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Transformation of D-Xylose to (1*R*,2*R*,3*R*,4*R*)-2,3,4-Trihydroxy-1-(hydroxymethyl)cyclopentane, Pseudo-β-D-arabinofuranose

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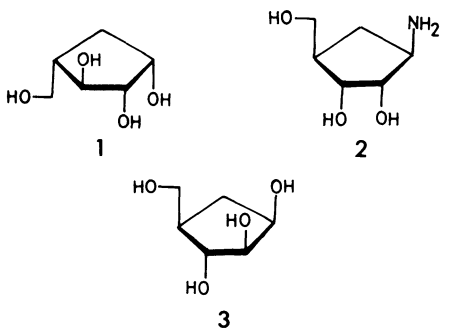
The known 3-*O*-benzyl-D-xylose was converted into methyl (4*S*,5*R*,6*R*)-4,6,7-triacetoxy-5-benzyloxy-2-(methoxycarbonyl)heptanoate (**8**) by employing Knoevenagel condensation of 2,4,5-tri-*O*-acetyl-3-*O*-benzyl-*aldehydo*-D-xylose with dimethyl malonate as a key reaction. *O*-Deacetylation of **8** and successive glycol cleavage followed by acetylation gave a mixture of (1*S*,4*R*,5*R*,6*R*)-5-acetoxy-6-benzyloxy-4-methoxycarbonyl-2-oxobicyclo[2.2.1]heptan-3-one and dimethyl (2*R*,3*R*,4*S*)-2,4-diacetoxy-3-benzyloxy-1,1-cyclopentanedicarboxylate (**12**), which was converted into **12** exclusively. This enantiomerically pure highly oxygenated cyclopentane dicarboxylate **12** was converted into (3*S*,4*S*)-3-benzyloxy-1-(*t*-butyldiphenylsilyloxymethyl)-4-hydroxy-1-cyclopentene (**15**) by 1) thermal demethoxycarbonylation accompanied by β-elimination of the acetoxyl group, 2) diisobutylaluminium hydride reduction, and 3) selective protection of thus formed 1-cyclopentene-1-methanol. Pyridinium chlorochromate oxidation of **15** followed by reduction with sodium borohydride gave a 6.4 : 1 mixture of (3*S*,4*R*)-3-benzyloxy-1-(*t*-butyldiphenylsilyloxymethyl)-4-hydroxy-1-cyclopentene (**18**) and **15**. Hydroboration of *O*-desilyl derivative of **18** proceeded stereoselectively from the less hindered α-face, and (1*R*,2*R*,3*R*,4*R*)-2,4-diacetoxy-1-acetoxymethyl-3-(benzyloxy)cyclopentane (**21**) was obtained after acetylation. Deprotection of **21** gave pseudo-β-D-arabinofuranose.

In our consecutive synthetic efforts on the access to enantiomerically pure highly oxygenated six- and five-membered carbocycles from carbohydrates, we developed several novel approaches to pseudo-sugars [stereoisomers of 2,3,4,5-tetrahydroxy-1-(hydroxymethyl)cyclohexane and those of 2,3,4-trihydroxy-1-(hydroxymethyl)cyclopentane][1a-f] and shikimate[1g] syntheses. In recent articles,[1e] we described the synthesis of (1*S*,2*S*,3*S*,4*S*)-2,3,4-trihydroxy-1-(hydroxymethyl)-cyclopentane, pseudo-β-L-arabinofuranose (**1**), starting from D-erythrose. The synthetic utility of **1** was verified by conversion of **1** into some enantiomerically pure pseudo-pentofuranoses and a key intermediate for the carbocyclic antibiotic (−)-aristeromycin synthesis, (1*R*,2*S*,3*R*,4*R*)-2,3-dihydroxy-4-hydroxymethyl-1-cyclopentanamine (**2**).[2] In this article, we describe a synthesis of (1*R*,2*R*,3*R*,4*R*)-2,3,4-trihydroxy-1-(hydroxymethyl)cyclopentane (**3**), an enantiomer of pseudo-β-L-arabinofuranose **1**. The synthesis of **3** was started from the known 3-*O*-benzyl-D-xylose, and the crucial cyclopentane ring formation was accomplished by an intramolecular aldol cyclization strategy, which has been developed in our laboratory for the synthesis of **1**.[1e]



Results and Discussion

The starting material, 3-*O*-benzyl-D-xylose (**4**), was prepared from D-glucose by a modified known procedure (Scheme).[3] Dithioacetal formation of **4** with ethanethiol in concd HCl followed by acetylation gave an acyclic diethyl dithioacetal **5** in 95% yield. An aldehyde group was regenerated by treatment of **5** with mercury(II) chloride in an aqueous acetonitrile giving 2,4,5-tri-*O*-acetyl-3-*O*-benzyl-*aldehydo*-D-xylose (**6**). The Knoevenagel condensation of **6** with dimethyl malonate in a mixture of acetic anhydride and pyridine resulted in a formation of α,β-unsaturated diester **7**, which was reduced with sodium borohydride at −15 °C to give the key intermediate **8** by a 1,4-conjugate addition of the hydride. The overall yield of **8** from **5** was 62%. *O*-Deacetylation of **8** with sodium methoxide provided an inseparable mixture of (4*S*,5*R*,6*R*)-5-benzyloxy-4,6,7-trihydroxy-2-(methoxycarbonyl)heptan-1,4-olide (**9**) and methyl (4*S*,5*R*,6*R*)-5-benzyloxy-4,6,7-trihydroxy-2-(methoxycarbonyl)heptanoate (**10**). The stereochemistry at C-2 of **9** was not determined. The glycols at C-6 and C-7 of the mixture **9** and **10** were cleaved by sodium periodate in an aqueous dioxane and the products were acetylated to give a mixture of (1*S*,4*R*,5*R*,6*R*)-5-acetoxy-6-benzyloxy-4-(methoxycarbonyl)-2-oxabicyclo[2.2.1]heptan-3-one (**11**) and dimethyl (2*R*,3*R*,4*S*)-2,4-diacetoxy-3-benzyloxy-1,1-cyclopentanedicarboxylate (**12**). The mixture was separated by silica-gel chromatography, and the ratio of **11** and **12** was approximately 8 : 1. As expacted, the desired intramolecular aldol cyclization occurred under the conditions of glycol cleavage. Based on this

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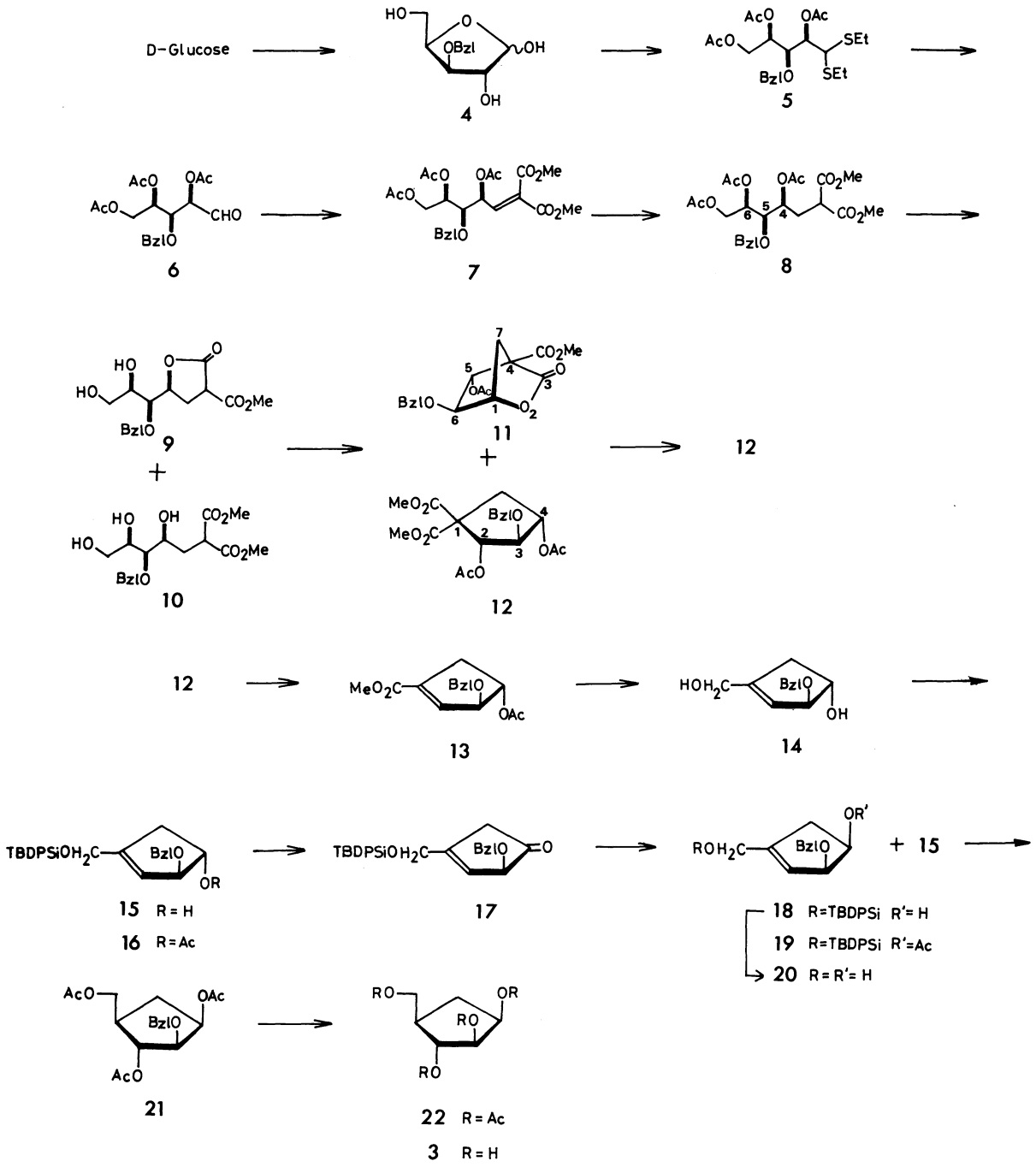

Scheme.

result, we assume that the ratio of **9** and **10** is same as that of **11** and **12**. On the ^{1}H NMR spectrum of **11**, H-5 (H-C-OAc) appeared at δ 5.56 as a broad singlet. This indicates that H-5 and H-6 (H-C-OBzl) is an endo-exo relationship as depicted.[4] The stereochemistry of the newly introduced chiral center on **12** (C-2) was assigned to be (R) based on the ^{1}H NMR spectrum, in which H-2 appeared at δ 5.90 as a doublet with $J_{2,3}$=3 Hz.[5] When a methanol solution of the mixture **11** and **12** in the presence of Amberlite IR-120 (H^+) resin was refluxed, the bicyclic compound **11** was converted into **12** after acetylation. The overall yield of **12** from **8** was 59% without separation of the mixture **11** and **12**. The fact that the sterically less crowded products **11** and **12** were formed predominantly on the aldol cyclization is parallel to our previous result on the aldol cyclization performed for the similar model.[1e]

Thermal demethoxycarbonylation of **12** in an aqueous DMSO at 110—160 °C in the presence of NaCl accompanied a β-elimination of the acetoxyl group to give methyl (3*S*,4*S*)-4-acetoxy-3-benzyloxy-1-cyclopentene-1-carboxylate (**13**) as a somewhat volatile liquid. The crude **13** was reduced with diisobutylaluminium hydride (DIBAL-H) at −78 °C to give (3*S*,4*S*)-3-benzyloxy-4-hydroxy-1-cyclopentene-1-methanol (**14**) in 75% yield. The primary hydroxyl group in **14** was

protected as a silyl ether with *t*-butylchlorodiphenylsilane and imidazole to provide **15** in 73% yield. Compound **15** was oxidized with pyridinium chlorochromate (PCC) giving (3*S*)-3-benzyloxy-1-(*t*-butyldiphenylsilyloxymethyl)-1-cyclopenten-4-one (**17**), which was reduced with sodium borohydride in methanol solution. The reduction gave (3*S*,4*R*)-1-cyclopentene-1-methanol **18** and **15** in 64 and 10% yield, respectively. The stereoselectivity of the reduction was 6.4:1 with preferential hydride attack from the less hindered α-side. The inversion at C-4 in **15** to *R* configuration was apparent by comparing the ^{1}H NMR sectra of the corresponding acetates **16** and **19**, both of which were prepared by acetylation of **15** and **18**. The *t*-butyldiphenylsilyl group was deprotected with tetrabutylammonium fluoride to give **20** as crystals in 90% yield. Hydroboration of **20** with borane-THF complex, oxidation of the product with hydrogen peroxide in an aqueous NaOH solution followed by acetylation gave a fully protected pseudo-β-D-arabinofuranose, (1*R*,2*R*,-3*R*,4*R*)-2,4-diacetoxy-1-acetoxymethyl-3-(benzyloxy)-cyclopentane (**21**), in 65% yield. The hydroboration occurred stereoselectively from the less hindered α-face of **20**, and the (1*S*,2*S*,3*R*,4*R*)-diastereomer, a derivative of pseudo-α-L-ribofuranose, was not detected. Removal of the benzyl group in **21** with cyclohexene in the presence of 20% $Pd(OH)_2$ on charcoal[6] followed by acetylation gave a fully acetylated pseudo-β-D-arabinofuranose **22** in 90% yield. The ^{1}H NMR spectrum of **22** was identical with that of the L-enantiomer,[1e] and the $[\alpha]_D$ value of **22** ($[\alpha]_D^{23}$ −4.8°) coincided with that of the L-enantiomer ($[\alpha]_D^{23}$ +4.1°). *O*-Deacetylation of **22** with sodium methoxide gave pseudo-β-D-arabinofuranose (**3**) in a quantitative yield.[7]

Experimental

Gereral. Reactions were carried out at room temperature unless otherwise described. Reaction mixture, extracts, and fraction of column chromatography were concentrated under a reduced pressure at below 40 °C with a bath. Melting points were determined with a Mitamura Riken micro melting point apparatus and are uncorrected. Specific rotation was measured by a Jasco DIP-4 polarimeter with a 10 mm cell. Column chromatography was performed with Silicagel 60 (Katayama Chemicals, K070), and thin-layer chromatography (TLC) by a glass plate coated with Kieselgel 60 GF_{254} (Merck), followed by UV light detection and charred with sulfuric acid. IR spectra were recorded with a Hitachi 225 spectrometer or with a Jasco A-202 spectrometer. ^{1}H NMR spectra were recorded with a Varian EM-390 (90 MHz) spectrometer for solutions in $CDCl_3$ with an internal standard of Me_4Si. High resolution mass spectra were obtained by a Hitachi M-80 spectrometer.

Dichloromethane and *N*,*N*-dimethylformamide (DMF) were dried over CaH_2 and distilled. Pyridine was distilled over NaOH. Tetrahydrofuran (THF) was distilled over $LiAlH_4$ and then over Na-benzophenone.

3-*O*-Benzyl-D-xylose (4). This compound was prepared from D-glucose according to the reported procedure.[3] In our case, acid hydrolysis of the intermediate, 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-xylofuranose, was performed in refluxing 80% aqueous acetic acid in place of the reported sulfuric acid in refluxing 50% methanol. The overall yield of **4** from 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose was 51%. **4**: Mp 115—116 °C, lit,[3] 89—91 °C. Found: C, 59.92; H, 6.67%. Calcd for $C_{12}H_{16}O_5$: C, 59.99; H, 6.71%.

2,4,5-Tri-*O*-acetyl-3-*O*-benzyl-D-xylose Diethyl Dithioacetal (5). A solution of **4** (23.5 g, 98.0 mmol) in concd HCl (80 ml) in the presence of ethanethiol (120 ml) was stirred at −15 °C for 30 min, and neutralized by addition of aqueous ammonia. The solution was concentrated, and the residue was suspended in ethanol, then concentrated. Ethanol (1 l) was added to the residue, and insoluble solids were removed by filtration, washed with ethanol (1 l). The combined filtrate and washing were concentrated, and the residue was acetylated with acetic anhydride (100 ml) in pyridine (100 ml) for 13 h. The mixture was concentrated, and the residue was chromatographed on silica gel (500 g, ethyl acetate-hexane=1:15), and the fraction corresponding to R_f 0.78 (ethyl acetate-hexane=1:3) was concentrated to give **5** (44.1 g, 95%) as a colorless syrup. **5**: $[\alpha]_D^{24.5}$ −5.3° (*c* 0.71, $CHCl_3$); IR $\nu_{max}^{CHCl_3}$ 2950, 2860, 1740, 1490, 1450, 1370, 1210, 1110, 1070 cm^{-1}; ^{1}H NMR δ=1.21, 1.23 (3H×2, each t, *J*=6 Hz, 2×$SCH_2C\underline{H}_3$), 2.01, 2.04, 2.10 (3H×3, each s, 3×$OCOCH_3$), 2.48—2.86 (4H, m, 2×$SC\underline{H}_2CH_3$), 3.93—4.53 (4H, m, H-1,3,5, 5′), 4.73 (2H, s, $OC\underline{H}_2C_6H_5$), 5.18—5.39 (2H, m, H-2,4), 7.31 (5H, s, $OCH_2C_6\underline{H}_5$). Found: C, 56.00; H, 6.73%. Calcd for $C_{22}H_{32}O_7S_2$: C, 55.91; H, 6.83%.

Methyl (4*S*,5*R*,6*R*)-4,6,7-Triacetoxy-5-benzyloxy-2-(methoxycarbonyl)heptanoate (8). A solution of **5** (8.39 g, 17.6 mmol) in a mixture of acetonitrile (200 ml) and water (200 ml) in the presence of mercury(II) chloride (48.2 g, 176.0 mmol) and calcium carbonate (20.25 g, 202 mmol) was stirred for 30 min. Insoluble solids were removed by filtration with a Celite-pad, washed with ethyl acetate (1 l). The combined filtrate and washing were washed with 1 mol dm^{-3} aqueous KI solution (400 ml×5), 20% aqueous sodium thiosulfate solution (400 ml×3), and brine (400 ml×2) successively. The organic layer was dried over Na_2SO_4 and concentrated to give crude **6**, which was subjected to the Knoevenagel condesation directly. **6**: ^{1}H NMR δ=2.00, 2.19 (6H and 3H, each s, 3×$OCOCH_3$), 3.90—4.45 (3H, m, H-3, 5,5′), 4.70 (2H, s, $OC\underline{H}_2C_6H_5$), 5.20—5.45 (2H, m, H-2, 4), 7.36 (5H, s, $OCH_2C_6\underline{H}_5$), 9.60 (1H, s, CHO).

A solution of the crude **6** and dimethyl malonate (20.1 ml, 176 mmol) in a mixture of acetic anhydride (63 ml) and pyridine (90 ml) was stirred for 36 h. The mixture was diluted with ethyl acetate (900 ml) and washed with water (300 ml×3). The aqueous layer was extracted with ethyl acetate (300 ml×3). The combined organic layers were dried over Na_2SO_4 and concentrated to give crude **7**, which was used to next step without purification. In a separate small scale experiment, the crude **7** was purified on silica-gel chromatography (ethyl acetate-hexane=1:3). **7** as a colorless syrup, TLC R_f 0.31 (ethyl acetate-hexane=1:3): $[\alpha]_D^{24}$ +10.0° (*c* 1.15, $CHCl_3$); IR $\nu_{max}^{CHCl_3}$ 2925, 1730, 1650, 1490, 1425, 1360, 1210, 1060^{-1}; ^{1}H NMR δ=2.00, 2.05 (3H and 6H, each s, 3×$OCOCH_3$), 3.79 (6H, s, 2×$COOCH_3$), 3.66—4.53 (3H, m, H-5,7,7′), 4.65 (2H, s, $OC\underline{H}_2C_6H_5$), 5.10—5.53 (1H, m, H-6), 5.72—5.95 (1H, m, H-4), 6.92 (1H, d, *J*=7 Hz, H-3), 7.33 (5H, s, $OCH_2C_6\underline{H}_5$).

A solution of the crude **7** in methanol (150 ml) containing

sodium borohydride (799 mg, 21.1 mmol) was stirred at −15 °C for 30 min. After concentration of the mixture to ca. 50 ml, water (300 ml) was added. This aqueous solution was extracted with dichloromethane (300 ml×3), and the extracts were dried over Na_2SO_4, then concentrated. The residue was chromatographed on silica gel (500 g, ethyl acetate-hexane=1 : 5). The fraction corresponding to R_f 0.47 (ethyl acetate-hexane=2 : 3) was concentrated to give **8** (5.24 g, 62%) as a colorless syrup. **8**: $[\alpha]_D^{25.5}$ −0.6° (*c* 1.32, $CHCl_3$); IR $\nu_{max}^{CHCl_3}$ 2950, 1735, 1435, 1370, 1225 cm^{-1}; ^1H NMR δ=1.98, 2.01, 2.05 (3H×3, each s, 3×$OCOCH_3$), 1.86—2.30 (2H, m, H-3,3′), 3.30 (1H, dd, *J*=6 and 9.5 Hz, H-2), 3.61—4.45 (3H, m, H-5,7,7′), 3.70, 3.72 (3H×2, each s, 2×$COOCH_3$), 4.65 (2H, s, $OCH_2C_6H_5$), 5.00—5.45 (2H, m, H-4, 6), 7.32 (5H, s, $OCH_2C_6H_5$). Found: C, 57.16; H, 6.26%. Calcd for $C_{23}H_{30}O_{11}$: C, 57.26; H, 6.27%.

Dimethyl (2*R*,3*R*,4*S*)-2,4-Diacetoxy-3-benzyloxy-1,1-cyclopentanedicarboxylate (12). A solution of **8** (6.50 g, 13.5 mmol) in methanol (160 ml) containing sodium methoxide (1 mol dm^{-3} in methanol, 20.0 ml, 20.0 mmol) was stirred at 0 °C for 2 h. The mixture was neutralized with Amberlite IR-120 (H^+), and the resin was removed by filtration, washed with methanol. The combined filtrate and washing were concentrated to give an approximately 8 : 1 mixture of **9** and **10**, which was used directly to next step.

To a solution of the mixture of **9** and **10** in dioxane (190 ml), an aqueous solution (22 ml) of sodium periodate (4.28 g, 20.0 mmol) was added with stirring. After stirring the mixture for 50 min, an aqueous solution (15 ml) of the oxidizing reagent (2.89 g, 13.5 mmol) was added. The mixture was stirred additional 1 h, and insoluble solids were removed by filtration. The filtrate was diluted with water (500 ml), and extracted with dichloromethane (800 ml×3). The extract was dried over Na_2SO_4 and concentrated. The residue was acetylated with acetic anhydride (60 ml) in pyridine (60 ml) for 18 h. The mixture was concentrated, and the residue was dissolved in toluene and then concentrated to give a mixture of **11** and **12**, which was subjected to next step without separation. In a separate experiment, **8** (456 mg) was converted to the mixture of **11** and **12** by the same procedure as described above. The mixture was separated by chromatography on silica gel (ethyl acetate-hexane=1 : 10) to give **11** (147 mg, 47%) and **12** (24 mg, 6%). **11** as a colorless syrup, TLC R_f 0.55 (ethyl acetate-hexane=1 : 2): $[\alpha]_D^{25}$ +87.8° (*c* 1.32, $CHCl_3$); IR $\nu_{max}^{CHCl_3}$ 2960, 1800, 1740, 1450, 1440, 1375, 1350, 1330, 1310, 1280, 1220, 1165, 1090 cm^{-1}; ^1H NMR δ=2.10 (3H, s, $OCOCH_3$), 2.53—2.72 (2H, m, H-7,7′), 3.66—4.00 (1H, m, H-6), 3.79 (3H, s, $COOCH_3$), 4.62 (1H, broad s, H-1), 4.70 (2H, ABq, *J*=11 Hz, $OCH_2C_6H_5$), 5.56 (1H, broad s, H-5), 7.32 (5H, s, $OCH_2C_6H_5$). Found: C, 61.04; H, 5.57%. Calcd for $C_{17}H_{18}O_7$: C, 61.05; H, 5.43%.

A solution of the crude mixture of **11** and **12** in methanol (200 ml) was refluxed in the presence of Amberlite IR-120 (H^+) (30 g). The resin was added after 6 h (20 g), 12 h (30 g), 16 h (15 g), 17 h (20 g), and 19 h (20 g) successively, and the mixture was refluxed additional 4 h. After removal of the resin by filtration and washing with methanol, the combined filtrate and washing were concentrated. The residue was acetylated with acetic anhydride (110 ml) in pyridine (110 ml) for 18 h. The mixture was concentrated with toluene. The residue was chromatographed on silica gel (130 g, ethyl acetate-hexane=1 : 7), and the fraction corresponding to R_f 0.59 (ethyl acetate-hexane=1 : 2) was concentrated to give **12** (3.26 g, 59%) as a colorless syrup. **12**: $[\alpha]_D^{27}$ +40.8° (*c* 0.53, $CHCl_3$); IR $\nu_{max}^{CHCl_3}$ 2950, 2910, 2850, 1730, 1430, 1370, 1230 cm^{-1}; ^1H NMR δ=2.02 (6H, s, 2×$OCOCH_3$), 2.30—2.45, 2.75—3.10 (1H×2, each m, H-5,5′), 3.69, 3.73 (3H×2, each s, 2×$COOCH_3$), 3.97 (1H, t, *J*=3 Hz, H-3), 4.63 (2H, d, *J*=1.5 Hz, $OCH_2C_6H_5$), 4.83—5.15 (1H, m, H-4), 5.90 (1H, d, *J*=3 Hz, H-2), 7.30 (5H, s, $OCH_2C_6H_5$). Found: C, 58.58; H, 6.04%. Calcd for $C_{20}H_{24}O_9$: C, 58.82; H, 5.92%.

(3*S*,4*S*)-3-Benzyloxy-4-hydroxy-1-cyclopentene-1-methanol (14). A solution of **12** (556 mg, 1.36 mmol) in a mixture of DMSO (44 ml) and water (2 ml) containing NaCl (239 mg, 4.09 mmol) was heated from 110 to 160 °C for 2 h. The mixture was heated at 160 °C additional 4 h. After cooling to room temperature, water (300 ml) was added. The aqueous mixture was extracted with dichloromethane (300 ml×2). The extract was dried over Na_2SO_4 and concentrated at below 9 °C until ca. 10 ml volume. The remaining liquid contained **13**, which was reduced directly. In a separate experiment, the crude **13** was purified on silica gel chromatography (ethyl acetate-hexane=1 : 15). **13** as a somewhat volatile colorless liquid, TLC R_f 0.73 (ethyl acetate-hexane=1 : 2): $[\alpha]_D^{27}$ +94.7° (*c* 0.44, $CHCl_3$): IR $\nu_{max}^{CHCl_3}$ 2950, 1720, 1630, 1435, 1370, 1290, 1240, 1220, 1170 cm^{-1}; ^1H NMR δ=2.01 (3H, s, $OCOCH_3$), 2.25—2.60, 3.04—3.40 (1H×2, each m, H-5,5′), 3.75 (3H, s, $COOCH_3$), 4.53—4.70 (1H, m, H-3), 4.63 (2H, s, $OCH_2C_6H_5$), 5.20—5.39 (1H, m, H-4), 6.60—6.75 (1H, m, H-2), 7.33 (5H, s, $OCH_2C_6H_5$). High-resolution mass spectrum, Found: *m/z* 290.1147, Calcd for $C_{16}H_{18}O_5$: M, 290.1152.

To a solution of the above concentrate in dichloromethane (14 ml), DIBAL-H (1.5 mol dm^{-3} in toluene, 18.1 ml, 27.2 mmol) was added at −78 °C with stirring under an argon atmosphere. The reducing reagent was added after 100 min (18.1 ml), 140 min (18.1 ml), and 160 min (9.1 ml) successively at −78 °C. The mixture was stirred at the same temperature additional 80 min and diluted with water (70 ml). The resulting insoluble solids were removed by filtration. The filtrate was diluted with water (200 ml) and extracted with dichloromethane (300 ml×6). The extract was dried over Na_2SO_4 and concentrated. The residue was chromatographed on silica gel (15 g, ethyl acetate-hexane=2 : 3) and the fraction corresponding to R_f 0.18 (ethyl acetate-hexane=1 : 1) was concentrated to give **14** (225 mg, 75%) as a colorless syrup. **14**: $[\alpha]_D^{25}$ +100.0° (*c* 0.99, $CHCl_3$); IR $\nu_{max}^{CHCl_3}$ 3350, 2900, 2850, 1650, 1490, 1455 cm^{-1}; ^1H NMR δ=1.95—2.26, 2.50—2.87 (1H×2, each m, H-5,5′), 3.15—3.65 (2H, broad s, 2×OH), 4.01 (2H, s, CH_2OH), 4.20—4.43 (2H, m, H-3,4), 4.54 (2H, s, $OCH_2C_6H_5$), 5.60 (1H, broad s, H-2), 7.30 (5H, s, $OCH_2C_6H_5$). High-resolution mass spectrum, Found: *m/z* 220.1097, Calcd for $C_{13}H_{16}O_3$: M, 220.1073.

(3*S*,4*S*)-3-Benzyloxy-1-(*t*-butyldiphenylsilyloxymethyl)-4-hydroxy-1-cyclopentene (15). To a solution of **14** (218 mg, 0.99 mmol) in DMF (4 ml), *t*-butylchlorodiphenylsilane (0.16 ml, 0.60 mmol) and imidazole (81 mg, 1.19 mmol) were added with stirring. Each 0.08 ml of the silylating reagent and 40.5 mg of imidazole was added after 5, 24, and 29 h. The mixture was stirred totally 31 h, and diluted with ethyl acetate (300 ml). The solution was washed with water (50 ml×3). The organic layer was dried over Na_2SO_4 and concentrated. The residue was chromatographed on silica gel (15 g, ethyl acetate-hexane=1 : 8), and the fraction corresponding to R_f 0.45 (ethyl acetate-hexane=1 : 3) was concentrated to give **15** (332 mg, 73%) as a colorless syrup. **15**: $[\alpha]_D^{20}$

+50.4° (*c* 1.00, $CHCl_3$); IR $\nu_{max}^{CHCl_3}$ 3420, 3075, 3055, 2960, 2940, 2860, 1590, 1500, 1470, 1460, 1430, 1390, 1360 cm^{-1}; ^1H NMR δ=1.02 (9H, s, $OSiC(CH_3)_3$), 1.88—2.22 (2H, m, H-5, OH), 2.45—2.82 (1H, m, H-5′), 4.08 (2H, s, CH_2OSi), 4.13—4.40 (2H, m, H-3,4), 4.49 (2H, s, $OC\underline{H}_2C_6H_5$), 5.60 (1H, m, H-2), 7.20—7.75 (15H, m, $OCH_2C_6\underline{H}_5$, $OSi(C_6\underline{H}_5)_2$). Found: C, 76.02; H, 7.55%. Calcd for $C_{29}H_{34}O_3Si$: C, 75.94; H, 7.47%.

(3*S*,4*S*)-4-Acetoxy-3-benzyloxy-1-(*t*-butyldiphenylsilyloxymethyl)-1-cyclopentene (16). Compound **15** (15 mg, 0.032 mmol) was acetylated with acetic anhydride (1 ml) in pyridine (1 ml) for 2 h. The mixture was concentrated, and the residue was purified on preparative TLC (20×20 cm, Merck Kieselgel 60 PF_{254}, ethyl acetate-hexane=1 : 3). The band corresponding to R_f 0.85 (ethyl acetate-hexane=1 : 3) was extracted with $CHCl_3$ and concentrated to give **16** (14 mg, 87%) as a colorless syrup. **16**: $[\alpha]_D^{19.5}$ +45.8°(*c* 0.65, $CHCl_3$); IR $\nu_{max}^{CHCl_3}$ 2930, 2860, 1725, 1450, 1430, 1370, 1250, 1170, 1110 cm^{-1}; ^1H NMR δ=0.85 (9H, s, $OSiC(CH_3)_3$), 1.83 (3H, s, $OCOCH_3$), 1.75—2.10, 2.50—2.90 (1H×2, each m, H-5,5′), 4.00 (2H, s, CH_2OSi), 4.20—4.50 (1H, m, H-3), 4.41 (2H, d, *J*=3 Hz, $OC\underline{H}_2C_6H_5$), 4.98—5.23 (1H, m, H-4), 5.55 (1H, d, *J*=2 Hz, H-2), 7.10—7.60 (15H, m, $OCH_2C_6\underline{H}_5$, $OSi(C_6H_5)_2$). Found: C, 74.18; H, 7.32%. Calcd for $C_{31}H_{36}O_4Si$: C, 74.36; H, 7.25%.

(3*S*,4*R*)-3-Benzyloxy-1-(*t*-butyldiphenylsilyloxymethyl)-4-hydroxy-1-cyclopentene (18). To a solution of **15** (251 mg, 0.55 mmol) in dichloromethane (24 ml), PCC (2.36 g, 10.9 mmol) and molecular sieves (4A, powder, 1 g) were added. The mixture was stirred for 30 min. The mixture was applied on silica-gel column (40 g), and eluted with ether. The fraction corresponding to R_f 0.79 (ethyl acetate-hexane =1 : 4) was concentrated to give **17** (223 mg) as a colorless syrup. To a solution of **17** in methanol (8 ml), sodium borohydride (31 mg, 0.82 mmol) was added with stirring at 0 °C. After stirring at 0 °C for 1 h, the mixture was neutralized with 1 mol dm^{-3} HCl and diluted with water (50 ml). The solution was extracted with dichloromethane (80 ml×4), and the extracts were combined, dried over Na_2SO_4, and concentrated. The residue was chromatographed on silica gel (11 g, ethyl acetate-hexane=1 : 25), and the fraction corresponding to R_f 0.53 (ethyl acetate-hexane=1 : 4) was concentrated to give **18** (160 mg, 64%) as a colorless syrup. The fraction corresponding to R_f 0.33 was concentrated to give **15** (25 mg, 10%) **18**: $[\alpha]_D^{21.5}$ +33.1° (*c* 1.17, $CHCl_3$); IR $\nu_{max}^{CHCl_3}$ 3550, 2940, 2860, 1650, 1590, 1470, 1430, 1390, 1160, 1110 cm^{-1}; ^1H NMR δ=1.09 (9H, s, $OSiC(CH_3)_3$), 2.28—2.50 (2H, m, H-5,5′), 2.00—3.00 (1H, broad, OH), 4.15—4.50 (4H, m, CH_2OSi, H-3,4), 4.66 (2H, s, $OC\underline{H}_2C_6H_5$), 5.70—5.85 (1H, m, H-2), 7.25—7.75 (15H, m, $OCH_2C_6\underline{H}_5$, $OSi(C_6H_5)_2$). Found: C, 75.67; H, 7.50%. Calcd for $C_{29}H_{34}O_3Si$: C, 75.94; H, 7.47%.

(3*S*,4*R*)-4-Acetoxy-3-benzyloxy-1-(*t*-butyldiphenylsilyloxymethyl)-1-cyclopentene (19). Compound **18** (11 mg, 0.024 mmol) was acetylated with acetic anhydride (1 ml) in pyridine (1 ml) for 13 h. The mixture was concentrated, and the residue was chromatographed on silica gel (1 g, ethyl acetate-hexane=1 : 30). The fraction corresponding to R_f 0.47 (ethyl acetate-hexane=1 : 8) was concentrated to give **19** (11 mg, 90%) as a colorless syrup. **19**: $[\alpha]_D^{22.5}$ +35.1° (*c* 0.49, $CHCl_3$); IR $\nu_{max}^{CHCl_3}$ 3000, 2960, 2930, 2860, 1725, 1250, 1170, 1110 cm^{-1}; ^1H NMR δ=1.05 (9H, s, $OSiC(CH_3)_3$), 2.03 (3H, s, $OCOCH_3$), 2.40—2.65 (2H, m, H-5,5′), 4.21 (2H, s, CH_2OSi), 4.50—4.68 (3H, m, $OC\underline{H}_2C_6H_5$, H-3), 5.30 (1H, q, *J*=6.5 Hz, H-4), 5.73—5.86 (1H, m, H-2), 7.30—7.80 (15H, m, $OCH_2C_6\underline{H}_5$, $OSi(C_6H_5)_2$). Found: C, 74.46; H, 7.28%. Calcd for $C_{31}H_{36}O_4Si$: C, 74.36; H, 7.25%.

(3*S*,4*R*)-3-Benzyloxy-4-hydroxy-1-cyclopentene-1-methanol (20). To a solution of **18** (156 mg, 0.34 mmol) in THF (10 ml), tetrabutylammonium fluoride (1 mol dm^{-3} in THF, 0.51 ml, 0.51 mmol) was added with stirring. After stirring for 2 h, the mixture was concentrated. The residue was chromatographed on silica gel (6 g, ethyl acetate-hexane=1 : 2), and the fraction corresponding to R_f 0.14 (ethyl acetate-hexane=1 : 1) was concentrated to give crystals of **20** (68 mg, 90%), mp 74—75 °C. **20**: $[\alpha]_D^{23}$ +75.4° (*c* 0.985, $CHCl_3$), IR $\nu_{max}^{CHCl_3}$ 3400, 2925, 2860, 1650, 1495, 1450, 1395, 1330, 1210, 1160 cm^{-1}; ^1H NMR δ=2.39 (2H, broad s, H-5,5′), 2.91 (2H, broad s, 2×OH), 4.10 (2H, broad s, CH_2OH), 4.25—4.50 (2H, m, H-3,4), 4.60 (2H, s, $OC\underline{H}_2C_6H_5$), 5.69 (1H, broad s, H-2), 7.34 (5H, s, $OCH_2C_6\underline{H}_5$). High-resolution mass spectrum, Found: *m/z* 220.1104, Calcd for $C_{13}H_{16}O_3$: M, 220.1098.

(1*R*,2*R*,3*R*,4*R*)-2,4-Diacetoxy-1-acetoxymethyl-3-(benzyloxy)cyclopentane (21). To a solution of **20** (65 mg, 0.29 mmol) in THF (5 ml), borane-THF complex (1 mol dm^{-3} in THF, 1.19 ml, 1.19 mmol) was added at 0 °C with stirring under an argon atmosphere. After 90 min stirring, borane-THF (0.59 ml) was added. The mixture was stirred additional 90 min at 0 °C, and water (1.8 ml), aqueous NaOH (3 mol dm^{-3}, 2.1 ml) and aqueous hydrogen peroxide (35%, 2.3 ml) were added successively. After stirring at room temperature for 3 h, saturated aqueous sodium sulfite (2.5 ml) was added and the mixture was concentrated with ethanol. The residue was passed through a short column of silica gel (3 g), and eluted with ethanol. The fraction corresponding to R_f 0.35 (ethanol-toluene=1 : 5) was concentrated. The residue was acetylated with acetic anhydride (5 ml) in pyridine (5 ml) for 18 h. The mixture was diluted with water (50 ml) and extracted with dichloromethane (50 ml×3). The extracts were dried over Na_2SO_4 and concentrated. The residue was chromatographed on silica gel (6 g, ethyl acetate-hexane=1 : 10), and the fraction corresponding to R_f 0.42 (ethyl acetate-hexane=1 : 3) was concentrated to give **21** (71 mg, 65%) as a colorless syrup. **21**: $[\alpha]_D^{23.5}$ −2.2° (*c* 0.9, $CHCl_3$); IR $\nu_{max}^{CHCl_3}$ 2930, 1740, 1730, 1450, 1365, 1230, 1220 cm^{-1}; ^1H NMR δ=2.03, 2.06 (6H, 3H, each s, 3×$OCOCH_3$), 1.95—2.40 (3H, m, H-1,5,5′), 3.89 (1H, t, *J*=4.5 Hz, H-3), 4.18 (2H, dd, *J*=3 and 6 Hz, $C\underline{H}_2OAc$), 4.59 (2H, s, $OC\underline{H}_2C_6H_5$), 5.00—5.30 (2H, m, H-2,4), 7.31 (5H, s, $OCH_2C_6\underline{H}_5$). Found: C, 62.75; H, 6.77%. Calcd for $C_{19}H_{24}O_7$: C, 62.63; H, 6.64%.

(1*R*,2*R*,3*R*,4*R*)-2,3,4-Triacetoxy-1-(acetoxymethyl)cyclopentane (22). A solution of **21** (68.5 mg, 0.19 mmol) in a mixture of ethanol (3 ml) and distilled cyclohexene (6.5 ml) in the presence of 20% $Pd(OH)_2$ on charcoal (150 mg) was refluxed for 4 h. The catalyst was removed by filtration with a Celite-pad, and the filtrate was concentrated. The residue was chromatographed on silica gel (3 g, ethyl acetate-hexane=1 : 4), and the fraction corresponding to R_f 0.19 (ethyl acetate-hexane=1 : 2) was concentrated. The residue was acetylated with acetic anhydride (1 ml) in pyridine (1 ml) for 2 h. The mixture was concentrated, and the residue was chromatographed on silica gel (3 g, ethyl acetate-hexane=1 : 6). The fraction corresponding to R_f 0.44 (ethyl acetate-hexane=1 : 2) was concentrated to give **22** (53.5 mg, 90%) as a colorless syrup. $[\alpha]_D^{23}$ −4.8° (*c* 0.87, $CHCl_3$), $[\alpha]_D^{23}$ +4.1° (*c* 1.07, $CHCl_3$) for the enantiomer of **22**.[1e] The IR and

^{1}H NMR spectra of **22** were identical with those of the (1*S*,2*S*,3*S*,4*S*)-enantiomer. Found: C, 53.37; H, 6.18%. Calcd for $C_{14}H_{20}O_8$: C, 53.16; H, 6.34%.

(1*R*,2*R*,3*R*,4*R*)-2,3,4-Trihydroxy-1-(hydroxymethyl)cyclopentane, Pseudo-β-D-arabinofuranose (3). To a solution of **22** (47 mg, 0.15 mmol) in methanol (2 ml), sodium methoxide (1 mol dm^{-3} in methanol, 0.45 ml, 0.45 mmol) was added at 0 °C with stirring. After stirring at 0 °C for 2 h, the mixture was neutralized by addition of Amberlite IR-120 (H^+). The resin was removed by filtration, washed with methanol. The filtrate and washing were concentrated to give **3** (22 mg, quantitatively). An analytical sample was obtained by PTLC (chloroform-methanol=2:1). **3** as a colorless syrup, TLC R_f 0.41 (chloroform-methanol=2:1): $[\alpha]_D^{22}$ +9.7° (*c* 0.72, MeOH), $[\alpha]_D^{14}$ −8.8° (*c* 0.56, MeOH) for the (1*S*,2*S*,3*S*,4*S*)-enantiomer **1**.[1e,8] The ^{1}H NMR sepctrum of **3** was identical with that of **1**. High-resolution mass spectrum, Found: *m/z* 149.0781. Calcd for $C_6H_{13}O_4$: M+H, 149.0812.

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7) Compound **1**, the L-enantiomer of **3**, was obtained as crystals (mp 103—104 °C),[1e] however, we can not crystallize compound **3** up to now.

8) In the previous paper,[1e] the $[\alpha]_D$ of compound **1** was incorrectly presented. Remeasurement of the crystalline (mp 103—104 °C) **1** gave $[\alpha]_D$ value described in this article.