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SYNTHESIS OF METHYL DL-(1,3/2,4,5)- AND DL-(1,3,4/2,5)-2,3,4,5-TETRAHYDROXYCYCLOHEXANE-1-CARBOXYLATES*

SEIICHIRO OGAWA**, YOSHIMASA YATO, KAZUFUMI NAKAMURA, MAKOTO TAKATA, AND TOHEI TAKAGAKI

Department of Applied Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi, Kohoku-ku, Yokohama 223 (Japan)

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ABSTRACT

Two new diastereoisomers of the pseudo-hexuronate methyl 2,3,4,5-tetrahydroxycyclohexane-1-carboxylate, having (1,3/2,4,5)- (**8**) and (1,3,4/2,5)-configurations (**16**), have been synthesised from the readily available bromo-lactone (**1**) of the *endo*-adduct of furan and acrylic acid. Treatment of **1** with 20% hydrogen bromide in acetic acid at 80° resulted in regioselective cleavage of the 1,4-anhydro ring to give DL-(1,3,5/2,4)-2,3-diacetoxy-4,5-dibromocyclohexane-1-carboxylic acid (**2**). Debromination of **2** with zinc dust gave DL-(1,3/2)-2,3-diacetoxycyclohex-4-ene-1-carboxylic acid (**5**). The methyl ester (**6**) of **5** was oxidised with osmium tetraoxide and hydrogen peroxide, followed by acetylation, to give the tetra-acetate of **8**. Epoxidation of **6** gave two isomeric epoxides, each of which gave **16** on hydrolysis followed by *O*-deacetylation.

INTRODUCTION

Carbohydrates containing hexopyranuronic acid residues occur in various polysaccharides and sugar conjugates, and much interest has been stimulated in the biological role of these compounds[2,3]. As part of our study[1] of the chemistry and biochemistry of pseudo-sugars, we now describe a synthesis of two stereoisomers of methyl pseudo-DL-hexopyranuronate starting from the Diels–Alder *endo*-adduct of furan and acrylic acid.

(1,2,3,4/5)-Tetrahydroxycyclohexane-1-carboxylic acid was first used as the synthetic intermediate for a total synthesis of shikimic acid[4,5] and later for a synthesis of pseudo-α-DL-talopyranose[6]. However, little is known of its stereoisomers and their biological properties.

*Pseudo-sugars, Part XII. For Part XI, see ref. 1.
**To whom correspondence should be addressed.

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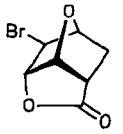
RESULTS AND DISCUSSION

The bromo-lactone[7] **1**, which is readily available from 7-oxabicyclo[2.2.1]hept-5-ene-2-carboxylic acid[8], was treated with 20% hydrogen bromide in acetic acid at 80° for 2 days to give a 64% yield of the crystalline dibromide **2**, which was converted quantitatively into the methyl ester **3** by treatment with diazomethane in ether. Two dibromides could be formed by cleavage of the 1,4-anhydro ring in **1**, but only one was formed and its structure was established as follows. Treatment of **2** with methanolic sodium methoxide and acetylation of the product gave 59% of a crystalline epoxide (**4**), the ^{1}H-n.m.r. spectrum ($CDCl_3$) of which contained signals at δ 4.35 (dd, J 1.5, 6, and 12 Hz) and 5.26 (d, J 10.5 Hz) attributed to H-5 and H-2, respectively. Therefore, the structure of **4** was established and that of **3** was assigned as shown in the formula.

Debromination of **2** and **3** with excess of zinc dust in acetic acid at 70° gave the corresponding cyclohexene derivatives **5** and **6**, respectively, in good yield. Compound **5** was easily converted into **6** by esterification, and their structures were confirmed on the basis of elemental analyses and ^{1}H-n.m.r. spectra.

Treatment of **6** with osmium tetraoxide and hydrogen peroxide in *tert*-butyl alcohol at 40° and acetylation of the product gave 61% of the crystalline tetra-acetate **7** and 7% of the enone **9**. The ^{1}H-n.m.r. spectrum (270 MHz, $CDCl_3$) of **7** contained signals for H-4 and H-5 at δ 4.88 (dd, J 9.9 and 3 Hz) and 5.39 (bq, J 4.3, 3, and 2.2 Hz), respectively, supporting the *α-gluco* configuration. This configura-



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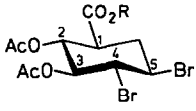

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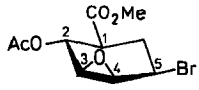
3 R = Me



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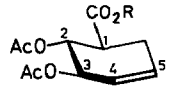

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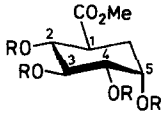

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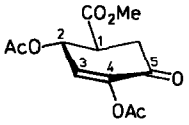

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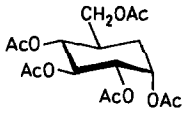

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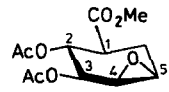

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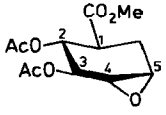

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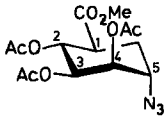

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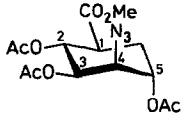

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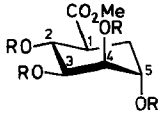

15 R = Ac
16 R = H

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

tion was confirmed by the conversion of **7** into the known pseudo-α-DL-glucopyranose penta-acetate[9] (**10**) by reduction with lithium aluminum hydride in tetrahydrofuran, followed by acetylation. Treatment of **7** with methanolic sodium methoxide gave the methyl carboxylate **8** quantitatively. The structure of **9** was deduced from the ^{1}H-n.m.r. spectrum, which contained signals for H-2 and H-3 at δ 6.00 (dd, *J* 9 and 3 Hz) and 6.46 (d, *J* 3 Hz), respectively.

Epoxidation of **6** with *m*-chloroperbenzoic acid in 1,2-dichloroethane in the presence of phosphate buffer (pH 8) at 50° gave two crystalline epoxides **11** (66%) and **12** (28%). Their ^{1}H-n.m.r. spectra (270 MHz, $CDCl_3$) were almost first order, but it was difficult to differentiate the structures only on the basis of the $J_{3,4}$ values (0 and 2.2 Hz). According to the empirical rules[10], $J_{3,4}$ for the *trans*-epoxide **12** should be ~0 Hz. Treatment of **11** and **12** with an excess of sodium azide in the presence of ammonium chloride in refluxing aqueous 10% 2-methoxyethanol, followed by acetylation of the products, gave the azides **13** (44%) and **14** (35%), respectively. The ^{1}H-n.m.r. spectra of **13** and **14** contained signals at δ 3.98 (td, *J* 3.9, 7.5, and 7.5 Hz) and 4.00 (t, *J* 3.5 Hz), which were attributed to the axial protons on the carbon atoms bearing azido groups. Therefore, they should be formed through a diaxial opening of the epoxide rings as expected under these reaction conditions, and the structures of **11** and **12** were therefore assigned as shown.

Then, **11** was hydrolysed by refluxing aqueous acetone containing sulfuric acid, the product was acetylated, and 82% of the tetra-acetate **15** was obtained; the expected (1,3,4/2,5)-configuration of **15** was clearly assigned by the ^{1}H-n.m.r. spectrum. Compound **15** was also obtained (74%) by similar treatment of **12**. *O*-Deacetylation of **15** with methanolic sodium methoxide afforded the crystalline methyl carboxylate **16**.

EXPERIMENTAL

General methods. — Melting points were determined with a MEL-TEMP capillary melting-point apparatus and are uncorrected. Unless otherwise noted, ^{1}H-n.m.r. spectra were recorded for solutions in $CDCl_3$ (internal Me_4Si) with a Varian EM-390 (90 MHz) spectrometer. Spectra at 270 MHz were recorded with a Jeol GX-1 instrument. T.l.c. was performed on Wakogel B-10 (Wako Co., Osaka, Japan) with detection by charring with 10% sulfuric acid. Organic solutions were dried over anhydrous Na_2SO_4 and concentrated at <50° under diminished pressure.

DL-*(1,3,5/2,4)-2,3-Diacetoxy-4,5-dibromocyclohexane-1-carboxylic acid* (**2**). — A mixture of finely powdered DL-2-*exo*-bromo-4,8-dioxatricyclo[4.2.1.0^{3,7}]nonan-5-one[7] (**1**; 5.0 g, 23 mmol) and 20% hydrogen bromide in acetic acid (15 mL) was heated in a sealed tube at 80° for 2 days. The cooled mixture was poured into ice–water, and the precipitate was collected and recrystallised from ethanol to give **2** (5.4 g, 61%), as prisms, m.p. 206–207°. ^{1}H-N.m.r. data (90 MHz, CD_3OD): δ 2.04 and 1.96 (2 s, each 3 H, 2 OAc).

Anal. Calc. for $C_{11}H_{14}Br_2O_6$: C, 32.86; H, 3.51; Br, 39.75. Found: C, 33.10; H, 3.64; Br, 39.47.

Methyl DL-*(1,3,5/2,4)-2,3-diacetoxy-4,5-dibromocyclohexane-1-carboxylate* (**3**). — A mixture of **2** (1.0 g, 2.5 mmol), methanol (20 mL), and acetyl chloride (0.3 mL) was boiled under reflux for 2 h, then neutralised with sodium hydrogencarbonate, and concentrated. The residue was treated with acetic anhydride (5 mL) and pyridine (5 mL) at room temperature overnight. The mixture was concentrated, and a solution of the residue in ethyl acetate (20 mL) was washed with M hydrochloric acid, aqueous sodium hydrogencarbonate, and water, dried, and concentrated. The residue was recrystallised from ethanol to give **3** (0.99 g, 96%), as needles, m.p. 132.5–134.5°. ^{1}H-N.m.r. data (90 MHz): δ 3.70 (s, 3 H, Me), 2.66 and 2.00 (2 s, each 3 H, 2 OAc).

Anal. Calc. for $C_{12}H_{16}Br_2O_6$: C, 34.65; H, 3.88; Br, 38.42. Found: C, 34.86; H, 3.93; Br, 38.12.

Methyl DL-*(1,3,4,5/2)-2-acetoxy-5-bromo-3,4-epoxycyclohexane-1-carboxylate* (**4**). — To a stirred solution of **3** (1.0 g, 2.4 mmol) in chloroform (1.7 mL) and methanol (1.7 mL) was added methanolic M sodium methoxide (3.5 mL). The mixture was kept at room temperature for 3.5 h, then neutralised with M hydrochloric acid, and concentrated. The product was acetylated in the usual way to give **4** (0.42 g, 59%), as prisms, m.p. 68–70° (from ethanol). ^{1}H-N.m.r. data (90 MHz): δ 5.26 (d, 1 H, $J_{1,2}$ 10.5 Hz, H-2), 4.35 (ddd, 1 H, $J_{4,5}$ 1.5, $J_{5,6a}$ 12, $J_{5,6e}$ 6 Hz, H-5), 3.69 (s, 3 H, Me), 3.50 (dd, 1 H, $J_{3,4}$ 3.6 Hz, H-4), 3.28 (d, 1 H, H-3), 2.47 (ddd, 1 H, $J_{1,6a}$ 13.5, $J_{1,6e}$ 3 Hz, H-1), 2.09 (s, 3 H, OAc).

Anal. Calc. for $C_{10}H_{13}BrO_5$: C, 40.98; H, 4.47; Br, 27.26. Found: C, 41.14; H, 4.46; Br, 27.03.

DL-*(1,3/2)-2,3-Diacetoxycyclohex-4-ene-1-carboxylic acid* (**5**). — To a stirred mixture of **2** (5.0 g, 12.4 mmol) and acetic acid (100 mL) at 70° was added zinc dust (8.1 g, 124 mmol) in several portions. The mixture was then stirred at 70° for 0.5 h, the insoluble material was removed, and the filtrate was concentrated. A solution of the residue in ethyl acetate (100 mL) was washed with M hydrochloric acid and water, dried, and concentrated. Recrystallisation of the residue from carbon tetrachloride gave **5** (2.5 g, 83%), as prisms, m.p. 110–113°. ^{1}H-N.m.r. data (90 MHz): δ 8.73 (bs, 1 H, CO_2H), 5.92 (dt, 1 H, $J_{3,4}$ 3, $J_{4,5}$ 8.4 Hz, H-4), 5.60–5.28 (m, 3 H, H-2,3,5), 2.96 (ddd, 1 H, $J_{1,2}$ 15, $J_{1,6a}$ 7.5, $J_{1,6e}$ 3 Hz, H-1), 2.54–2.42 (m, 2 H, H-6*a*,6*e*), 2.04 (s, 6 H, 2 OAc).

Anal. Calc. for $C_{11}H_{14}O_6$: C, 54.54; H, 5.83. Found: C, 54.25; H, 5.75.

Methyl DL-*(1,3/2)-2,3-diacetoxycyclohex-4-ene-1-carboxylate* (**6**). — (*a*) A mixture of **3** (0.50 g, 1.2 mmol), zinc dust (0.8 g, 12 mmol), and acetic acid (15 mL) was stirred vigorously at 70° for 1 h, and then processed as described in the preparation of **5**. The product was crystallised from ethanol to give **6** (0.26 g, 84%), as prisms, m.p. 67–68.5°. ^{1}H-N.m.r. data (90 MHz): δ 5.87 (dt, 1 H, $J_{3,4}$ 3.8, $J_{4,5}$ 9.6, $J_{4,6}$ 3.8 Hz, H-4), 5.65–5.26 (m, 3 H, H-2,3,5), 3.67 (s, 3 H, Me), 2.93 (dt, 1 H, $J_{1,2}$ 10.7, $J_{1,6} = J_{1,6'} = 8.6$ Hz, H-1), 2.60–2.33 (m, 2 H, H-6,6'), 2.03 and 2.00 (2 s, each 3 H, 2 OAc).

Anal. Calc. for $C_{12}H_{16}O_6$: C, 56.25; H, 6.29. Found: C, 56.05; H, 6.30.

(*b*) Compound **5** (2.0 g, 8.3 mmol) was converted into **6** (2.2 g) quantitatively by treatment with diazomethane in methanol in the usual way.

Methyl DL-*(1,3/2,4,5)-2,3,4,5-tetra-acetoxycyclohexane-1-carboxylate* (**7**) *and methyl* DL-*(1/2,4)-2,4-diacetoxy-5-oxo-3-cyclohexene-1-carboxylate* (**9**). — A mixture of **6** (0.60 g, 2.3 mmol), aqueous 30% hydrogen peroxide (2.7 mL), and *tert*-butyl alcohol (16 mL) containing osmium tetraoxide (25 mg) was stirred at room temperature for 24 h. The mixture was then diluted with water (10 mL), and sodium sulfite was added to decompose the excess of hydrogen peroxide. The mixture was concentrated and the residue was acetylated in the usual way. The products were eluted from a column of silica gel [Wakogel C-300 (300 Mesh), 5 g] with 2-butanone–toluene (1:8) to give, first, **7** (0.54 g, 61%), as prisms, m.p. 150–152° (from ethanol). ^{1}H-N.m.r. data (270 MHz): δ 5.39 (bq, 1 H, $J_{4,5}$ 3, $J_{5,6a}$ 2.2, $J_{5,6e}$ 4.3 Hz, H-5), 5.32 (t, 1 H, $J_{2,3} = J_{3,4}$ = 9.9 Hz, H-3), 5.21 (dd, 1 H, $J_{1,2}$ 10.8 Hz, H-2), 4.88 (dd, 1 H, H-4), 3.62 (s, 3 H, Me), 2.94 (ddd, 1 H, $J_{1,6a}$ 14, $J_{1,6e}$ 4.3 Hz, H-1), 2.10 (dt, 1 H, J_{6gem} 14 Hz, H-6*e*), 2.07, 1.94, and 1.92 (3 s, 3, 6, and 3 H, 4 OAc), 1.83 (ddd, 1 H, H-6*a*).

Anal. Calc. for $C_{16}H_{22}O_{10}$: C, 51.34; H, 5.92. Found: C, 51.59; H, 5.98.

Eluted second was **9** (0.04 g, 7%), as prisms, m.p. 104–106° (from ethanol). ^{1}H-N.m.r. data (90 MHz): δ 6.46 (d, 1 H, $J_{2,3}$ 3 Hz, H-3), 6.00 (dd, 1 H, $J_{1,2}$ 9 Hz, H-2), 3.73 (s, 3 H, Me), 3.30 (symmetrical m, 1 H, H-1), 2.85–2.55 (m, 2 H, H-6,6′), 2.23 and 2.10 (2 s, each 3 H, 2 OAc).

Anal. Calc. for $C_{12}H_{14}O_7$: C, 53.33; H, 5.22. Found: C, 53.07; H, 5.24.

Methyl DL-*(1,3/2,4,5)-2,3,4,5-tetrahydroxycyclohexane-1-carboxylate* (**8**). — A mixture of **7** (100 mg, 0.26 mmol), methanolic M sodium methoxide (0.32 mL), and methanol (0.32 mL) was stirred at room temperature for 2 h, then neutralised with Amberlite IR-120B (H^+) resin, and concentrated. Crystallisation of the residue from ethanol gave **8** (33 mg, 62%), as prisms, m.p. 124.5–126°.

Anal. Calc. for $C_8H_{14}O_6$: C, 46.60; H, 6.84. Found: C, 46.53; H, 6.74.

DL-*(1,2,4/3,5)-1,2,3,4-Tetra-acetoxy-5-acetoxymethylcyclohexane* (**10**). — Compound **7** (100 mg, 0.26 mmol) was treated with lithium aluminum hydride (40 mg) in tetrahydrofuran (2 mL) at room temperature for 4 h. The mixture was processed in the usual way and the product was acetylated with acetic anhydride and pyridine at room temperature. The crude product was crystallised from ethanol to give **10** (54 mg, 52%), as prisms, m.p. 106–107°; lit.[9] m.p. 110–111°. The ^{1}H-n.m.r. spectrum was superposable on that of an authentic sample[9].

Methyl DL-*(1,3,4,5/2)-* (**11**) *and* DL-*(1,3/2,4,5)-2,3-diacetoxy-4,5-epoxycyclohexane-1-carboxylate* (**12**). — To a stirred mixture of **6** (100 mg, 0.39 mmol), 1,2-dichloroethane (3 mL), and phosphate buffer (5 mL, pH 8) at 50° was added a solution of *m*-chloroperbenzoic acid (0.15 g, 0.8 mmol) in 1,2-dichloroethane (2 mL). The mixture was stirred for 20 h at the same temperature, then treated with M sodium thiosulfate until the peroxy acid disappeared, and extracted with chloroform (30 mL). The extract was washed with aqueous sodium hydrogencarbo-

nate and water, and then concentrated. The products were eluted from a column of silica gel (Wakogel C-300, 5 g) with 2-butanone–toluene (1:8) to give, first, **11** (30 mg, 28%), as prisms, m.p. 104.5–105.5° (from ethanol). ^{1}H-N.m.r. data (270 MHz): δ 5.36 (dd, 1 H, $J_{1,2}$ 10.8, $J_{2,3}$ 8.4 Hz, H-2), 5.20 (dd, 1 H, $J_{3,4}$ 2.2 Hz, H-3), 3.63 (s, 3 H, Me), 3.38 (dd, 1 H, $J_{4,5}$ 3.6 Hz, H-4), 3.31 (ddd, 1 H, $J_{5,6a} = J_{5,6e}$ = 2.4 Hz, H-5), 2.70 (dt, $J_{1,6a} = J_{1,6e}$ = 9 Hz, H-1), 2.30 (dd, 2 H, H-6*a*,6*e*), 2.08 and 1.95 (2 s, each 3 H, 2 OAc).

Anal. Calc. for $C_{12}H_{16}O_7$: C, 52.95; H, 5.92. Found: C, 52.85; H, 5.88.

Eluted second was **12** (70 mg, 66%), as prisms, m.p. 56–57° (from ethanol). ^{1}H-N.m.r. data (270 MHz): δ 5.10 (dd, 1 H, $J_{1,2}$ 11.4, $J_{2,3}$ 8.7 Hz, H-2), 4.96 (d, 1 H, $J_{3,4}$ ~0 Hz, H-3), 3.60 (s, 3 H, Me), 3.26 (bs, 1 H, H-5), 3.00 (d, 1 H, $J_{4,5}$ 3.3 Hz, H-4), 2.62 (td, 1 H, $J_{1,6a}$ 11.4, $J_{1,6e}$ 5.2 Hz, H-1), 2.40 (ddd, 1 H, $J_{5,6e}$ 2.2, J_{6gem} 14.2 Hz, H-6*e*), 2.11 (ddd, 1 H, $J_{5,6}$ 1.8 Hz, H-6*a*), 2.02 and 1.92 (2 s, each 3 H, 2 OAc).

Anal. Found: C, 52.95; H, 5.78.

Methyl DL-*(1,3,4/2,5)-2,3,4-triacetoxy-5-azidocyclohexane-1-carboxylate* (**13**). — A mixture of **11** (50 mg, 0.18 mmol), sodium azide (14 mg, 0.22 mmol), ammonium chloride (9.6 mg, 0.36 mmol), and aqueous 10% 2-methoxyethanol (5 mL) was stirred at 110° for 2 h, and then concentrated, and the residue was acetylated in the usual way. The product was eluted from a column of silica gel (Wakogel C-300, 10 g) with 2-butanone–toluene (1:15) to give **13** (34 mg, 44%), m.p. 74–75°. ^{1}H-N.m.r. data (90 MHz): δ 5.45 (t, 1 H, $J_{1,2} = J_{2,3}$ = 6.8 Hz, H-2), 5.30–5.10 (m, 2 H, H-3,4), 3.98 (td, 1 H, $J_{4,5}$ 3.9, $J_{5,6a} = J_{5,6e}$ = 7.5 Hz, H-5), 3.73 (s, 3 H, Me), 2.73 (td, 1 H, $J_{1,2} = J_{1,6a}$ = 7.2, $J_{1,6e}$ 4.5 Hz, H-1), 2.12, 2.07, and 2.02 (3 s, 3, 3, and 3 H, 3 OAc).

Anal. Calc. for $C_{14}H_{19}N_3O_8$: C, 47.06; H, 5.36; N, 11.76. Found: C, 47.15; H, 5.51; N, 11.40.

Methyl DL-*(1,3,4/2,5)-2,3,5-triacetoxy-4-azidocyclohexane-1-carboxylate* (**14**). — Compound **12** (50 mg, 0.18 mmol) was treated with sodium azide as described in the preparation of **13**. T.l.c. revealed two products [R_F 0.50 and 0.59 in 2-butanone–toluene (1:2)]. Elution of the mixture from a column of silica gel (Wakogel C-300, 10 g) with 2-butanone–toluene (1:6) gave mainly the slower-moving component (22 mg), which was acetylated in the usual way to give **14** (27 mg, 35%), which spontaneously crystallised as prisms, m.p. 92.5–94°. ^{1}H-N.m.r. data (90 MHz): δ 5.52 (t, 1 H, $J_{1,2} = J_{2,3}$ = 9 Hz, H-2), 5.20 (dd, 1 H, $J_{3,4}$ 3.5 Hz, H-3), 5.07 (q, 1 H, $J_{4,5} = J_{5,6a} = J_{5,6e}$ = 3.6 Hz, H-5), 4.00 (t, 1 H, H-4), 3.72 (s, 3 H, Me), 2.87 (td, $J_{1,6a}$ 10.5, $J_{1,6e}$ 5.3 Hz, H-1), 2.17, 2.12, and 2.07 (3 s, 3, 3, and 3 H, 3 OAc).

Anal. Calc. for $C_{14}H_{19}N_3O_8$: C, 47.06; H, 5.36; N, 11.76. Found: C, 46.94; H, 5.39; N, 11.03.

Methyl DL-*(1,3,4/2,5)-2,3,4,5-tetra-acetoxycyclohexane-1-carboxylate* (**15**). — (*a*) A mixture of **11** (50 mg, 0.18 mmol) and acetone (1.3 mL) containing 10% sulfuric acid (0.2 mL) was boiled under reflux for 3 h, then neutralised with sodium

hydrogencarbonate, and concentrated. The residue was acetylated in the usual way and the product was eluted from a column of silica gel (Wakogel C-300, 3 g) with 2-butanone–toluene (1:8) to give **15** (55 mg, 82%) as a syrup. ^{1}H-N.m.r. data (90 MHz): δ 5.46 (t, 1 H, $J_{1,2} = J_{2,3} = 9.4$ Hz, H-2), 5.33–5.17 (m, 2 H, H-3,4), 5.07 (q, 1 H, $J_{4,5} = J_{5,6a} = J_{5,6e} = 3$ Hz, H-5), 3.70 (s, 3 H, Me), 2.87 (td, 1 H, $J_{1,6a}$ 9.4, $J_{1,6e}$ 6 Hz, H-1), 2.12, 2.01, and 1.99 (3 s, 6, 3, and 3 H, 4 OAc).

Anal. Calc. for $C_{16}H_{22}O_{10}$: C, 51.34; H, 5.92. Found: C, 51.57; H, 5.96.

(*b*) Compound **12** (100 mg, 0.36 mmol) was treated with aqueous acetone containing sulfuric acid as described above. The acetylated products were eluted from a column of silica gel (Wakogel C-300, 9 g) with 2-butanone–toluene (1:8) to give mainly **15** (100 mg, 74%), together with an unidentified syrupy compound (10 mg).

Methyl DL-*(1,3,4/2,5)-2,3,4,5-tetrahydroxycyclohexane-1-carboxylate* (**16**). — Compound **15** (150 mg, 0.40 mmol) was treated with methanolic sodium methoxide as described in the preparation of **8** to give, after recrystallisation from ethanol, **16** (30 mg, 36%), as prisms, m.p. 148–149°.

Anal. Calc. for $C_8H_{14}O_6$: C, 46.60; H, 6.84. Found: C, 46.88; H, 6.81.

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