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ACETONATION OF D-GLUCOSE WITH 2,2-DIMETHOXYPROPANE–*N,N*-DIMETHYLFORMAMIDE–*p*-TOLUENESULFONIC ACID*

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ABSTRACT

Acetonation of D-glucose with 2,2-dimethoxypropane in *N,N*-dimethylformamide containing a trace of *p*-toluenesulfonic acid at room temperature gave 4,6-*O*-isopropylidene-D-glucopyranose almost exclusively. However, when this reaction was conducted at 95°, 5,6-*O*-isopropylidene-D-glucofuranose, 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose, and an acyclic di-*O*-isopropylidene derivative were obtained as major products. Such variation of products with temperature presumably reflects pyranose–furanose equilibria in which D-glucose exists mainly in the pyranose forms at room temperature, but in the furanose and acyclic ones at 95°; this suggests that this reaction is controlled kinetically, with favored attack by the reagent at the primary hydroxyl group.

INTRODUCTION

In the previous papers[1–3] in this series, we have mainly described the reaction of various *N*-substituted 2-amino-2-deoxy-D-aldohexoses with the 2,2-dimethoxypropane reagent, and its potential utility for syntheses in the amino sugar field. When this reagent was used with non-nitrogeneous aldohexoses[3], some interesting results were obtained; D-glucose gave 4,6-*O*-isopropylidene-D-glucopyranose (which could not be synthesized by the conventional acetonation methods), whereas D-mannose afforded the well known 2,3:5,6-di-*O*-isopropylidene-D-mannofuranose.

We now report further studies of the acetonation of D-glucose with the 2,2-dimethoxypropane reagent, and discuss the reaction mechanism in comparison with the thermodynamically controlled one associated with conventional acetonation methods.

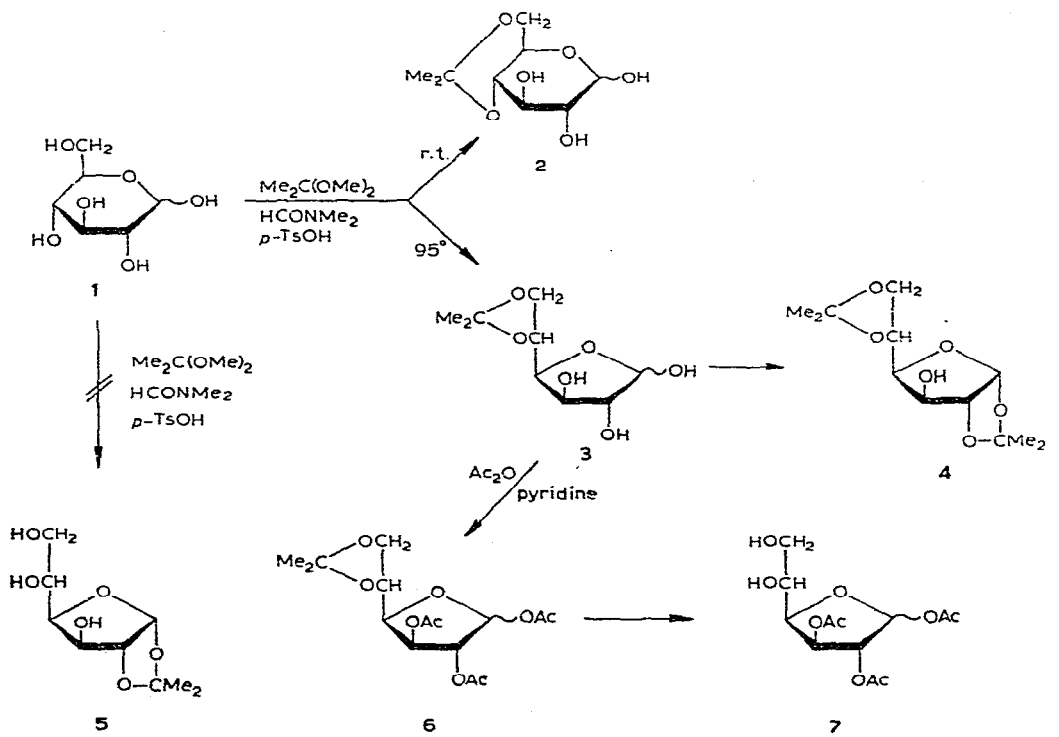
RESULTS AND DISCUSSION

Treatment of D-glucose (**1**) with 2.9 mole-equivalents of 2,2-dimethoxypropane in dry *N,N*-dimethylformamide in the presence of a trace of *p*-toluenesulfonic acid

*The Behavior of Some Aldoses with 2,2-Dialkoxypropane–*N,N*-Dimethylformamide–*p*-Toluenesulfonic Acid, Part IV. For Part III, see ref. 1.

at room temperature gave 4,6-*O*-isopropylidene-D-glucopyranose (**2**) in high yield (80%). Small proportions of 5,6-*O*-isopropylidene-D-glucofuranose (**3**) and 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**4**) were also isolated by column chromatography. When this treatment was performed for 30 min at 95° (reaction *A*), two major products, **4** and **8**, were obtained in 43 and 42% yields, respectively, with traces of mono-*O*-isopropylidene derivatives. However, the well known 1,2-*O*-isopropylidene-α-D-glucofuranose (**5**) was not isolated.

To examine the acetonation mechanism in this reaction system, **1** was treated with 1.2 mole-equivalents of 2,2-dimethoxypropane for 10 min at 95° (reaction *B*), to give a mixture from which **2** (9.2%), **3** (25%), **4** (14%), and **8** (14%) were isolated, and 36% of **1** was recovered unchanged. The subsequent addition of 1.7 mole-equivalents of 2,2-dimethoxypropane to the mixture obtained by reaction *B* (total amount, 2.9 moles/mole of **1**) and continuation of the reaction for another 20 min at 95° gave almost the same result as reaction *A*. These experimental results indicate that 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**4**) was formed *via* 5,6-*O*-isopropylidene-D-glucofuranose (**3**), instead of *via* the 1,2-*O*-isopropylidene-α-D-glucofuranose (**5**) associated with the conventional acetonation methods (see Scheme 1).



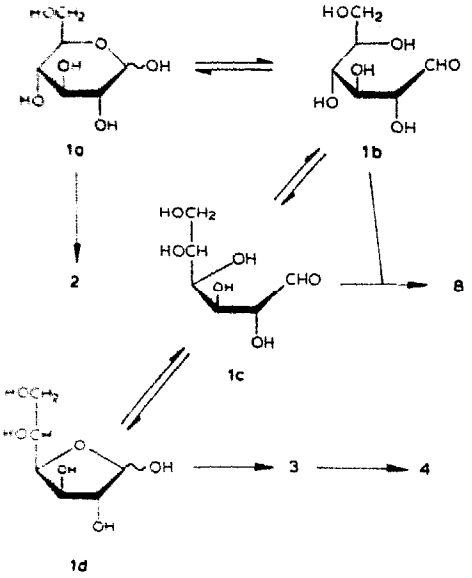
Scheme 1.

The structure of **2** was determined on the basis of chemical evidence in a preceding paper[3], and more-detailed characterization of **2** was reported in a related study using ethyl isopropenyl ether[4].

The product **3** was eluted slightly faster than **2** by column chromatography on silicic acid; it had the elemental composition $C_9H_{16}O_6$ (corresponding to the mono-*O*-isopropylidene derivative of D-glucose), but the infrared spectrum was clearly different from those of **2** and **5**. This product reduced Fehling solution, and consumed two moles of periodate per mole. In the n.m.r. spectrum of **3** in dimethyl sulfoxide-d_6, at lowest field, the 1-OH protons of the two anomeric forms appeared as a doublet of doublets due to the couplings with H-1α ($J_{1\alpha,OH}$ 8.1 Hz) and H-1β ($J_{1\beta,OH}$ 7 Hz) at δ 5.75–5.93, and their intensity ratio indicated an approximately equimolar, anomeric mixture. After D_2O treatment, the only signals remaining below δ 4.78 were a narrow doublet at δ 5.23 (H-1α, $J_{1,2}$ 3.9 Hz) and a singlet at δ 4.95 (H-1β, $J_{1,2}$ ~0 Hz), indicating an anomeric mixture of furanoid structures. The mass spectrum of **3** was identical with that reported by Morgenlie[5]. Acetylation of **3** gave a syrupy tri-*O*-acetyl derivative (**6**) (see Scheme 1), the n.m.r. signals for H-1 being shifted to much lower field (δ 6.02, H-1β; 6.32, H-1α). The signals of H-2 and H-3 were also shifted to lower field (δ 5.08–5.63), and their assignments were confirmed by decoupling techniques. Hydrolytic removal of the isopropylidene group under mild conditions gave a syrupy product (**7**), which consumed one mole of periodate per mole.

An n.m.r. signal for the anomeric proton of the unknown product **8** was not observed, and treatment of **8** with 60% aqueous acetic acid at 55–60° gave a quantitative yield of D-glucose, indicating that **8** exists in an acyclic structure readily convertible into D-glucose. In the mass spectrum of **8**, the peak at *m/e* 245 represents the loss of a methyl group from a di-*O*-isopropylidenehexose[6,7], whereas that at *m/e* 187 may be due to further loss of an isopropylidene group, as acetone. The highest peak, at *m/e* 101, is strongly indicative of the presence of a 5,6-*O*-isopropylidene group, and the peak at *m/e* 231 most likely represents the loss of an aldehyde group. Thus, the mass-spectral data strongly suggest the structure of 2,3:5,6- or 3,4:5,6-di-*O*-isopropylidene-*aldehydo*-D-glucose (**9**). The i.r. and n.m.r. data, however, showed the absence of an aldehyde group, suggesting a structure such as the aldehydrol, or its dimerized form, which is readily convertible into **9** by dehydration. Similar aldehydrol derivatives were also isolated from the reaction mixture of D-xylose with the 2,2-dimethoxypropane reagent[8].

Scheme 2 illustrates the behaviour of D-glucose with the 2,2-dimethoxypropane reagent. The existence of such equilibria in the reaction solution accounts satisfactorily for the variation of products with temperature. It appears that, at room temperature, D-glucose exists almost exclusively in the pyranose form (**1a**), and that the proportion of the acyclic forms (**1b**, **1c**) as well as of the furanose one (**1d**) is extremely small. However, it is known that the pyranose–furanose equilibria can be markedly altered by changes in temperature, or in such solvents as *N*,*N*-dimethylformamide[9,10] and dimethyl sulfoxide[11,12]. Indeed, products **3**, **4**, and **8** were obtained as major products at 95°; this means that the proportions of **1b**, **1d** increase with rise in temperature.



Scheme 2.

It is most likely, therefore, that this acetonation reagent operates under kinetic control, with favored attack at the primary hydroxyl group on C-6 to form the 4,6- or 5,6-*O*-isopropylidene derivative as the initial step. This is in contrast to the conventional acetonation methods involving the initial formation of the 1,2-*O*-isopropylidene derivative. Similar interesting phenomena were also observed in the acetonation of 2-(acylamido)-2-deoxy-D-glucose with this reagent[13].

EXPERIMENTAL

General methods. — Melting points were determined with a Yanagimoto micro melting-point apparatus and are uncorrected. Specific rotations were determined with a Yanagimoto OR-50 polarimeter, and i.r. spectra were recorded with a Jasco IRA-1 spectrophotometer. N.m.r. spectra were recorded at 60 MHz and 90 MHz with Hitachi R-24 and R-22 spectrometers for solutions in chloroform-*d*, unless otherwise noted; tetramethylsilane was used as the internal standard and the sample temperature was ~35°. Chemical shifts are given in δ values, and the couplings recorded are first-order spacings. Mass spectra were recorded with a Hitachi RMU-6M spectrometer operating at 70 eV. *N*,*N*-Dimethylformamide was distilled, and dried over Drierite.

Acetonation of D-*glucose* (**1**). — (*a*) *At room temperature* (~20°). To a stirred solution of anhydrous D-glucose (**1**) (4.0 g, 22.2 mmoles) in *N*,*N*-dimethylformamide (50 ml) were added *p*-toluenesulfonic acid monohydrate (85 mg) and then 2,2

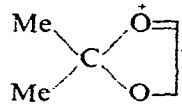
dimethoxypropane (8 ml, 64.6 mmoles, 2.9 moles/mole of **1**). The mixture was stirred for 2 h at room temperature and then treated with Amberlite IRA-410 (OH^-) ion-exchange resin to remove the acid; this deacidification must be complete, because 5,6-*O*-deisopropylidenation occurs very readily under slightly acidic conditions. The resin was filtered off, and washed with methanol. The combined filtrate and washings were evaporated *in vacuo* (~60° bath), and the syrupy residue was chromatographed on a column (4 cm diam.) of silicic acid (160 g) with chloroform, and then with chloroform–methanol (100:1, 50:1, and 30:1). The 100:1 eluate yielded 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**4**) (52 mg, 0.90%). Two monoisopropylidene acetals, 5,6-*O*-isopropylidene-D-glucofuranose (**3**) (460 mg, 9.4%) and 4,6-*O*-isopropylidene-D-glucopyranose (**2**) (3.7 g, 76%), were obtained as crystals from the 30:1 eluate.

(*b*) *At* 95° (*reaction* A). A stirred solution of anhydrous D-glucose (**1**) (4.0 g) and *p*-toluenesulfonic acid monohydrate (85 mg) in *N*,*N*-dimethylformamide (50 ml) was heated to 95°, and then 2,2-dimethoxypropane (8 ml, 2.9 moles/mole of **1**) was gradually added; stirring was continued for 30 min at 95°. The mixture was cooled, and treated with Amberlite IRA-410 (OH^-) ion-exchange resin; the resin was filtered off and washed with methanol. The combined filtrate and washings were evaporated *in vacuo* (~60° bath), and the syrupy residue was chromatographed on a column of silicic acid. The chloroform–methanol (100:1 and 50:1) eluates yielded **4** (2.5 g, 43%) and **8** (2.5 g, 42%). Amounts of **3** (150 mg, 3.1%) and **2** (400 mg, 8.2%) were obtained from the 30:1 eluate.

(*Reaction* B). A stirred solution of **1** (4.0 g) and *p*-toluenesulfonic acid monohydrate (85 mg) in *N*,*N*-dimethylformamide (50 ml) was heated to 95°, and then 2,2-dimethoxypropane (3.31 ml, 1.2 moles/mole of **1**) was added; stirring was continued for 10 min at 95°. The mixture was treated as described in reaction *A*, followed by column chromatography on silicic acid. The chloroform–methanol (100:1 and 50:1) eluates yielded **4** (800 mg, 14%) and **8** (830 mg, 14%), and the 30:1 eluate yielded **3** (1.2 g, 25%) and **2** (450 mg, 9.2%). D-Glucose (**1**) (1.4 g, 36%) was recovered unchanged.

4,6-O-Isopropylidene-D-glucopyranose (**2**). — The white, crystalline mass of **2** was recrystallized from ethanol–ether, to give colorless needles (m.p. 170°), with some amorphous material which started to melt at 164°. Recrystallization of the latter from methanol–hexane gave powdery granules, m.p. 164–167°, $[\alpha]_D^{25}$ −7.2° (*c* 2, equil., water) (lit.[4] −7.3°, lit.[14] −4°); ν_{max}^{Nujol} 3520, 3380 (OH), and 860 cm^{-1} (Me_2C); n.m.r. data at 90 MHz (in dimethyl sulfoxide-d_6 containing a trace of water): δ (before D_2O treatment) 1.29 and 1.44 (2 s, Me_2C), 2.7–3.8 (m, ring protons), 4.37 (d of d, $J_{1,2}$ 7.6, $J_{1,OH}$ 6.4 Hz, H-1β), 4.6 (d, *J* 6.4 Hz, OH), 4.7–5.05 (m, H-1α and OH), 6.35 (d, $J_{1,OH}$ 4.6 Hz, 1-OHα), and 6.69 (d, $J_{1,OH}$ 6.4 Hz, 1-OHβ) (for the n.m.r. data in dry dimethyl sulfoxide-d_6, see ref. 4); mass-spectral data: *m/e* 205 (37, $M^+ - Me$), 187 (3.3, $205 - H_2O$), 145 (4.8, 205 − AcOH), 131 (29), 127 (7.9), 103 (9.5), 102 (11), 101 (9.2), 85 (8.3), 73 (29), 69 (7.6), 61 (10), 60 (9.7), 59 (100, $Me_2\dot{C}OH$), 45 (6.5), 44 (7.6), and 43 (30, $Me_2\dot{C}O$).

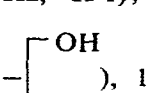
Anal. Calc. for $C_9H_{16}O_6$: C, 49.08; H, 7.32. Found: C, 49.13; H, 7.45.

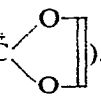
5,6-O-Isopropylidene-D-glucofuranose (**3**). — The crude, crystalline **3** was recrystallized twice from ethyl acetate, to give colorless, fine needles, m.p. 117.5–118.5° (lit.[5] 124–125°), $[\alpha]_D^{25}$ +7° (*c* 2, equil., water) (lit[5]. +9°); ν_{max}^{Nujol} 3360 (OH) and 860 cm^{-1} (Me_2C); n.m.r. data at 90 MHz (in dimethyl sulfoxide-d_6 containing a trace of water): δ (before D_2O treatment) 1.28 and 1.32 (2 s, Me_2C), 3.55–4.45 (m, H-2,H-6$\alpha\beta$), 4.83 (d, *J* 5.4 Hz, 2- or 3-OHβ), 4.92 (d, $J_{1,OH}$ 7 Hz, H-1β), 4.98 (d, *J* 4.9 Hz, 2- or 3-OHα), 5.08 (d, *J* 4.2 Hz, 2- or 3-OHα), 5.18 (d, *J* 4 Hz, 2- or 3-OHβ), 5.2 (d of d, $J_{1,OH}$ 8.1 Hz, $J_{1,2}$ 3.9 Hz, H-1α), 5.8 (d, $J_{1,OH}$ 7 Hz, 1-OHβ), and 5.84 (d, $J_{1,OH}$ 8.1 Hz, 1-OHα); δ (after D_2O treatment) 1.30 and 1.34 (2 s, Me_2C), 3.6–4.5 (m, H-2,H-6$\alpha\beta$), 4.95 (s, $J_{1,2}$ ~0 Hz, H-1), and 5.23 (d, $J_{1,2}$ 3.9 Hz, H-1α); mass-spectral data: *m/e* 205 (19, $M^+ - Me$), 187 (3.8, $205 - H_2O$), 145 (5.3, 205 − AcOH), 131 (5.8), 127 (12), 115 (3.8), 103 (5.0), 102 (5.6), 101 (100, ), 85 (12), 73 (21), 72 (7.8), 69 (5.1), 61 (8.8), 59 (23, $Me_2\overset{+}{C}OH$), 57 (7.5), and 43 (61, $Me_2\overset{+}{C}O$).

Anal. Calc. for $C_9H_{16}O_6$: C, 49.08; H, 7.32. Found: C, 48.96; H, 7.59.

1,2:5,6-Di-O-isopropylidene-α-D-glucofuranose (**4**). — The crude needles of **4** were recrystallized from benzene–hexane, to give colorless needles, m.p. 106–107° (lit.[5] 106–109°), $[\alpha]_D^{20}$ −18.4° (*c* 0.6, water); ν_{max}^{Nujol} 3400 (OH), 843, and 855 cm^{-1} (Me_2C); n.m.r. data at 60 MHz: δ 1.31, 1.36, 1.44, and 1.49 (4 s, Me_2C), 2.83 (d, $J_{3,OH}$ 4 Hz, 3-OH), 4.56 (d, $J_{1,2}$ 3.5 Hz, H-2), and 5.98 (d, $J_{1,2}$ 3.5 Hz, H-1). This compound was also synthesized by the conventional acetonation methods[15], both using acetone–sulfuric acid and acetone–$ZnCl_2$.

Anal. Calc. for $C_{12}H_{20}O_6$: C, 55.37; H, 7.75. Found: C, 55.18; H, 7.95.

1,2-O-Isopropylidene-α-D-glucofuranose (**5**). — A solution of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**4**) in 60% aqueous acetic acid was stirred for 1.5 h at 30–35°, and evaporated *in vacuo* (~35° bath) to a crystalline mass, which was recrystallized from acetone to give colorless needles of **5** in quantitative yield; m.p. 159.5–160.5° (lit.[15] 159–161°), $[\alpha]_D^{20}$ −11.5° (*c* 0.56, water) (lit.[16] −11.8°); ν_{max}^{Nujol} 3420 and 3300 (OH), and 855 cm^{-1} (Me_2C); n.m.r. data at 90 MHz (in dimethyl sulfoxide-d_6 containing a trace of water): δ (before D_2O treatment) 1.24 and 1.38 (2 s, Me_2C), 3.1–3.75 (m, H-5,6), 3.86 (d of d, $J_{3,4}$ 2–2.5 Hz, $J_{4,5}$ 8.2 Hz, H-4), 4.03 (d of d, $J_{3,OH}$ 4.5, $J_{3,4}$ 2–2.5 Hz, H-3), 4.37 (d, $J_{1,2}$ 4 Hz, H-2), 4.4 (t, $J_{6,OH}$ and $J_{6',OH}$ 5.5 Hz, 6-OH), 4.59 (d, $J_{5,OH}$ 5 Hz, 5-OH), 5.08 (d, $J_{3,OH}$ 4.5 Hz, 3-OH), and 5.78 (d, $J_{1,2}$ 4 Hz, H-1); δ (after D_2O treatment) 1.23 and 1.37 (2 s, Me_2C), 3.1–3.75 (m, H-5,6), 3.85 (d of d, H-4), 4.02 (d, $J_{3,4}$ 2–2.5 Hz, H-3), 4.37 (d, H-2), and 5.77 (d, $J_{1,2}$ 4 Hz, H-1); mass-spectral data: *m/e* 205 (40, $M^+ - Me$), 187 (0.84), 159 (53, $M^+ -$ ), 149 (4.2), 145 (3.0), 131 (5.3), 129 (5.9), 127 (15), 113 (14),

101 (10), 100 (12), 85 (29, ), 73 (66), 71 (12), 69 (7.8), 61 (8.5), 59 (100, $Me_2\dot{C}OH$), 57 (7.2), 55 (5.8), and 43 (26, $Me_2\dot{C}O$). Compound **5** was also isolated directly from the mixture obtained by reaction of D-glucose with acetone–sulfuric acid.

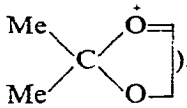
Anal. Calc. for $C_9H_{16}O_6$: C, 49.08; H, 7.32. Found: C, 49.24; H, 7.33.

*1,2,3-Tri-*O*-acetyl-5,6-*O*-isopropylidene-*D*-glucofuranose* (**6**). — Compound **3** (600 mg) was treated with pyridine (12 ml) and acetic anhydride (6 ml), and the solution was kept overnight at room temperature. It was then evaporated *in vacuo* to a syrupy residue, which was chromatographed on a column (2 cm diam.) of silicic acid (20 g) with chloroform, to yield **6** (850 mg, 89%) as a syrup; ν_{max}^{film} 1760 (OAc), 1220 (ester), and 850 cm^{-1} (Me_2C); n.m.r. data at 90 MHz: δ 1.2 and 1.26 (2 s, Me_2C), 2.04, 2.06, and 2.08 (3 s, AcO), 3.8–4.4 (m, H-4,H-6$\alpha\beta$), 5.12 (d, $J_{1,2}$ ~0 Hz, $J_{2,3}$ 1.3 Hz, H-2β), 5.17 (t, $J_{1,2}$ and $J_{2,3}$ 4.5 Hz, H-2α), 5.22 (d of d, $J_{2,3}$ 1.3 Hz, $J_{3,4}$ 4.5 Hz, H-3β), 5.55 (t, $J_{2,3} \simeq J_{3,4} = 4.5$ Hz, H-3α), 6.02 (s, $J_{1,2}$ ~0 Hz, H-1β), and 6.32 (d, $J_{1,2}$ 4.5 Hz, H-1α); anomeric ratio (α:β) was estimated at ~11:9 from the ratio of intensity of H-1α and H-1β. These n.m.r. data were confirmed by use of decoupling techniques.

Anal. Calc. for $C_{15}H_{22}O_9$: C, 52.02; H, 6.40. Found: C, 52.23; H, 6.31.

*1,2,3-Tri-*O*-acetyl-*D*-glucofuranose* (**7**). — A solution of compound **6** (700 mg) in 60% aqueous acetic acid was stirred for 1.5 h at 30–35°, and evaporated *in vacuo* (~35° bath) to a syrupy residue, which was chromatographed on a column (2 cm diam.) of silicic acid (20 g) with chloroform and then 70:1 chloroform–methanol. The 70:1 eluate yielded **7** (560 mg, 90%) as a syrup; ν_{max}^{film} 3460 (OH), 1750 (AcO), and 1230 cm^{-1} (ester); n.m.r. data at 90 MHz: δ 2.11, 2.13, 2.15, 2.17, 2.19, and 2.21 (6 s, AcO$\alpha\beta$), 2.6 and 3.05 (OH), 3.55–4.0 and 4.15–4.5 (m, H-4,H-6$\alpha\beta$), 5.19 (d, $J_{1,2}$ ~0 Hz, $J_{2,3}$ 0.75 Hz, H-2β), 5.29 (d of d, $J_{1,2}$ 4.5 Hz, $J_{2,3}$ 3.1 Hz, H-2α), 5.38 (d of d, $J_{2,3}$ 0.75 Hz, $J_{3,4}$ 4.2 Hz, H-3β), 5.55 (d of d, $J_{2,3}$ 3.1 Hz, $J_{3,4}$ 4.9 Hz, H-3α), 6.09 (s, $J_{1,2}$ ~0 Hz, H-1β), and 6.42 (d, $J_{1,2}$ 4.5 Hz, H-1α). This sample consumed one mole of periodate per mole.

Anal. Calc. for $C_{12}H_{18}O_9$: C, 47.06; H, 5.92. Found: C, 47.31; H, 6.02.

Unknown product (**8**). — The crude sample of **8** was rechromatographed on a column of silicic acid, to give a colorless, amorphous material, $[\alpha]_D^{20}$ −2.4° (*c* 0.5, methanol); ν_{max}^{Nujol} 3420 (OH) and 860 cm^{-1} (Me_2C); this sample was homogeneous by g.l.c. (2% of OV-1; glass column, 1 m × 3 mm i.d.); n.m.r. data at 60 MHz: δ 1.15–1.65 (Me_2C), 2.0–4.0 (OH), and 3.8–4.65 (ring protons); mass spectral data: *m/e* 245 (65, $M^+ - Me$), 231 (23, $M^+ - CHO$), 187 (26), 173 (31), 159 (4.0), 145 (3.9), 129 (12), 127 (9.9), 115 (14), 109 (3.9), 101 (100, ), 100 (4.7), 85 (11), 73 (10), 72 (7.6), 71 (7.8), 59 (30, $Me_2\dot{C}OH$), and 43 (21, $Me\dot{C}O$).

Anal. Found for **8**: C, 54.90; H, 8.44.

A solution of this sample in 60% aqueous acetic acid was stirred for 30 min at 55–60°, and evaporated *in vacuo* to a white, crystalline mass, which was recrystallized from methanol–benzene, m.p. ~157°; the i.r. and n.m.r. spectra were identical with those of D-glucose.

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