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SYNTHESIS OF (1,2,3,4,5/0)-5-HYDROXYMETHYL-1,2,3,4-CYCLOHEXANETETROL: PSEUDO-β-DL-TALOPYRANOSE*

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ABSTRACT

The remaining unknown diastereoisomer of 5-hydroxymethyl-1,2,3,4-cyclohexanetetrol with the (1,2,3,4,5/0)-configuration has been synthesised as the penta-acetate from DL-(1,2/3,4,5)-1,3,4-triacetoxy-5-acetoxymethyl-2-bromocyclohexane. In addition, a new synthesis of three pseudo-sugars having the α- and β-*galacto* and α-*talo* configurations is also described.

INTRODUCTION

The discovery[2] of the production of the antibacterial (1*S*)-(1,2/3,4,5)-5-hydroxymethyl-1,2,3,4-cyclohexanetetrol (pseudo-α-D-galactose) from *Streptomyces* sp. MA-4145 has stimulated interest in the biological properties of pseudo-sugars. Pseudo-β-DL-glucopyranose[3] and pseudo-β-DL-fructopyranose[4] are almost as sweet as the corresponding true sugars, and pseudo-α-DL-glucopyranose, but not the β isomer, inhibits glucokinase activity and glucose-stimulated insuline release[5],

Sixteen diastereoisomers (racemic) are theoretically possible for the pseudo-sugar DL-5-hydroxymethyl-1,2,3,4-cyclohexanetetrol and all except that with the (1,2,3,4,5/0)-configuration have been synthesised[6–15]. We now describe a synthesis of the last remaining diastereoisomer, pseudo-β-DL-talopyranose (**1**), as the penta-acetate (**2**) from DL-(1,2/3,4,5)-1,3,4-triacetoxy-5-acetoxymethyl-2-bromocyclohexane[11] (**3**), together with a new synthesis of three diastereoisomers with (1,3,4,5/2)- (**9**), (1,2/3,4,5)- (**10**), and (1/2,3,4,5)-configurations (**11**).

Fifteen of the sixteen diastereoisomeric pseudo-sugars are obtainable from the cycloaddition *endo*-adduct of furan with acrylic acid[10]. Since the adduct can be readily optically resolved[14], fifteen of the pseudo-sugars should be accessible in D or L forms, as illustrated by synthesis of pseudo-α-D-galactopyranose and pseudo-β-D-glucopyranose[14].

*Pseudo-sugars. Part XIII. For Part XII, see ref. 1.
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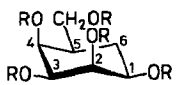

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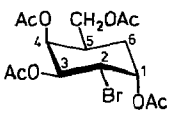

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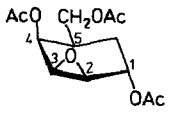

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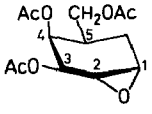

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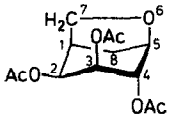

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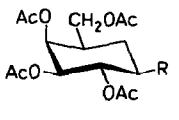

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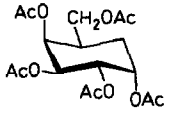
8 R = NHAc
9 R = OAc



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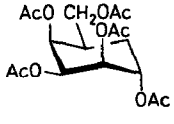

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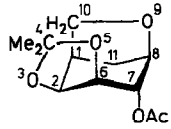

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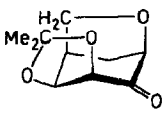

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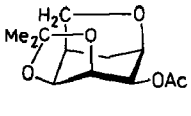

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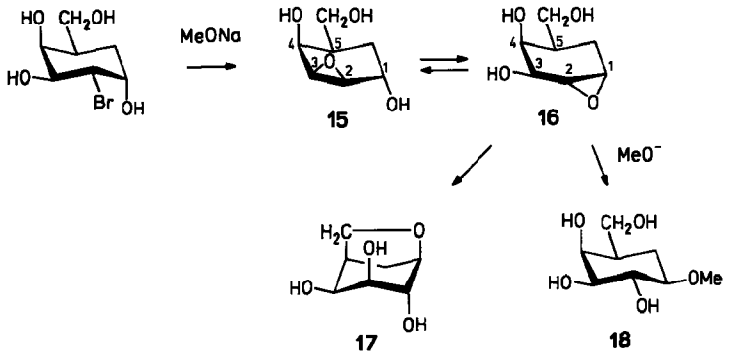
All compounds described in this paper are racemic, but, for convenience, only single enantiomers are depicted.

RESULTS AND DISCUSSION

Treatment of the bromide **3**[11] with 2 mol of sodium methoxide in methanol at reflux temperature, followed by acetylation, gave, after column chromatography, three anhydro compounds **4**–**6** and the methyl ether **7**. The yields of the products depended on the time of reaction and on the temperature at which the reaction mixture was neutralised with acetic acid. When the mixture was heated for 20 min and then neutralised after cooling, 15% of **4** and 85% of **5** were obtained. After heating for 40 min, 28% of **5** and of 26% **6** were isolated. When the reaction was quenched by the addition of acetic acid, **4** and **5** were obtained preferentially. Only **6** was obtained (54%) after boiling under reflux with 3 mol of sodium methoxide for 2 h. The structures **4**–**7** were assigned readily on the basis of ^{1}H-n.m.r. data.

Mechanistically, the initially formed 2,3-epoxide **15** undergoes an epoxide group migration to give the 1,2-epoxide **16**, and an equilibrium mixture of **15** and **16** may be formed under these conditions. The more reactive **16** is attacked intramolecularly or by a methoxide ion to produce **17** or **18**. Therefore, a prolonged reaction time would improve the yield of **17**.

Treatment of **5** with excess of sodium azide and ammonium chloride in aqueous 10% 2-methoxyethanol resulted in a preferential attack by azide ion at C-1 to give a single azido compound which was then hydrogenated, and the product was acetylated to give 24% of DL-(1,2,4,6/3)-4-acetamido-1,2,3-triacetoxy-6-acetoxymethylcyclohexane (**8**). The structure of **8** was indicated by its ^{1}H-n.m.r.



spectrum. Therefore, the epoxide **5** may be a versatile intermediate for the preparation of pseudo-β-galactopyranosyl compounds. On the other hand, **4** and **5** were hydrolysed with conc. sulfuric acid in aqueous acetone and the products were acetylated to give the pseudo-sugar penta-acetates having *α-galacto*[7] (**10**, 57%) and *α-talo*[6] configurations (**11**, 73%), respectively. A neighboring-group participation of the acetoxyl group vicinal and *trans* to the epoxide ring is involved in these hydrolyses. Treatment of **6** with acetic anhydride–acetic acid–conc. sulfuric acid (40:40:1) at 50° gave, selectively, 66% of pseudo-β-DL-galactopyranose penta-acetate[9] (**9**). In this reaction, the anhydro ring was cleaved at C-7 by an acetate ion.

O-Deacetylation of **6** with methanolic sodium methoxide and treatment of the resulting triol with excess of 2,2-dimethoxypropane in *N,N*-dimethylformamide in the presence of toluene-*p*-sulfonic acid at 80° gave, after acetylation, 65% of the isopropylidene derivative **12**. The ^{1}H-n.m.r. spectrum of **12** contained a signal at δ 4.98 (bd, *J* 3 Hz) which was attributed to H-7 and was consistent with the assigned structure. Deacetylation of **12** and oxidation of HO-7 with ruthenium dioxide and sodium metaperiodate in dichloromethane gave 53% of the crystalline ketone **13**. The ^{1}H-n.m.r. spectrum of **13** contained signals at δ 4.31 (d) and 4.20 (d) attributable to H-6 and H-8, respectively. Catalytic (Pt/C) hydrogenation of **13** gave an alcohol, which was characterised as the acetate (**14**, 59%) that was different from **12**. Acetolysis of the alcohol gave a new pseudo-sugar penta-acetate (**2**, 35%), m.p. 117–119°. The ^{1}H-n.m.r. spectrum of **2** contained signals at δ 5.50 (t), 5.40 (t), 4.93 (t), and 4.93 (ddd, *J* 3 Hz), attributable to H-2 (H-4), H-4 (H-2), H-3, and H-1, respectively, indicating the all-*cis* configuration (*β-talo* configuration) of the five substituents on the cyclohexane ring. Compound **2** was also obtained in a reasonable yield (70%) by acetolysis of **14**. In this reaction, the anhydro ring was cleaved selectively at C-10 by an acetate ion.

EXPERIMENTAL

General methods. — Melting points were determined with a Büchi 510 capillary melting-point apparatus and are uncorrected. ^{1}H-N.m.r. spectra were

recorded for solutions in $CDCl_3$ (internal Me_4Si) with a Varian EM-360A (60 MHz) or EM-390 (90 MHz) spectrometer. Column chromatography was conducted on Wakogel C-200 (200 Mesh) or C-300 (300 Mesh) (Wako Co., Osaka, Japan). Organic solutions were dried over anhydrous Na_2SO_4 and concentrated at <50° under diminished pressure.

Reaction of DL-*(1,2/3,4,5)-1,3,4-triacetoxy-5-acetoxymethyl-2-bromocyclohexane*[11] (**3**) *with methanolic sodium methoxide.* — (*a*) A mixture of **3** (3.0 g, 7.3 mmol), methanolic M sodium methoxide (15 mL), and methanol (150 mL) was boiled under reflux for 20 min, then cooled to room temperature, stored at ~5° for 1 h, neutralised with acetic acid, and then concentrated. The residue was treated with acetic anhydride (20 mL) in pyridine (20 mL) at room temperature overnight. Insoluble material was removed, the filtrate was concentrated, and the residue was eluted from a column of silica gel (40 g, C-200) with 2-butanone–toluene (1:5) to give, first, DL-(1/2,3,4,5)-1,4-diacetoxy-5-acetoxymethyl-2,3-epoxycyclohexane (**4**; 0.32 g, 15%), as prisms, m.p. 119–120° (from ethanol). ^{1}H-N.m.r. data (90 MHz): δ 5.38 (bq, 1 H, $J_{1,2} = J_{1,6} = J_{1,6'} = \sim 3$ Hz, H-1), 5.20 (t, 1 H, $J_{3,4} = J_{4,5} = 4.5$ Hz, H-4), 4.10 (dd, 1 H, $J_{5,7}$ 9, $J_{7,7}$ 11.3 Hz, H-7), 3.92 (dd, 1 H, $J_{5,7'}$ 6.5 Hz, H-7′), 3.54 (t, 1 H, $J_{2,3}$ 3.5 Hz, H-3), 3.23 (bt, 1 H, H-2), 2.10 and 2.02 (2 s, 6 and 3 H, 3 OAc).

Anal. Calc. for $C_{13}H_{18}O_7$: C, 54.54; H, 6.34. Found: C, 54.23; H, 6.23.

Eluted second was crude DL-(1,2/3,4,5)-3,4-diacetoxy-5-acetoxymethyl-1,2-epoxycyclohexane (**5**; 1.8 g, 85%) as a syrup. An analytical sample was obtained by elution from a column of silica gel (C-300) with 2-butanone–toluene (1:5). ^{1}H-N.m.r. data (90 MHz): δ 5.29 (bd, 1 H, $J_{3,4}$ 4.5 Hz, H-4), 4.95 (d, 1 H, H-3), 3.88 (d, 2 H, $J_{5,7}$ 6.5 Hz, CH_2OAc), 3.36 (bd, 1 H, $J_{1,2}$ 3.8 Hz, H-2), 3.01 (dd, 1 H, $J_{1,6}$ 2 Hz, H-1), 2.07 and 2.03 (2 s, 3 and 6 H, 3 OAc).

Anal. Found: C, 54.85; H, 6.46.

(*b*) A mixture as described in (*a*) was boiled under reflux for 40 min and then processed. The resulting mixture of acetylated products was eluted from a column of silica gel (40 g, C-200) with 2-butanone–toluene (1:5) to give, first, **5** (0.60 g, 28%) as a syrup. Eluted second was (1*RS*,2*SR*,3*SR*,4*SR*,5*RS*)-2,3,4-triacetoxy-6-oxabicyclo[3.2.1]octane (**6**; 0.55 g, 26%) as a syrup. ^{1}H-N.m.r. data (90 MHz): δ 5.27–5.00 (m, 2 H, H-2,3), 4.88 (bd, $J_{3,4}$ 4.5 Hz, H-4), 4.40–4.20 (m, 1 H, H-5), 4.29 (d, 1 H, $J_{7,7}$ 9 Hz, H-7*endo*), 3.70 (dd, 1 H, $J_{1,7exo}$ 4.5 Hz, H-7*exo*), 2.60–2.40 (m, 1 H, H-1), 2.12, 2.07, and 2.00 (3 s, 3, 3, and 3 H, 3 OAc).

Anal. Found: C, 54.23; H, 6.44.

(*c*) A mixture of **3** (1.0 g, 2.4 mmol), methanolic M sodium methoxide (5 mL), and methanol (20 mL) was boiled under reflux for 20 min, then neutralised with acetic acid, and processed as in (a). The acetylated products were eluted from a column of silica gel (35 g, C-200) with 2-butanone–toluene (1:5) to give a mixture (0.36 g, 25%) of **4** and **5**, **5** (74 mg, 11%), **4** (36 mg, 5%), and DL-(1,3,4,5/2)-2,3,4-triacetoxy-5-acetoxymethyl-1-methoxycyclohexane (**7**; 22 mg, 2.4%). ^{1}H-N.m.r. data (90 MHz) for **7**: δ 5.20–4.90 (m, 3 H, H-2,3,4), 4.22–4.00 (m, 2 H, CH_2OAc), 3.56–3.40 (m, 1 H, H-1), 3.45 (s, 3 H, OMe), 2.09, 2.06, and 2.03 (3 s, 6, 3, and 3 H, 4 OAc).

Anal. Calc. for $C_{16}H_{24}O_9$: C, 53.33; H, 6.71. Found: C, 53.68; H, 6.73.

(*d*) A mixture as in (*c*) was boiled under reflux for 40 min and then processed as in (*a*). The resulting acetylated products were eluted from a column of silica gel to give **4** (0.76 g, 36%), **5** (78 mg, 4%), and **6** (0.10 g, 5%).

(*e*) A mixture of **3** (1.0 g, 2.4 mmol), methanolic M sodium methoxide (10 mL), and methanol (40 mL) was boiled under reflux for 2 h, and then processed as in (*a*). Elution of the products from a column of silica gel with 2-butanone–toluene (1:6) gave **6** (0.45 g, 54%).

DL-*(1,2,4,6/3)-4-Acetamido-1,2,3-triacetoxy-6-acetoxymethylcyclohexane* (**8**). — A mixture of **5** (0.55 g, 1.9 mmol), sodium azide (0.50 g, 7.7 mmol), ammonium chloride (0.41 g, 7.7 mmol), and aqueous 10% 2-methoxyethanol (18 mL) was boiled under reflux for 24 h and then concentrated, and the residue was acetylated in the usual way. The product was eluted from a column of alumina (5 g) with chloroform to give the azido compound (0.58 g) as a crude syrup, which was shown to be homogeneous by t.l.c. A solution of the azide (0.54 g) in ethanol (20 mL) containing acetic anhydride (0.7 mL) was hydrogenated in the presence of Raney nickel T-4[16] (0.5 mL) in a Parr apparatus (initial hydrogen pressure of 3.4 kg/cm^2) at room temperature for 17 h. The product crystallised from ethanol–ether to give **8** (0.13 g, 24%), as prisms, m.p. 174–175°. ^{1}H-N.m.r. data (60 MHz): δ 5.89 (d, 1 H, $J_{4,NH}$ 8.2 Hz, NH), 5.41 (t, 1 H, $J_{1,2} = J_{1,6} = 2.8$ Hz, H-1), 5.22 (t, 1 H, $J_{2,3} = J_{3,4} = 10$ Hz, H-3), 4.84 (dd, 1 H, H-2), 4.33 (dt, 1 H, $J_{4,5a}$ 10, $J_{4,5e}$ 7.8 Hz, H-4), 4.05–3.70 (m, 2 H, CH_2OAc), 2.10, 2.03, 2.01, 1.98, and 1.92 (5 s, 3, 3, 3, 3, and 3 H, NAc and 4 OAc).

Anal. Calc. for $C_{17}H_{25}NO_9$: C, 52.70; H, 6.50; N, 3.61. Found: C, 52.94; H, 6.45; N, 3.73.

DL-*(1,2/3,4,5)-1,2,3,4-Tetra-acetoxy-5-acetoxymethylcyclohexane* (**10**). — A mixture of **4** (0.49 g, 3.5 mmol) and acetone (25 mL) containing aqueous 10% sulfuric acid (2.5 mL) was boiled under reflux for 1.5 h, then neutralised with aqueous sodium hydrogencarbonate, and concentrated. The residue was acetylated in the usual way and the product was eluted from a column of silica gel (20 g, C-200) with 2-butanone–toluene (1:8). The product crystallised from ethanol to give **10** (0.38 g, 57%), m.p. 115–118°; lit.[7] m.p. 123–124°. The ^{1}H-n.m.r. spectrum was superposable on that of an authentic sample[11].

DL-*(1/2,3,4,5)-1,2,3,4-Tetra-acetoxy-5-acetoxymethylcyclohexane* (**11**). — Compound **5** (0.13 g, 0.46 mmol) was hydrolysed as described in the preparation of **10**. The product was acetylated and then eluted from a column of silica gel (6 g, C-300) with 2-butanone–toluene (1:8) to give **11** (0.11 g, 73%), m.p. 95–98°; lit.[6] m.p. 111–112°. The ^{1}H-n.m.r. spectrum was superposable on that of an authentic sample[6].

DL-*(1,3,4,5/2)-1,2,3,4-Tetra-acetoxy-5-acetoxymethylcyclohexane* (**9**). — A mixture of **6** (79 mg, 0.28 mmol) and 40:40:1 acetic anhydride–acetic acid–conc. sulfuric acid (5 mL) was heated at 50° for 2 days, then poured into ice–water, and extracted with ethyl acetate (100 mL). The extract was washed with aqueous

sodium hydrogencarbonate and water, dried, and concentrated. The product was eluted from a column of silica gel (5 g, C-300) with 2-butanone–toluene (1:8) to give **9** (60 mg, 66%), as prisms, m.p. 115–118° (from ethanol); lit.[9] m.p. 123–124°. The ^{1}H-n.m.r. spectrum was superposable on that of an authentic sample[9].

*(1*RS,*2*SR,*6*SR,*7*SR,*8*RS*) - 7 - Acetoxy - 4,4 - dimethyl - 3,5,9 -trioxatricyclo - [6.2.1.0^{2,6}]undecane* (**12**). — To a solution of **6** (0.45 g, 1.6 mmol) in methanol (10 mL) was added methanolic M sodium methoxide (1.5 mL). The mixture was stirred at room temperature for 0.5 h, neutralised with Amberlite IR-120 (H^+) resin (2.5 mL), and then concentrated. To a solution of the dried residue in *N,N*-dimethylformamide (6 mL) were added 2,2-dimethoxypropane (3 mL) and toluene-*p*-sulfonic acid (10 mg). The mixture was stirred at 80° for 20 h, neutralised with sodium hydrogencarbonate, and then concentrated. The residue was acetylated in the usual way and the product was crystallised from ethanol to give **12** (0.25 g, 65%), m.p. 75–75.5°. ^{1}H-N.m.r. data (90 MHz): δ 4.98 (bd, 1 H, $J_{6,7}$ 0, $J_{7,8}$ 3 Hz, H-7), 4.04 (d, 1 H, $J_{1,10endo}$ 0, $J_{1,10exo}$ 4.5 Hz, H-10*endo*), 4.32 (bdd, 1 H, $J_{10,10}$ 9 Hz, H-10*exo*), 2.49 (q, 1 H, $J_{1,11endo}$ 0, $J_{1,11exo}$ 4.5 Hz, H-1), 2.03 (s, 3 H, OAc), 1.52 and 1.31 (2 s, each 3 H, CMe_2).

Anal. Calc. for $C_{12}H_{18}O_5$: C, 59.49; H, 7.49. Found: C, 59.48; H, 7.33.

*(1*RS,*2*SR,*6*SR,*8*RS*)-4,4-Dimethyl-3,5,9-trioxatricyclo[6.2.1.0^{2,6}]undecan-7-one* (**13**). — A solution of **12** (243 mg, 1.0 mmol) in methanolic 0.1M sodium methoxide (20 mL) was kept at room temperature for 0.5 h, then treated with Amberlite IR-120 (H^+) resin (3 mL), and concentrated. The residue was vigorously stirred with ruthenium dioxide (20 mg), aqueous 5% sodium metaperiodate (10 mL), sodium hydrogencarbonate (0.5 g), and chloroform (9 mL) at room temperature for 2 h. After the addition of 2-propanol (5 mL), insoluble material was removed, and the filtrate was washed with water, dried, and concentrated. Crystallisation of the residue from ethanol gave **13** (0.11 g, 53%), as prisms, m.p. 123–126°. ^{1}H-N.m.r. data (90 MHz): δ 4.57 (dd, 1 H, $J_{1,2}$ 6, $J_{2,6}$ 7.5 Hz, H-2), 4.31 (d, 1 H, H-6), 4.24 (d, 1 H, $J_{1,10endo}$ 0, $J_{10,10}$ 9 Hz, H-10*endo*), 4.20 (d, 1 H, $J_{8,11}$ 5.3 Hz, H-8), 3.79 (dd, 1 H, $J_{1,10exo}$ 5 Hz, H-10*exo*), 2.79 (q, 1 H, H-1), 2.24 (dt, 1 H, $J_{8,11exo}$ 5.3, $J_{11,11}$ 13.5 Hz, H-11*exo*), 1.83 (d, 1 H, H-11*endo*), 1.53 and 1.37 (2 s, each 3 H, CMe_2).

Anal. Calc. for $C_{10}H_{14}O_4$: C, 60.60; H, 7.12. Found: C, 60.88; H, 7.24.

*(1*RS,*2*SR,*6*SR,*7*RS,*8*RS*) - 7 - Acetoxy - 4,4 - dimethyl - 3,5,9 -trioxatricyclo - [6.2.1.0^{2,6}]undecane* (**14**). — A solution of **13** (88 mg, 0.44 mmol) in methanol (9 mL) was hydrogenated in the presence of 10% Pt/C (10 mg) as described for the preparation of **8**. The product was acetylated in the usual way and then crystallised from ethanol to give **14** (64 mg, 59%), as prisms, m.p. 118–120°. ^{1}H-N.m.r. data (90 MHz): δ 4.80–4.45 (m, 2 H), 4.32–3.90 (m, 3 H), 3.67 (dd, 1 H, $J_{1,10exo}$ 4.5, $J_{10,10}$ 9 Hz, H-10*exo*), 2.41 (q, 1 H, $J_{1,2} = J_{11exo}$ = 4.5 Hz, H-1), 1.55 and 1.30 (2 s, each 3 H, CMe_2).

Anal. Calc. for $C_{12}H_{18}O_5 \cdot 0.25\ H_2O$: C, 58.40; H, 7.55. Found: C, 58.39; H, 7.39.

DL-*(1,2,3,4,5/0)-1,2,3,4-Tetra-acetoxy-5-acetoxymethylcyclohexane* (**2**). — (*a*) The alcohol derived by hydrogenation of **13** (77 mg, 0.39 mmol) was, without isolation, acetolysed as described in the preparation of **9**. The product was eluted from a column of silica gel (5 g, C-300) with 2-butanone–toluene (1:4) to give **2** (53 mg, 35%), as prisms, m.p. 117–119° (from ethanol). ^{1}H-N.m.r. data (90 MHz): δ 5.50 (t, 1 H, *J* 3 Hz) and 5.40 (t, 1 H, *J* 3 Hz) (H-2,4), 4.93 (bddd, $J_{1,6a}$ 10, $J_{1,6e}$ 6 Hz, H-1), 4.93 (t, 1 H, H-3), 4.12 (dd, 1 H, $J_{5,7}$ 7.5, $J_{7,7}$ 10.5 Hz, H-7), 3.91 (dd, 1 H, $J_{5,7'}$ 6 Hz, H-7'), 2.09, 2.06, 2.03, 2.01, and 1.98 (5 s, 3, 3, 3, 3, and 3 H, 5 OAc).

Anal. Calc. for $C_{17}H_{24}O_{10}$: C, 52.58; H, 6.23. Found: C, 52.48; H, 6.17.

(*b*) Compound **14** (87 mg, 0.36 mmol) was acetolysed with the reagent (12 mL) at 50° for 4 days, and then at 80° for 1 h. The reaction mixture was processed, and the product was crystallised from ethanol to give **2** (32 mg). The mother liquor was concentrated and the residue was eluted from a column of silica gel (8 g, C-300) with 2-butanone–toluene (1:5) to give additional crystals (65 mg; total yield, 70%) of **2**, m.p. 115–117°. The ^{1}H-n.m.r. spectrum was superposable on that obtained for the above compound.

The formation of **11** was not detected by t.l.c.

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