Carbohydrate Research, 182 (1988) 53–62
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

SYNTHESIS AND MASS SPECTRA OF 4-*O*-ACETYL-1,5-ANHYDRO-2,3,6-TRI-*O*-ETHYL-D-GLUCITOL AND THE POSITIONAL ISOMERS OF 4-*O*-ACETYL-1,5-ANHYDRO-DI-*O*-ETHYL-*O*-METHYL-D-GLUCITOL AND 4-*O*-ACETYL-1,5-ANHYDRO-*O*-ETHYL-DI-*O*-METHYL-D-GLUCITOL*

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(Received September 2nd, 1987; accepted for publication in revised form, March 16th, 1988)

ABSTRACT

Reductive cleavage of fully methylated, partially *O*-ethylated cellulose or fully ethylated, partially *O*-methylated cellulose and subsequent acetylation had previously been shown to produce 4-*O*-acetyl-1,5-anhydro-2,3,6-tri-*O*-methyl-, -6-*O*-ethyl-2,3-di-*O*-methyl-, -3-*O*-ethyl-2,6-di-*O*-methyl-, -2-*O*-ethyl-3,6-di-*O*-methyl-, -2,3-di-*O*-ethyl-6-*O*-methyl-, -2,6-di-*O*-ethyl-3-*O*-methyl-, -3,6-di-*O*-ethyl-2-*O*-methyl-, and -2,3,6-tri-*O*-ethyl-D-glucitol. Described herein is the independent synthesis of these derivatives, except for the first (which had been reported); and their ^{1}H-n.m.r. spectra, chemical-ionization (NH_3) mass spectra, and electron-impact mass spectra are tabulated.

INTRODUCTION

In a previous report[1], the applicability of the Reductive Cleavage Method[2] for establishing the positions of substitution of methoxy or ethoxy groups in partially-methylated or -ethylated cellulose was demonstrated. The strategy employed in these analyses was to ethylate *O*-methylcellulose fully and methylate *O*-ethylcellulose fully, and then to carry out reductive cleavage and acetylation in the usual way[3]. Subsequent g.l.c. analysis was expected to reveal the presence of only eight products (**1**–**8**) and, indeed, all eight were observed when commercial samples of *O*-methylcellulose and *O*-ethylcellulose were analyzed. The identities of these components were established by comparison to independently synthesized standards by g.l.c. retention-time and by their electron impact (e.i.) and chemical ionization (c.i.) mass spectra. Compound **1** was available from previous work[4]; consequently, reported herein is the synthesis of compounds **2**–**8**. Also reported herein are e.i.- and c.i.-mass-spectral data for compounds **2**–**8**, as an aid to those who may wish to use this method.

*This investigation was supported by Grant GM34710 awarded by the Department of Health and Human Services.
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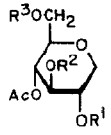


	R^1	R^2	R^3
1	Me	Me	Me
2	Me	Me	Et
3	Me	Et	Me
4	Et	Me	Me
5	Et	Et	Me
6	Et	Me	Et
7	Me	Et	Et
8	Et	Et	Et

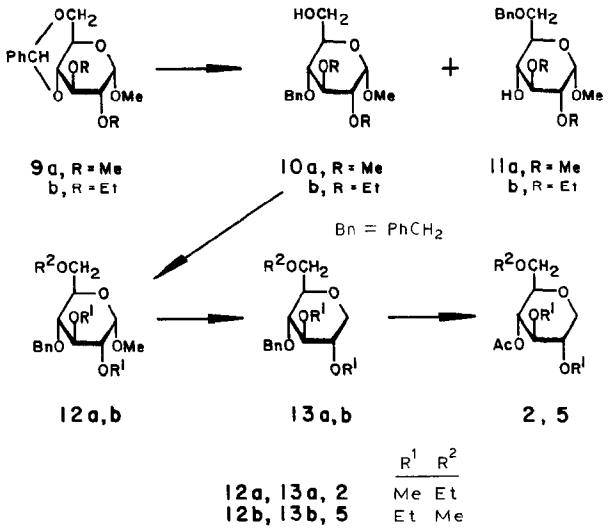
RESULTS AND DISCUSSION

Synthesis. — The various manipulations employed in the syntheses were standard, and therefore the intermediates were usually not isolated and fully characterized. The product of each reaction was, however, checked by ^{1}H-n.m.r. spectroscopy, to ensure completion of protection or deprotection.

4-*O*-Acetyl-1,5-anhydro-6-*O*-ethyl-2,3-di-*O*-methyl-D-glucitol (**2**) and 4-*O*-acetyl-1,5-anhydro-2,3-di-*O*-ethyl-6-*O*-methyl-D-glucitol (**5**) were prepared as shown in Scheme 1. Methylation[5] of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside gave **9a**, which was subsequently treated with a mixture of lithium aluminum hydride and aluminum chloride as described by Liptak *et al.*[6], to yield **10a** and its corresponding 6-*O*-benzyl regioisomer (**11a**) in the ratio of 7:3. Chromatography of this mixture on silica gel afforded pure **10a** and **11a**, which were distinguished by the ^{1}H-n.m.r. spectra of their acetates. The H-6 and H-6′ resonances of acetylated **10a** were observed at δ 4.25 as an apparent doublet (*J* 3.4 Hz), whereas the H-4 resonance of acetylated **11a** was observed at δ 4.95 as an apparent triplet (*J* 9.4 Hz). The conversion of **10a** into **2** was accomplished by sequential ethylation to produce **12a**, reductive cleavage[3] thereof to give **13a**, catalytic hydrogenolysis, and acetylation.

Compound **5** was produced by the same sequence of reactions shown in Scheme 1, with the exceptions that **9b** was formed by ethylation of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside, and **12b** was produced by methylation of **10b**. Reductive opening of the benzylidene acetal of **9b** was found to give a greater proportion (90%) of the favored regioisomer (**10b**) than was observed when **9a** was used as the starting material.

The synthesis of compounds **3, 4, 6**, and **7** was accomplished as outlined in Scheme 2. The strategy employed in these syntheses was the same as that for the synthesis of compounds **2** and **5** (see Scheme 1), in that reductive opening of a 4,6-*O*-benzylidene protecting group was used to derive a 4-*O*-benzyl protecting group. The strategy employed for synthesizing compounds **3, 4, 6**, and **7** differed, however, from that used in the synthesis of compounds **2** and **5**, in that it allowed independent alkylation of each of the 2-, 3-, and 6-hydroxyl groups. The syntheses therefore differed only in the sequence of methylation and ethylation reactions. The synthesis of 4-*O*-acetyl-1,5-anhydro-2-*O*-ethyl-3,6-di-*O*-methyl-D-glucitol (**4**) is



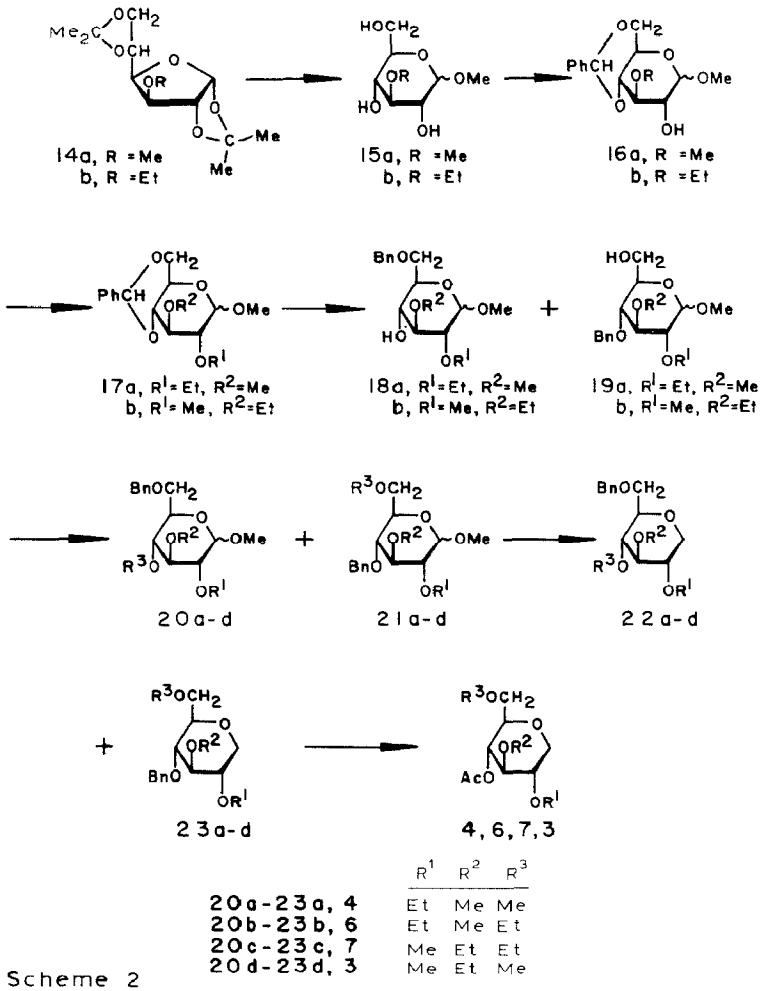
Scheme 1

representative. 1,2:5,6-Di-*O*-isopropylidene-3-*O*-methyl-α-D-glucofuranose (**14a**) was converted into **16a** by standard procedures. Ethylation[5] of **16a** afforded **17a**, which, upon treatment[6] with lithium aluminum hydride and aluminum chloride, gave the anomeric 6-*O*-benzyl (**18a**) and 4-*O*-benzyl (**19a**) regioisomers in the ratio of 3:7. The mixture of **18a** and **19a** was not separated, but was methylated[5], to yield a mixture of **20a** and **21a**. Reductive cleavage[3] of the mixture of **20a** and **21a** afforded a 3:7 mixture of **22a** and **23a** that was readily resolved by chromatography on silica gel. Debenzylation of **23a**, and acetylation of the product, afforded **4**.

The regiochemistry that was observed for reductive opening of the benzylidene acetal of **17a,b** was the same as was observed for **9a,b** (see Scheme 1); *i.e.*, the 4-*O*-benzyl and 6-*O*-benzyl regioisomers were produced in the ratio of 7:3 if a methoxy group was present at C-3, but in the ratio of 9:1 if an ethoxy group was present thereat. Due to the fact that each of the regioisomers was present as an anomeric mixture of glycosides, which made separation difficult, the syntheses were continued with the mixture (**18a** + **19a**, or **18b** + **19b**) of regioisomers until after reductive cleavage of the aglycon. In all cases, separation of regioisomers **22** and **23** was readily accomplished by chromatography on silica gel, and the 4-*O*-benzyl regioisomers (**23**) were selected for deprotection and acetylation.

Synthesis of the remaining 4-*O*-acetyl-1,5-anhydro-D-glucitol derivative (**8**) was accomplished from cyclomaltoheptaose by successive ethylation[5], reductive cleavage[3], and acetylation.

^{1}H-N.m.r. spectra. — The ^{1}H-n.m.r. spectra of compounds **2–8** were compared to the previously reported[4] spectrum of **1**. All spectra displayed the expected triplet (*J* 9.2 Hz) for H-4 at δ 4.8, which is characteristic[4,7,8] for 4-*O*-acetyl-1,5-



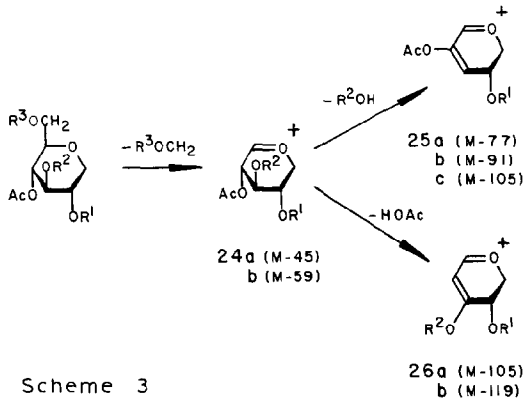
Scheme 2

anhydro-D-glucitol derivatives. Interestingly, the H-4 triplet was broadened in the spectra of derivatives (**2, 6–8**) that contained an ethoxy group at C-6, and this broadening may arise as a consequence of rotational preferences of the exocyclic ethoxymethyl group. All spectra also displayed the expected doublet of doublets (J 5 and 11 Hz) for H-1*e*, and this resonance was downfield (δ 4.105 ±0.010 p.p.m.) in the spectra of 2-*O*-methyl derivatives (**1–3**, and **7**) as compared to 2-*O*-ethyl derivatives (**4–6**, and **8**), where it was observed at δ 4.060 ±0.006 p.p.m. The chemical shift of the *O*-acetyl resonance was likewise found to depend upon the vicinal (O-3) substituent; *i.e.*, in 3-*O*-methyl derivatives (**1, 2, 4,** and **6**), the acetyl resonance was observed at δ 2.105 ±0.002 p.p.m., whereas, in 3-*O*-ethyl derivatives (**3, 5, 7,** and **8**), the acetyl resonance was observed slightly upfield at δ 2.091 ±0.005 p.p.m.

Analysis of the chemical shifts of the *O*-methyl resonances and the *C*-methyl resonances of the *O*-ethyl groups also revealed a pattern consistent with their positions of substitution. The 2-*O*-, 3-*O*-, and 6-*O*-methyl resonances were observed at δ 3.48, 3.54, and 3.35, respectively, and the chemical shifts of these resonances were independent of other substituents in the positional isomers. The *C*-methyl resonances of the *O*-ethyl groups were not quite as characteristic, however. The *C*-methyl resonances of 2-*O*-ethyl and 6-*O*-ethyl groups were consistently observed together, at δ 1.19, whereas the *C*-methyl resonances of 3-*O*-ethyl groups were observed slightly upfield, at δ 1.16.

The spectra of these derivatives are therefore fully in accord with the expected positions of substitution of all acetyl, methyl, and ethyl groups.

Mass spectra. — Some preliminary conclusions can be drawn that permit a distinction to be made among positional isomers. One of the major fragmentation pathways (see Scheme 3) for these derivatives begins with loss[9] of the exocyclic methoxymethyl group (M − 45) or ethoxymethyl group (M − 59), to give fragment ions **24a** or **24b**, respectively. The further elimination of methanol or ethanol from the (M − 45) ion (**24a**) gives rise to fragment ions **25a** (M − 77) and **25b** (M − 91), respectively, whereas the elimination of methanol or ethanol from the (M − 59) ion (**24b**) gives rise to fragment ions **25b** (M − 91) and **25c** (M − 105), respectively. A fragment ion (**26a**) at (M − 105) is also formed by elimination of acetic acid from the (M − 45) ion (**24a**), but elimination of acetic acid from the (M − 59) ion (**24b**) gives a fragment ion at (M − 119).



Scheme 3

It was anticipated that the further elimination of methanol or ethanol, as appropriate, from fragment ions **25a–c** would give rise to an ion at *m/z* 139; however, this ion was not observed in the mass spectrum of any of the positional isomers (**1–8**). Similarly, elimination of methanol or ethanol from fragment ion **26** would give rise to ions at *m/z* 111 (R^1 = Me) or *m/z* 125 (R^2 = Et). The latter ions were observed in low intensity in the mass spectra of compounds **1–8**, but they appeared to arise *via* fragmentation pathways either in addition to, or instead of, the one depicted in Scheme 3.

There was excellent correlation, however, between the presence or absence of fragment ions at (M − 45), (M − 59), (M − 77), (M − 91), and (M − 105) and the positions of substitution of *O*-methyl and *O*-ethyl groups (see Table I). For example, the (M − 45) fragment ion (**24a**) was present only in the mass spectra of 6-*O*-methyl derivatives, whereas the (M − 59) fragment ion (**24b**) was present only in the mass spectra of 6-*O*-ethyl derivatives. The further elimination of methanol or ethanol from fragment ions **24a,b** also displayed complete regiospecificity, *i.e.*, loss of the alkoxy group from C-3. The (M − 77) fragment-ion was therefore only observed in the spectra of derivatives (**1** and **4**) that contained methoxy groups at both C-3 and C-6. Similarly, the (M − 91) fragment ion was observed in the spectra of derivatives (**2** and **6**) that contained 3-methoxy and 6-ethoxy groups as well as derivatives (**3** and **5**) that contained 3-ethoxy and 6-methoxy groups. The (M − 105) fragment ion (**26a**), which arises by elimination of acetic acid from the (M − 45) fragment ion (**24a**), was present in the mass spectra of all 6-*O*-methyl derivatives (**1, 3, 4,** and **5**), as expected. The (M − 105) fragment-ion (**25c**) was also present in the mass spectra of both 3,6-di-*O*-ethyl derivatives (**7** and **8**) as a consequence of elimination of ethanol from the (M − 59) fragment-ion **24b**.

It should be pointed out that, because loss of the exocyclic methoxymethyl group or ethoxymethyl group (see Scheme 3) is a major fragmentation-pathway, compounds differing *only* in substitution at O-6 will give exactly the same series of fragment ions. For example, loss of the exocyclic methoxymethyl group of **1** gives an (M − 45) ion at *m/z* 203, whereas loss of the exocyclic ethoxymethyl group of **2** gives an (M − 59) ion at the same *m/z* value (203). Subsequent fragment-ions arising from the *m/z*-203 ion will obviously be identical. Identical results are obtained for the three other such pairs of compounds, namely, **4** and **6, 3** and **7**, and **5** and **8**. The mass spectra of the members of these pairs differ, however, in other ways, that allow a distinction to be made. Of particular significance, the *m/z* 45 ion ($MeOCH_2^+$) is always greater in intensity than the *m/z*-59 ion ($EtOCH_2^+$) in 6-*O*-methyl derivatives whereas the *m/z*-59 ion is greater in intensity than the *m/z*-45 ion in 6-*O*-ethyl derivatives. The members of these pairs are also readily distinguished by c.i.m.s., because, within each pair, each compound has a different molecular weight.

TABLE I

SELECTED FRAGMENTS OBSERVED IN THE ELECTRON-IMPACT MASS SPECTRA OF COMPOUNDS **1–8**

Compound	*Mol. wt.*	*(M − 45)*	*(M − 59)*	*(M − 77)*	*(M − 91)*	*(M − 105)*
1[a]	248	+	−	+	−	+
2	262	−	+	−	+	−
3	262	+	−	−	+	+
4	262	+	−	+	−	+
5	276	+	−	−	+	+
6	276	−	+	−	+	−
7	276	−	+	−	−	+
8	290	−	+	−	−	+

[a]Data from ref. 4.

EXPERIMENTAL

General. — Methylations and ethylations were conducted by a modification[5] of the Hakomori[10] procedure. Benzylidenations were performed as described by Evans[11]. Reductive cleavages were achieved with triethylsilane as the reducing agent and a mixture of trimethylsilyl methanesulfonate and boron trifluoride etherate as the catalyst, as previously described[3]. 1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranose and methyl 4,6-*O*-benzylidene-α-D-glucopyranoside were obtained from Pfanstiehl and Aldrich, respectively. Elemental analyses were performed by M-H-W Laboratories, Inc., Phoenix, Arizona, on samples purified by m.p.l.c. on a column (0.8 × 25 cm) of silica gel in 2:1 (v/v) hexane–ethyl acetate.

^{1}H-N.m.r. spectra were recorded with an IBM NR-200 AF n.m.r. spectrometer for solutions in $CDCl_3$, and were referenced to internal tetramethylsilane ($CHCl_3$ resonance at δ 7.262). G.l.c.-m.s. analyses were performed by using either a Finnigan 4000 mass spectrometer equipped with a VG Multispec data system or a VG Analytical Ltd Model VG 7070E-HF high-resolution, double-focusing mass spectrometer. Medium pressure liquid chromatography (m.p.l.c.) was carried out in an instrument consisting of a Rheodyne 7125 injector, Eldex model B-100-S4 pump, Scientific Systems model LP-21 pulse dampener, and Waters Associates differential refractometer. Chromatography was conducted on 40A silica gel (35–70 mesh) from Merck.

4-O-Acetyl-1,5-anhydro-6-O-ethyl-2,3-di-O-methyl-D-glucitol (**2**). — Methylation[5] of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside gave **9a** in 82% yield. Treatment of **9a** with a mixture of 5 equiv. of $LiAlH_4$ and 5 equiv. of $AlCl_3$ as described by Liptak *et al.*[6], afforded a 7:3 mixture of **10a** and **11a**, respectively, in 83% yield. Chromatography (m.p.l.c.) of the mixture of **10a** and **11a** on a column (2.1 × 30 cm) of silica gel and elution with hexane:ethyl acetate (2:1, v/v) afforded pure **10a** in 58% yield from **9a**. Ethylation[5] of **10a** gave **12a** (61%), which was converted to **13a** (78%) by reductive cleavage[3] in the presence of 5 equiv. each of triethylsilane and trimethylsilyl methanesulfonate and 1 equiv. of boron trifluoride etherate. Debenzylation of **13a** in EtOH with H_2 at 101 kPa in the presence of Pd for 18 h, and acetylation of the product, yielded **2** as an oil; ^{1}H-n.m.r.: δ 1.196 (t, 3 H, *J* 7.0 Hz, 6-*O*-ethyl CH_3), 2.103 (s, 3 H, AcO), 3.480 (s, 3 H, MeO-2), 3.530 (s, 3 H, MeO-3), 3.08–3.49 (complex, 8 H, H-1*a*,2,3,5,6,6′, ethyl CH_2), 4.11 (dd, 1 H, *J* 4.7, 10.9 Hz, H-1*e*), and 4.82 (broadened t, 1 H, *J* 9.3 Hz, H-4); g.l.c.–c.i.m.s. (NH_3, positive): *m/z* 263 (100) and 280 (48); g.l.c.–e.i.m.s.: *m/z* 43 (100), 45 (14), 58 (42), 59 (25), 97 (39), 101 (10), 111 (6), 129 (11), 143 (13), 171 (12), and 203 (7).

Anal. Calc. for $C_{12}H_{22}O_6$: C, 54.95; H, 8.45. Found: C, 54.90; H, 8.45.

4-O-Acetyl-1,5-anhydro-3-O-ethyl-2,6-di-O-methyl-D-glucitol (**3**). — Ethylation[5] of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose, and hydrolysis with 50% acetic acid for 24 h at reflux gave 3-*O*-ethyl-D-glucose, which was converted into the anomeric methyl 3-*O*-ethyl-α,β-D-glucopyranosides (**15b**) by refluxing for 24 h

with M HCl in methanol. Successive benzylidenation[11] and methylation[5] of **15b**, and reduction ($LiAlH_4$–$AlCl_3$)[6] of the product gave a mixture of the 6-*O*-benzyl (**18b**) and 4-*O*-benzyl (**19b**) regioisomers in 78% yield. The **18b, 19b** mixture was subjected to methylation[5] and reductive cleavage[3], to yield **22d** and **23d** in the ratio of 1:9 (69% yield). Chromatography (m.p.l.c.) of the mixture of **22d** and **23d** on a column (0.8 × 25 cm) of silica gel, and elution with 1:1 (v/v) hexane–ethyl acetate afforded pure **23d**. Debenzylation (H_2, Pd) of **23d**, and acetylation of the product, gave **3** as an oil; ^{1}H-n.m.r.: δ 1.159 (t, 3 H, *J* 7.0 Hz, 3-*O*-ethyl CH_3), 2.095 (s, 3 H, AcO), 3.352 (s, 3 H, MeO-6), 3.482 (s, 3 H, MeO-2), 3.07–3.84 (complex, 8 H, H-1*a*,2,3,5,6,6′, ethyl CH_2), 4.10 (dd, 1 H, *J* 4.3, 10.9 Hz, H-1*e*), and 4.797 (t, 1 H, *J* 9.2 Hz, H-4); g.l.c.–c.i.m.s. (NH_3, positive): *m/z* 263 (100) and 280 (58); g.l.c.–e.i.m.s.: *m/z* 43 (100), 45 (84), 57 (20), 58 (77), 59 (56), 60 (13), 69 (25), 71 (20), 74 (15), 85 (15), 87 (40), 88 (26), 89 (29), 97 (38), 99 (20), 111 (7), 117 (25), 125 (4), 129 (20), 143 (5), 157 (26), 171 (13), and 217 (5).

Anal. Calc. for $C_{12}H_{22}O_6$: C, 54.95; H, 8.45. Found: C. 55.25; H, 8.47.

*4-O-Acetyl-1,5-anhydro-2-O-ethyl-3,6-di-O-methyl-*D*-glucitol* (**4**). — Methylation[5] of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose and hydrolysis with 50% acetic acid for 24 h at reflux gave 3-*O*-methyl-D-glucose, which was converted into a mixture of **18a** and **19a** (80% yield) as described for **3**, except that ethylation was performed. The mixture of **18a** and **19a** was subjected to methylation[5] and reductive cleavage[3], to yield **22a** and **23a** in the ratio of 3:7 (78% yield). Chromatography (m.p.l.c.) of the mixture of **22a** and **23a** on silica gel as described previously for the synthesis of **3** afforded pure **23a**. Debenzylation of **23a** as already described, and acetylation of the product gave **4** as an oil; ^{1}H-n.m.r.: δ 1.198 (t, 3 H, *J* 7.0 Hz, 2-*O*-ethyl CH_3), 2.106 (s, 3 H, AcO), 3.354 (s, 3 H, MeO-6), 3.542 (s, 3 H, MeO-3), 3.11–3.71 (complex, 8 H, H-1*a*,2,3,5,6,6′, ethyl CH_2), 4.066 (dd, 1 H, *J* 5.1, 11.1 Hz, H-1*e*), and 4.798 (t, 1 H, *J* 9.0 Hz, H-4); g.l.c.–c.i.m.s. (NH_3, positive): *m/z* 263 (100) and 280 (55); g.l.c.–e.i.m.s.: *m/z* 43 (100), 44 (16), 45 (56), 59 (9), 71 (11), 74 (11), 114 (4), 125 (4), 143 (3), 157 (3), 185 (3), and 217 (2).

Anal. Calc. for $C_{12}H_{22}O_6$: C, 54.95; H, 8.45. Found: C, 55.03; H, 8.58.

*4-O-Acetyl-1,5-anhydro-2,3-di-O-ethyl-6-O-methyl-*D*-glucitol* (**5**). — Compound **5** was prepared as described for **2**, with the following exceptions. Ethylation[5] of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside gave **9b**, which was converted into a 9:1 mixture of **10b** and **11b**. Separation of this mixture was accomplished as described for the mixture of **10a** and **11a**, and the pure **10b** was then methylated to give **12b**; for **5**: ^{1}H-n.m.r.: δ 1.155 (t, 3 H, *J* 6.9 Hz, 3-*O*-ethyl CH_3), 1.189 (t, 3 H, *J* 6.6 Hz, 2-*O*-ethyl CH_3), 2.096 (s, 3 H, AcO), 3.354 (s, 3 H, MeO-6), 3.09–3.80 (complex, 10 H, H-1*a*,2,3,5,6,6′, and two ethyl CH_2), 4.058 (dd, 1 H, *J* 4.6, 10.9 Hz, H-1*e*), and 4.789 (t, 1 H, *J* 9.0 Hz, H-4); g.l.c.–c.i.m.s. (NH_3, positive): *m/z* 277 (100) and 294 (72); g.l.c.–e.i.m.s.: *m/z* 43 (100), 44 (20), 45 (42), 57 (11), 59 (14), 60 (11), 69 (13), 72 (33), 73 (22), 87 (10), 88 (12), 97 (15), 99 (10), 117 (10), 125 (6), 143 (11), 159 (5), 171 (12), 185 (6), 203 (2), and 231 (3).

Anal. Calc. for $C_{13}H_{24}O_6$: C, 56.51; H, 8.75. Found: C, 56.61; H, 8.61.

4-O-Acetyl-1,5-anhydro-2,6-di-O-ethyl-3-O-methyl-D-glucitol (**6**). — Compound **6** was prepared as described for compound **4**, with the exception that the mixture of **18a** and **19a** was ethylated[5] to yield a mixture of **20b** and **21b**. Reductive cleavage[3] of the **20b** + **21b** mixture yielded **22b** plus **23b** in the ratio of 3:7 (68% yield); for **6**: ^{1}H-n.m.r.: δ 1.197 (t, 6 H, J 7.0 Hz, 2- and 6-*O*-ethyl CH_3), 2.103 (s, 3 H, AcO), 3.543 (s, 3 H, MeO-3), 3.12–3.65 (complex, 10 H, H-1*a*,2,3,5,6,6′, two ethyl CH_2), 4.064 (dd, 1 H, J 5.1, 11.1 Hz, H-1*e*), and 4.809 (broadened t, 1 H, J 9.3 Hz, H-4); g.l.c.–c.i.m.s. (NH_3, positive): *m/z* 277 (100) and 294 (31); g.l.c.–e.i.m.s.: *m/z* 43 (100), 44 (17), 45 (18), 59 (21), 69 (16), 72 (36), 73 (22), 75 (17), 85 (13), 88 (10), 99 (26), 143 (16), 157 (8), 185 (6), and 217 (5).

Anal. Calc. for $C_{13}H_{24}O_6$: C, 56.51; H, 8.75. Found: C, 56.40; H, 8.60.

4-O-Acetyl-1,5-anhydro-3,6-di-O-ethyl-2-O-methyl-D-glucitol (**7**). — Compound **7** was prepared as described for compound **3**, with the exception that the mixture of **18b** and **19b** was ethylated[5], to yield a mixture of **20c** and **21c**. Reductive cleavage[3] of the **20c** + **21c** mixture yielded **22c** and **23c** in the ratio of 1:9 (85% yield); for **7**: ^{1}H-n.m.r.: δ 1.153 (t, 3 H, J 6.9 Hz, 3-*O*-ethyl CH_3), 1.187 (t, 3 H, J 7.0 Hz, 6-*O*-ethyl CH_3), 2.086 (s, 3 H, AcO), 3.474 (s, 3 H, MeO-2), 3.07–3.84 (complex, 10 H, H-1*a*,2,3,5,6,6′, two ethyl CH_2), 4.095 (dd, 1 H, J 4.2, 10.9 Hz, H-1*e*), and 4.808 (broadened t, 3 H, J 9.2 Hz, H-4): g.l.c.–c.i.m.s. (NH_3, positive): *m/z* 277 (100) and 294 (8); g.l.c.–e.i.m.s.: *m/z* 43 (100), 45 (23), 57 (18), 58 (43), 59 (41), 60 (12), 61 (10), 69 (21), 71 (16), 73 (15), 74 (13), 85 (30), 87 (25), 88 (21), 89 (43), 97 (61), 99 (31), 101 (88), 102 (15), 103 (18), 111 (17), 113 (13), 114 (14), 115 (18), 117 (34), 125 (15), 129 (40), 130 (12), 142 (23), 143 (15), 157 (70), 159 (15), 171 (51), and 217 (29).

Anal. Calc. for $C_{13}H_{24}O_6$: C, 56.51; H, 8.75. Found: C, 56.78; H, 8.61.

4-O-Acetyl-1,5-anhydro-2,3,6-tri-O-ethyl-D-glucitol (**8**). — Cyclomaltoheptaose was ethylated by the standard procedure and the product was re-ethylated to give the fully ethylated derivative in 78% yield. Minor, polar contaminants were removed by chromatography (m.p.l.c.) on a column (0.8 × 25 cm) of silica gel in 1:1 (v/v) hexane–ethyl acetate; reductive cleavage[3] then afforded 1,5-anhydro-2,3,6-tri-*O*-ethyl-D-glucitol (69%), which was acetylated. Chromatography (m.p.l.c.) under the same conditions afforded pure **8** as an oil; ^{1}H-n.m.r.: δ 1.152 (t, 3 H, J 6.9 Hz, 3-*O*-ethyl CH_3), 1.186, 1.193 (two t, 6 H, J 7.0 Hz, 2- and 6-*O*-ethyl CH_3), 2.092 (s, 3 H, AcO), 3.10–3.86 (complex, 12 H, H-1*a*,2,3,5,6,6′, three *O*-ethyl CH_2), 4.054 (dd, 1 H, J 4.9, 11.1 Hz, H-1*e*), and 4.804 (broadened t, 1 H, J 9.3 Hz, H-4); g.l.c.–c.i.m.s. (NH_3, positive): *m/z* 291 (100) and 308 (50); g.l.c.–e.i.m.s.: *m/z* 43 (100), 44 (20), 45 (17), 57 (16), 59 (21), 60 (11), 69 (14), 72 (37), 73 (25), 85 (12), 88 (13), 97 (23), 99 (13), 101 (20), 117 (12), 125 (9), 143 (22), 171 (14), 185 (14), 217 (3), and 231 (7).

Anal. Calc. for $C_{14}H_{26}O_6$: C, 57.91; H, 9.03. Found: C, 58.17; H, 9.01.

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