomeric acetals differing in the configuration of the methyl group on the 1,4-dioxane ring.



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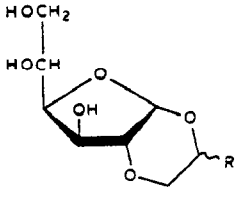

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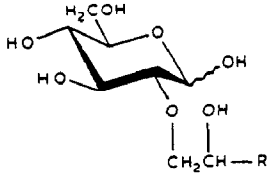

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For comparison with these data on the acetal–aldose equilibria in the D-glucose series, we have now examined the facility of 2-*O*-(2-hydroxyethyl)-D-mannose (**4**), the 2-epimer of **3**, to undergo acid-catalysed formation of cyclic acetals. Evidence that the D-mannose configuration is compatible with 1,2-acetal structures of this kind is available from gas–liquid chromatographic data obtained[7] during a study on *O*-(carboxymethyl) derivatives of guaran, a polymer composed of residues of D-mannose (as well as D-galactose). The analytical approach used, entailed reduction of 2-*O*-(carboxymethyl) substituents to 2-*O*-(2-hydroxyethyl) groups which, during subsequent workup, allowed for the formation[7] of a cyclic acetal of D-mannose. A fuller description of this acetalation reaction is offered here by characteristics observed for derivative **4**.

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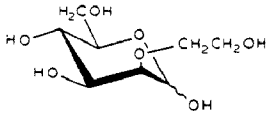
RESULTS AND DISCUSSION

Access to 2-*O*-(2-hydroxyethyl)-D-mannose (**4**) was by hydrolysis of methyl 2-*O*-(2-hydroxyethyl)-α-D-mannopyranoside (**5**), itself prepared by a series of reactions starting with methyl 4,6-*O*-benzylidene-α-D-mannopyranoside (**6**). Selective benzylation[8] of the dibutyltin oxide complex of **6** with benzyl bromide occurred to give the 3-benzyl ether (**7**), which permitted the introduction[9] of a 2-*O*-(2-methoxycarbonylmethyl) substituent (**8**) with methyl bromoacetate and sodium hydride. Reduction of the ester function[9] with lithium aluminum hydride then afforded the 2-*O*-(2-hydroxyethyl) derivative (**9**). The 3-*O*-benzyl and 4,6-*O*-benzylidene substituents of **9** were removed[10] simultaneously, by catalytic-transfer hydrogenolysis[10] with formic acid in the presence of palladium catalyst, giving the required ether-glycoside (**5**).



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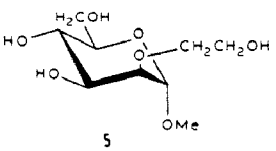

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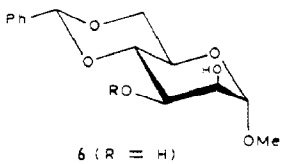
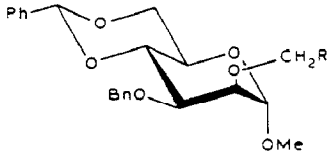
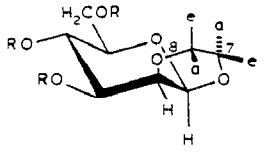


6 (R = H)
7 (R = Bn)

Hydrolysis of **5** with 0.5M sulfuric acid for 18 h at 100° gave, according to the ^{13}C-n.m.r. spectrum of the neutral product (Fig. 1A), a mixture of three compounds consisting of the α and β anomers of 2-*O*-(2-hydroxyethyl)-D-mannose (**4**) and a cyclic acetal (**10**). From the relative intensities of their anomeric ^{13}C resonances, in the region δ 94–97, these products were present in the ratio of 5:2:3, respectively. Designation of the C-1 signal of **10** to the central peak at δ 95.5 was facilitated by introducing sodium borohydride, because it was essentially the only signal remaining in that region following reduction of the anomeric aldoses (see Fig. 1B).



8 R = CO_2Me
9 R = CH_2OH



10 R = H
11 R = $COCH_3$

The mixture of **10** and the alditols was acetylated and fractionated by column chromatography, affording a triacetate of the acetal **11**. According to the ^1H-n.m.r. spectrum of **11** (Fig. 1D), which was analysed with the aid of the COSY version shown in Fig. 1E, the *O*-acetyl groups of **11** are located at positions 3 and 4 (as well as 6) as shown by the strong deshielding of H-3 and H-4. These data are consistent with a 1,2-acetal form of D-mannopyranose. In addition, the spin–spin coupling pattern (Table I) corresponds to that expected for close to a $^4C_1$ conformation of the pyranose ring,

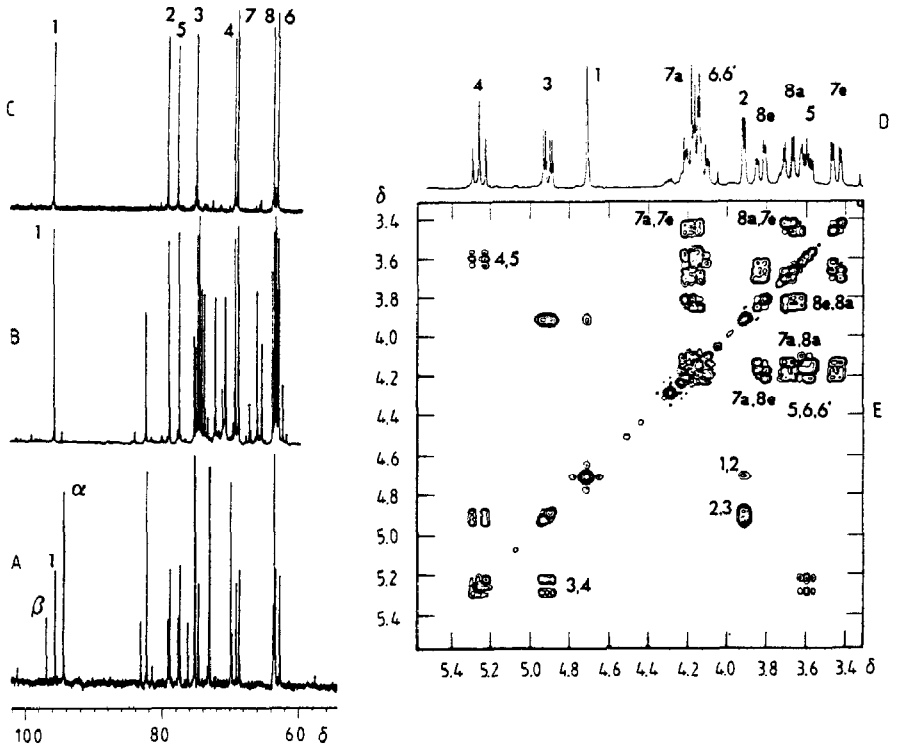


Fig. 1. ^{1}H-Decoupled ^{13}C-n.m.r. spectra (in D_2O) of (A) the hydrolysis products from methyl 2-*O*-(2-hydroxyethyl)-α-D-mannopyranoside (**5**), showing the presence of a mixture of cyclic acetal **10** and 2-*O*-(2-hydroxyethyl)-α- and -β-D-mannose (**4**) (the anomeric ^{13}C signals are designated); (B) the solution obtained following borohydride reduction of the mixture represented by (A); and (C) isolated acetal **10**. Fig. 1D is the ^{1}H-n.m.r. spectrum of **11** (in $CDCl_3$), the 3,4,6-tri-*O*-acetyl derivative of **10**, and Fig. 1E is the corresponding 2-dimensional ^{1}H–^{1}H correlation (COSY) spectrum of **11**; (the H-7*e* and H-8*e* assignments in Fig. 1D are based on the sloping cross-peak responses[21] observable in Fig. 1E).

especially the large values of $J_{3,4}$ and $J_{4,5}$ of ~10 Hz, characteristic for *trans*-diaxial orientations of H-3, -4, and -5. Spin–spin coupling interactions among the methylenic protons of the 1,4-dioxane ring, which are reflected in the cross-peak patterns in Fig. 1E, produce the two large spacings (11–12 Hz, Table I) of the multiplet at δ 3.67. We attribute this signal to H-8*a*, and one of these spacings to vicinal coupling with *antiperiplanar* H-7*a*, because the latter is so atypically[5] deshielded (δ ~4.2) that it is likely to be *synperiplanar* with respect to the C-1–O-1 bond in **11**. Geminal coupling (see Fig. 1E) accounts for the other large spacing, as well as those of the signals at δ 3.83 and 3.45 (Table I). Consequently, the data are in accord with the presence of a *cis*-fused 1,4-dioxane ring in which O-4 is down and O-2 is up, as depicted in formula **11**.

Discounting the possibility of a *trans*-bicyclic structure for **11** is the small value of $J_{1,2}$ (<0.5 Hz), which, although consistent[11,12] with a 1,2-*e*,*a* (*cis*) orientation of H-1 and H-2 in a 1,4-dioxane ring, is an order of magnitude less than that (~8–9 Hz) anticipated for an *antiperiplanar* disposition of the two protons. Also, molecular models suggest

TABLE I

^{1}H- and ^{13}C-N.m.r. data for 1,2-*O*-(1,2-ethanediyl)-*β*-D-mannopyranose (**10**) and its triacetate (**11**)

Proton[a]	*1*	*2*	*3*	*4*	*5*	*6,6′*	*7a*	*8e*	*8a*	*7e*
δ	4.71	3.92	4.91	5.25	3.60	4.1–4.2	4.1–4.2	3.83	3.67	3.45
J(Hz)	<0.5	3.3	10.2	10.2	2.4[b],5.1[b]	--	--	12.0,3.0	11.5,11.5	2.7,11.5
	(1,2)	(2,3)	(3,4)	(4,5)	(5,6)(5,6′)	--	--	(8*e*,8*a*)(8*e*,7*a*)	(8*a*,7*a*)(8*a*,8*e*)	(7*e*,8*a*)(7*e*,7*a*)
Carbon[c]	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*		
δ	95.5	78.8	74.6	69.0[d]	77.3	62.7	68.5[d]	63.3		
δ[e]	95.0	82.6	74.5	68.0	77.5	62.1				
δ[f]	91.8	81.6	71.0	68.3	73.3	62.1				
δ[g]	80.7	71.0	64.4							

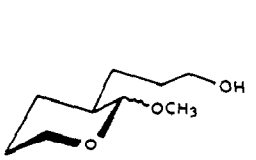
[a] For **11**, in $CDCl_3$. [b] Spacings. [c] For **10**, in D_2O. [d] Assigments may be reversed. [e,f] Data for 2-*O*-methyl-*β*-and -α-D-mannopyranose, respectively (ref. 13). [g] Data for methyl *β*-D-mannofuranoside (ref. 14).

that the *trans* isomer would contain either a non-chair pyranose conformation or a $^1C_4$ conformation in which O-3, O-4, and C-6 would be axially oriented. Not only are these less likely on thermodynamic grounds, but they cannot be accommodated in terms of the ^{1}H–^{1}H coupling patterns described.

^{13}C-Chemical-shift data (Fig. 1C, and Table I) for acetal **10**, examined following the O-deacetylation of **11**, provide additional support for the conclusions based on the ^{1}H-n.m.r. evidence. In particular, a comparison with chemical-shift data[13] for carbons 3–6 for 2-*O*-methyl α- and -β-D-mannopyranose (Table I) suggests a close analogy with ^{13}C shielding characteristics of a β-mannopyranose ring. A furanose acetal structure is also eliminated, because it would be characterized[14] by markedly different chemical shifts, especially that of C-4, which is far less strongly shielding in mannofuranosides than in pyranosides (Table I). It is worth noting that the ^{13}C spectrum of **10** (as well as the ^{1}H spectrum of **11**) clearly show that only *one* cyclic acetal was present as a significant contributor to the acid-catalysed equilibration of aldose **4**.

There is a large difference between this latter equilibrium and that[15] of the epimeric aldose, 2-*O*-(2-hydroxyethyl)-D-glucose (**3** R = H), inasmuch as little or no cyclic acetal is detected following equilibration of **3** with 0.5M sulfuric acid, as well as[3,4,6] in the corresponding hydrolysate of isolated 1,2-(1,2-ethanediyl)-α-D-glucofuranose (**2**, R = H). The pyranose bicyclic (6,6) ring system of the mannose acetal (**10**) also markedly differentiates it from the furanose (5,6) ring structure of the *gluco* diastereoisomer (**2**). In both instances, nevertheless, as the only acetals detected contain a *cis*-fused 1,4-dioxane ring, it is clear that the formation of their *trans* isomers is strongly disfavored.

Related types of bicyclic acetals of tetrahydropyran derivatives occur[16,17] as mixtures of *cis*- and *trans*-isomers. For example, compounds **13** and **14** were found in an equilibrium ratio of 11:9 following the solvolysis of methoxytetrahydropyran **12** in methanol–HCl. This was taken[16] as an indication that the *cis* isomer, in which the anomeric C–O bond is axial, incorporates an anomeric effect[18] of 1.4 kcal/mol. Although the corresponding bond in the D-mannose acetal (**10**) is equatorial and entails no analogous stabilization, the fact that the *trans* isomer was not observed is attributable, presumably, to a geometry that would be inherently unstable, as already suggested.



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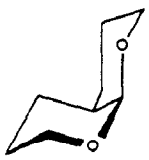

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These findings tend to emphasize the fact that acid-catalysed equilibrations in the D-glucose series yield only *cis* acetals, irrespective of whether the aldose unit is pyranose (**1**) or furanose (**2**). This would require a far larger anomeric effect than found for the tetrahydropyran *cis* acetals, or else the presence of severe destabilizing interactions in

the *trans* isomers of **1** and **2**. There is no apparent reason why either possibility should apply. Among other striking features of these equilibria are wide differences in product ratios associated with the presence (and orientation) of a 1′-methyl group on the 1,4-dioxane ring. For example, 2-*O*-(2-hydroxypropyl)-D-glucose [**3**, R = CH_3, substituent in the (*R*) configuration] was converted[6] in 81% yield into 1,2-*O*-[1-methyl-(*R*)-1,2-ethanediyl]-α-D-glucopyranose (**1**, R = eq. CH_3) and a trace of the corresponding furanose acetal. By contrast, the equilibrated mixture obtained from the (*S*) diasteroisomer of **3** consisted of 65% of the aldose, 24% of the furanose acetal, and only 11% of the pyranose acetal. Although the methyl group of **1** (R = CH_3), being equatorial in the (*R*) isomer and axial in the (*S*) isomer, undoubtedly diminishes the relative stability of the latter, it also appears to account for much higher populations of the pyranose forms than found with the 2-hydroxyethyl analogs. Such diverse characteristics suggest that the bicyclic acetals of aldoses of the class considered here, incorporate stabilizing or destabilizing factors, some large in magnitude, that have yet to be recognized.

Whether or not hydrolysates of *O*-(2-hydroxypropyl) guaran[19,20] are analogous to those of the cellulose derivative, and contain bicyclic acetals of D-mannose, corresponding to **10**, remains to be determined.

EXPERIMENTAL

General methods. — N.m.r. spectra (^1H and ^{13}C) were recorded at room temperature with Varian XL-200 and XL-300 spectrometers, with the latter being used to acquire the COSY spectra[21]; ^1H chemical shifts (δ) are reported for solutions in $CDCl_3$ or acetone-d_6 with reference to Me_4Si, and those for ^{13}C with reference to internal acetone (δ 28.9). Optical rotations were determined at room temperature with a Jasco-DIP 140 digital polarimeter. Mass spectrometry was performed by the Biomedical Mass Spectrometry Unit, using a ZAB-HS instrument and a glycerol matrix for the f.a.b mode. Silica gel 60 (Merck, 230–400 mesh) was used for column chromatography, and silica gel sheets (Merck) were used for t.l.c.

Methyl 4,6-O-benzylidene-3-O-benzyl-α-D-mannopyranoside (**7**). — A solution of methyl 4,6-*O*-benzylidene-α-D-mannopyranoside[22] (0.2 g, 0.7 mmol) and dibutyltin oxide (0.18 g, 0.7 mmol) in MeOH (25 mL) was refluxed (60°) for 1 h. The solvent was removed under diminished pressure and the residue was dissolved in *N*,*N*-dimethylformamide (5 mL). Benzyl bromide (0.143 mL, 1.2 mmol) was added and the solution was heated to 100°. After 25 min. t.l.c. indicated the presence of only one product (R_F 0.67, 3:2 EtOAc–hexane), which was purified by chromatography to give 0.22 g (84%) of a colourless syrup; ^1H-n.m.r. data (acetone-d_6): δ 7.68–7.27 (m, 10 H, 2 C_6H_5), 5.7 (s, 1 H, H-C-Ph), 4.76 (s, 2 H, CH_2-Ph), 4.71 (d, $J_{1,2}$ 1.3 Hz, H-1), 4.08 (dd, $J_{2,3}$ 3.3 Hz, H-2), 3.79 (dd, $J_{3,4}$ 9.4 Hz, H-3), and 3.36 (s, 3 H, OCH_3).

Methyl-4,6-O-benzylidene-3-O-benzyl-2-O-(methoxycarbonylmethyl)-α-D-mannopyranoside (**8**). — To a solution of **7** (0.28 g, 0.75 mmol) in dry THF (10 mL) were added NaH (0.181 g, 7.52 mmol), imidazole (10 mg), and Bu_4NBr (10 mg). The mixture

was refluxed for 0.5 h. Methyl bromoacetate (0.71 mL, 7.5 mmol) was then added and the solution was refluxed overnight. T.l.c. indicated the presence of only one product (R_F 0.50 (7:3 hexane–EtOAc) as compared to 0.38 for the starting compound. To the cooled mixture, MeOH (2 mL) was added dropwise followed by dilute aq. HCl (0.12% v/v), and the solution was then extracted with CH_2Cl_2 (2 × 25 mL). The organic layer was washed consecutively with dilute solutions of $NaHCO_3$ and brine, dried over $MgSO_4$, and concentrated. The residue was purified by chromatography (5.7:1 hexane–EtOAc) to give 0.19 g (57%) of **8** (ref. 8); ^{1}H-n.m.r. data (acetone-d_6): δ 7.60–7.25 (m, 10 H, 2 C_6H_5), 5.73 (s, 1 H, CH-Ph), 4.98 (d, $J_{1,2}$ 1.6 Hz, H-1), 4.85, 4.75 (2 d, AB, 2 H, O-CH_2-Ph, J 11.7 Hz), 4.44, 4.40 (2 d, AB, 2H, OCH_2CO, J 16 Hz), 3.92 (dd, $J_{2,3}$ 2.9 Hz, H-2), 3.86 (dd, $J_{3,4}$ 9.8 Hz, H-3), 3.69 (s, 3 H, CO_2CH_3), and 3.38 (s, 3 H, OCH_3).

*Methyl 4,6-O-benzylidene-3-O-benzyl-2-O-(2-hydroxyethyl)-α-*D*-mannopyranoside* (**9**). — Compound **8** (0.110 g, 0.25 mmol) was dissolved in tetrahydrofuran (20 mL) and treated with $LiAlH_4$ (0.04 g, 1.1 mmol). After refluxing the mixture for 18 h, t.l.c. indicated that a more-polar compound (R_F 0.11 vs R_F 0.54 for **7**; 2:3 EtOAc–hexane) had been formed exclusively. Excess $LiAlH_4$ was decomposed with EtOAc (3 mL), 20% NaOH (4 mL), and water (7 mL) were introduced, and the aq. layer was extracted with two portions of ether (10 mL). The combined ether extract was washed with brine, dried over $MgSO_4$ and evaporated to dryness. The residue was purified by flash chromatography, affording 0.074 g (71%) of **9** as a colourless syrup; ^{1}H-n.m.r. data (acetone-d_6): δ 7.58–7.27 (m, 10 H, 2 C_6H_5), 5.7 (s, 1 H, H-C-Ph), 4.82, 4.73 (2 d, AB, 2 H, O-CH-Ph), 4.78 (s, H-1), 3.87 (dd, H-2), and 3.55 (s, 3 H, OCH_3).

*Methyl 2-O-(2-hydroxyethyl)-α-*D*-mannopyranoside* (**5**). — A mixture of 10% palladium-on-charcoal (1.8 g) in MeOH (25 mL) containing 10% v/v HCO_2H was stirred under N_2 for 5 min. To this was added **9** (0.32 g, 0.78 mmol) in MeOH (25 mL) containing 10% v/v HCO_2H. After 14 h t.l.c. indicated that the reaction was complete, the catalyst was filtered off, and successively washed with MeOH and water. The filtrate was concentrated to give 0.15 g (79%) of **5** as a syrup; $[\alpha]_D^{25}$ +17.5° (*c* 2.1, H_2O); ^{1}H-n.m.r. data δ (D_2O): 4.76 (d, $J_{1,2}$ 1.4 Hz, H-1), and 3.26 (s, 3 H, OCH_3); f.a.b.-mass spectrum (glycerol): *m/z* 261.095 [(M($C_9H_{18}O_7$) + Na]$^+$, 100%).

*Acid hydrolysis of methyl 2-O-(2-hydroxyethyl)-α-*D*-mannopyranoside.* — Compound **5** (0.075 g, 0.32 mmol), dissolved in 0.5M H_2SO_4 (10 mL), was heated for 18 h at 95°. The solution was made neutral with Dowex 1X8 (HCO_3-form) ion-exchange resin, the resin was filtered off and the solvent removed under diminished pressure. ^{13}C-N.m.r. spectroscopy indicated the presence of three products, in a ratio of 5:2:3, corresponding to **4α**, **4β**, and **10**, respectively; ^{13}C-n.m.r. data (D_2O): δ 96.8 (C-1, **4β**), 95.5 (C-1, **10**) and 94.2 (C-1, **4α**) (see Fig. 1A).

*Reduction of a mixture containing 1,2-O-(1,2-ethanediyl)-β-*D*-mannopyranose* (**10**) *and 2-O-(2-hydroxyethyl)-α,β-*D*-mannopyranose* (**4**) *with sodium borohydride.* — To an aqueous solution of **10**, **4α**, and **4β** (0.03 g in 5 mL) was added $NaBH_4$ (0.02 g) at room temperature; t.l.c. (9:4:2 EtOAc–2-propanol–water) indicated the disappearance of the lower-R_F components corresponding to the aldoses. The solution was then treated with Amberlite IR-120 (H^+) ion-exchange resin, the filtrate was concentrated,

and the residue was repeatedly dissolved in MeOH (20 mL) which was evaporated; ^{13}C-n.m.r. data (D_2O): δ 95.5 (C-1 of **10**) (see Fig. 1B).

*1,2-O-(1,2-Ethanediyl)-3,4,5-tri-O-acetyl-β-*D*-mannopyranose* (**11**). — The reduced mixture was treated with pyridine (1.0 mL) and Ac_2O (1.5 mL) for 4 h with stirring; t.l.c. (3:2 EtOAc–hexane) showed the presence of a component (R_F 0.40) which, when isolated by column chromatography, was shown by ^{1}H-n.m.r. spectroscopy (300 MHz, see Figs. 1D and 1E and Table I) to be a relatively pure specimen of the desired product.

*1,2-O-(1,2-ethanediyl)-β-*D*-mannopyranose* (**10**). — Compound **11** was dissolved in anhydrous MeOH (1.0 mL) and treated with 0.5N NaOMe (100 μL) for 4 h at room temperature. Amberlite IR-120 (H^+) ion-exchange resin (250 mg) and water (1.0 mL) were added to the mixture, which was then filtered and concentrated; $[\alpha]_D^{25}$ +12.7° (*c* 0.55, D_2O) ^{13}C-n.m.r. data (75.4 MHz) are presented in Fig. 1C, which verifies the relatively high purity of **10**, and in Table I. F.a.b.-mass spectrum (glycerol): *m/z* 229.0689 [$M(C_8H_{14}O_6)$ + Na]$^+$, 22%.

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