Syntheses of Optically Active Pentaacetates of Pseudo-β-L-allopyranose and Pseudo-α-D-mannopyranose

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Diisobutylaluminium hydride reduction of D-glucose-derived chiral synthon, (1*R*,6*R*,8*R*,9*R*)-8,9-isopropylidenedioxy-7-oxabicyclo[4.3.0]non-4-en-3-one (**1**), gave a 7:1 mixture of (1*R*,3*S*,6*R*,8*R*,9*R*)- and (1*R*,3*R*,6*R*,8*R*,9*R*)-8,9-isopropylidenedioxy-7-oxabicyclo[4.3.0]non-4-en-3-ol, (**2**) and (**2′**). Introduction of cis-diol to the double bond of 3-*O*-acetyl derivatives of **2** and **2′** by osmium tetraoxide oxidation provided the diastereomeric mixture of (1*R*,3*S*,4*R*,5*S*,6*S*,8*R*,9*R*)-3-acetoxy-8,9-isopropylidenedioxy-7-oxabicyclo[4.3.0]-nonane-4,5-diol (**5**) and (1*R*,3*R*,4*S*,5*R*,6*S*,8*R*,9*R*) diastereomer. Compound **5** was transformed to optically active pseudo-β-L-allopyranose effectively via (1*R*)-1-[(1*S*,2*S*,3*S*,4*R*,5*S*)-3,4,5-tris(benzyloxy)-2-hydroxycyclohexyl]-1,2-ethanediol (**9**). Cyclohexanecarbaldehyde formed by glycol cleavage of **9** was treated with methanesulfonyl chloride and reduced with lithium aluminium hydride to give (3*S*,4*R*,5*S*)-3,4,5-tris(benzyloxy)-1-cyclohexene-1-methanol (**13**). Compound **13** was efficiently converted to pseudo-α-D-mannopyranose pentaacetate by stereoselective hydroboration as a key reaction. The Wharton reaction of (1*R*,4*S*,5*S*,6*S*,8*R*,9*R*)-4,5-epoxy-8,9-isopropylidenedioxy-7-oxabicyclo[4.3.0]nonan-3-one derived from **1** gave (1*R*,5*R*,6*S*,8*R*,9*R*)-8,9-isopropylidenedioxy-7-oxabicyclo[4.3.0]non-3-en-5-ol, into which (3*S*,4*S*)-diol was stereoselectively introduced by oxidation with osmium tetraoxide.

The pseudo-sugars, 1-hydroxymethyl-2,3,4,5-cyclohexanetetrols, are found in components of antibiotics and enzyme inhibitors.[1] Optically active pseudo-sugars have currently been investigated by several subtle approaches to these carbocyclic analogues of carbohydrates.[2] This situation made us use chiral synthon as a starting compound for the pseudo-sugar synthesis. In the previous papers,[3] we demonstrated a practicable access to the chiral synthon **1**, from which some optically active pseudo-sugars and pseudo-2-amino sugars were synthesized by stereoselective introduction of triol or azido diol on the cyclohexenone moiety of **1**. In our further study of synthesizing the optically active carbocyclic natural products and pseudo-sugars,[4] we described another approach to pseudo-sugars starting from synthon **1**. The approach features a stereoselective cis-diol introduction to the double bond of two allyl acetates **4** and **19**, both of which are easily prepared from **1**, to give (3*S*,4*R*,5*S*)- and (3*S*,4*S*,5*S*)- protected triols **5** and **20**. Compound **5** was transformed to pentaacetyl derivatives of pseudo-α-L-allopyranose and pseudo-α-D-mannopyranose, **11** and **15**, efficiently.

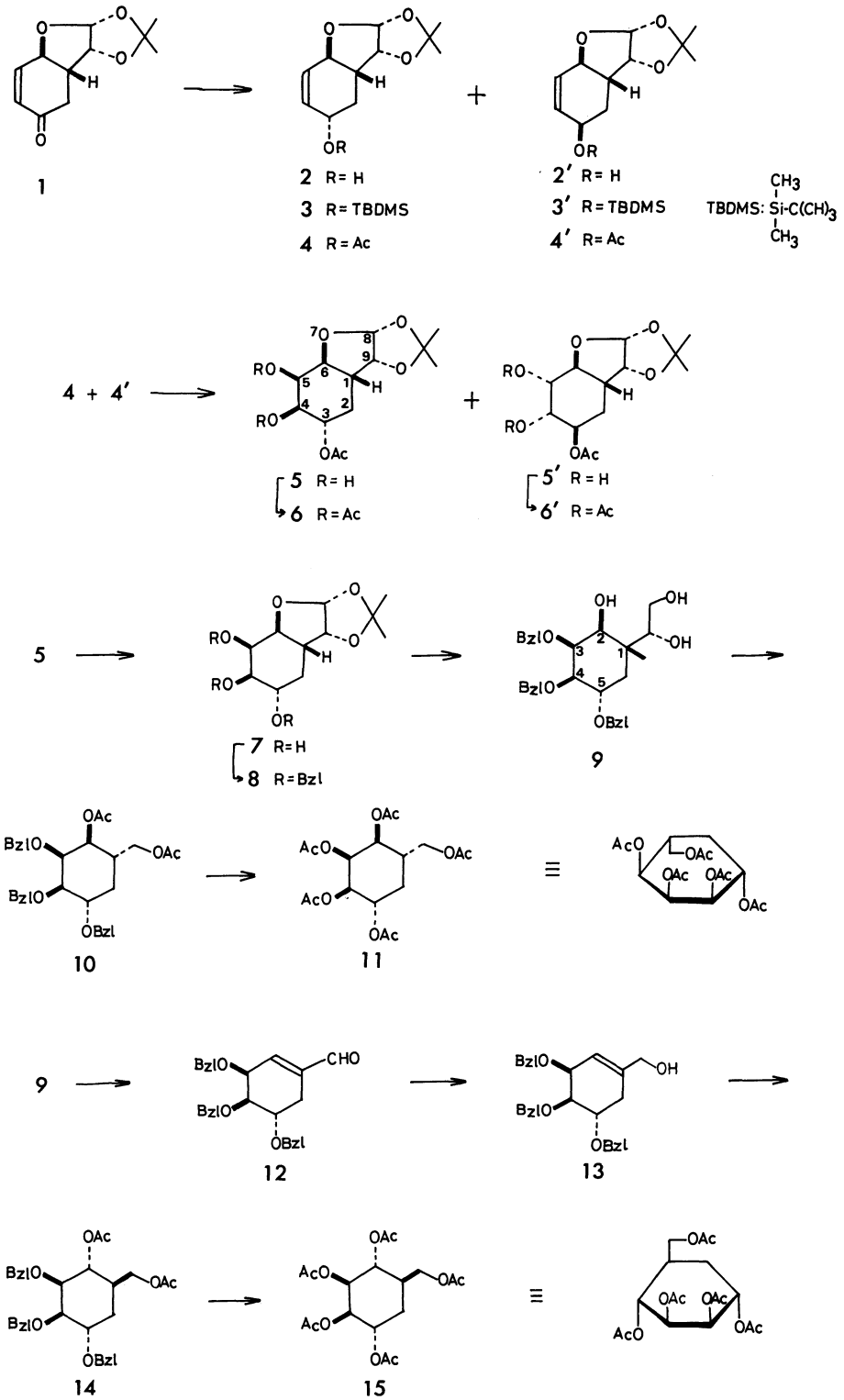
Results and Discussion

Synthesis of Pentaacetates of Pseudo-β-L-allopyranose and Pseudo-α-D-mannopyranose, (11) and (15) (Scheme 1). Diisobutylaluminium hydride (DIBAL-H) reduced chiral synthon **1**, which was prepared from 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose by seven-steps reaction in an overall yield of 37%,[3] at −78 °C to give an inseparable mixture of allyl alcohols **2** and **2′** in 69% yield. The ratio of **2** to **2′** was 7:1 by conversion of the mixture to *t*-butyldimethylsilyl ethers **3** and **3′**, which were separated by silica-gel chromatography.[5] Although we were unable to confirm stereochemically C-3 (H-C-OH) of **2** and **2′** unambigously by ^{1}H NMR analysis of **3** and **3′**, the configuration of C-3 of the main product **2** was tentatively assigned to be (*S*), as was confirmed later. Osmium tetraoxide oxidation of an inseparable mixture of allyl acetates **4** and **4′**, which was prepared by acetylation of a mixture of **2** and **2′**, with aqueous hydrogen peroxide in *t*-butyl alcohol at room temperature gave (1*R*,3*S*,4*R*,5*S*,6*S*,8*R*,9*R*)- and (1*R*,3*R*,4*S*,5*R*,6*S*,8*R*,9*R*)-3-acetoxy-8,9-isopropylidenedioxy-7-oxabicyclo[4.3.0]nonane-4,5-diol, (**5**) and (**5′**), in 53 and 6% yield, respectively. The structure of main product **5** was verified by ^{1}H NMR spectrum of tri-*O*-acetyl derivative **6**, which was prepared in 96% yield. In the ^{1}H NMR spectrum of **6**, H-6 signal appeared at δ 3.85 as a double doublet with $J_{1,6}$=10.5 Hz and $J_{5,6}$=3 Hz, indicating that 5-acetoxyl group is axial. Three acetoxyl methyl signals of **6** appeared at δ 2.00, 2.03, and 2.12 indicate that acetoxyl groups on C-3, 4, and 5 are equatorial, equatorial, and axial, respectively.[6] The configurations at C-3 to C-5 are, therefore, (3*S*,4*R*,5*S*) as depicted. The structure of **5′**, (3*R*,4*S*,5*R*), was also confirmed by ^{1}H NMR spectrum of acetyl derivative **6′** obtained in 97% yield. In the ^{1}H NMR spectrum, H-6 of **6′** appeared at δ 4.02 as a triplet with $J_{1,6}$=$J_{5,6}$=9.5 Hz, indicating that 5-acetoxyl group is equatorial. Three acetoxyl methyl signals of **6′** appeared at δ 2.00 (3H) and 2.10 (6H), indicating that acetoxyl groups on C-3, 4, and 5 are axial, axial, and equatorial.[6] Stereoselective cis-diol introduction was thus achieved for both allyl acetates **4** and **4′**, and osmate formation in both cases occurred from the opposite side of acetoxyl group, providing **5** from **4** and **5′** from **4′**.[7]

Pseudo-sugar **11** was synthesized from **5** as follows. *O*-Deacetylation of **5** and successive benzylation with excess benzyl bromide in the presence of sodium

hydride gave tri-*O*-benzyl derivative **8** in 88% yield. Hydrolysis of **8** with 80% aqueous acetic acid to remove *O*-isopropylidene group, followed by reduction with sodium borohydride, gave pseudo-heptopyranose **9** in 56% yield. The glycol cleavage of **9** with sodium periodate, reduction of the resulting aldehyde group with sodium borohydride, and acetylation gave a fully protected pseudo-β-L-allopyranose **10** in 85% yield. Finally, hydrogenolysis of **10** in the presence of palladium-black to remove *O*-benzyl groups and successive acetylation gave compound **11** as crystals in 79% yield. The ^{1}H NMR spectrum of **11** was identical with that of authentic DL-**11**.[8]

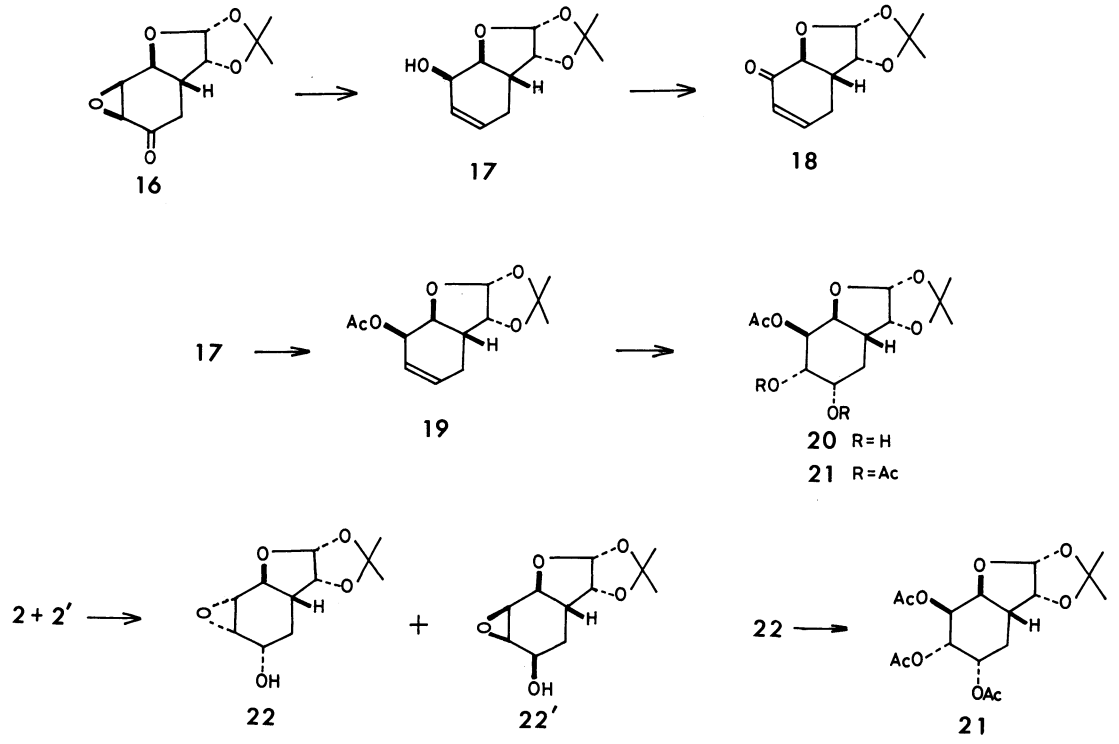
The synthesis of pseudo-α-D-mannopyranose pen-



Scheme 1.

taacetate (**15**) from compound **9** was achieved as follows. The glycol cleavage of **9** as described above and successive treatment of the resulting cyclohexanecarbaldehyde with excess methanesulfonyl chloride at room temperature gave α,β-unsaturated 1-cyclohexene-1-carbaldehyde, which was reduced with lithium aluminium hydride to give 1-cyclohexene-1-methanol **13** in 37% yield from **9**. Hydroboration of **13** with borane-THF complex, treatment with alkaline hydrogen peroxide, and acetylation gave a fully protected pseudo-α-D-mannopyranose **14** in 47% yield. Since pseudo-β-L-allopyranose **10** was not detected in the reaction mixture, hydroboration of **13** seems to proceed stereoselectively from less-hindered side opposite to the benzyloxy groups on C-3 and C-4.[9] Hydrogenolysis of **14** in the presence of palladium-black followed by acetylation gave compound **15** as crystals in 56% yield. The ^{1}H NMR spectrum of **15** was identical with that of authentic DL-**15**.[10]

Synthesis of (1*R*,5*R*,6*S*,8*R*,9*R*)-8,9-Isopropylidenedioxy-7-oxabicyclo[4.3.0]non-3-en-5-ol (17) and Stereoselective Introduction of Two Hydroxyl Groups to the Double Bond in Acetate (19) of 17 (Scheme 2). Our next interest was to investigate stereoselectivity of introduction of two hydroxyl groups to the double bond located at C-3 and C-4 in the appropriate model **17**. Compound **17** was synthesized by the Wharton reaction[11] of known epoxy ketone **16**, which was obtained by stereoselective epoxidation of **1**.[3] Treatment of **16** in ethanol with each 5 molar equivalent of hydrazine hydrate and acetic acid at room temperature for 2.5 min gave compound **17** in 74% yield. Longer reaction time decreased the yield. In the ^{1}H NMR spectrum of **17**, H-6 signal appeared at δ 3.72 as a double doublet with $J_{1,6}$=10.5 Hz and $J_{5,6}$=4.5 Hz. Meanwhile, oxidation of **17** with pyridinium chlorochromate (PCC) gave (1*S*,6*S*,8*R*,9*R*)-8,9-isopropylidenedioxy-7-oxabicyclo[4.3.0]non-3-en-5-one (**18**) in 87% yield. In the ^{1}H NMR spectrum of **18**, H-6 signal appeared at δ 4.45 as a doublet with $J_{1,6}$=12 Hz. From these spectral data, it was concluded that hydroxyl group in the Wharton reaction product is at C-5 with (R)-configuration (a pseudo-axial orientation). Treatment of allyl acetate **19**, which was prepared by acetylation of **17** in 98% yield, with osmium tetraoxide in *t*-butyl alcohol in the presence of hydrogen peroxide gave cis diol **20** as a sole product in 35% yield. No stereoisomer was detected. The structure of **20** was estimated from the ^{1}H NMR spectrum of tri-*O*-acetyl derivative **21**, where H-6 signal appeared at δ 4.05 as a double doublet with $J_{1,6}$=10.5 Hz and $J_{5,6}$=3 Hz, indicating that 5-acetoxyl group is axial. Three acetoxyl methyl signals of **21** appeared at δ 1.99 (3H) and 2.10 (6H) and those signals were assigned to one equatorial and two axial acetoxyl groups.[6] Based on the results of oxidation of compound **4** and **4'** catalysed with osmium tetraoxide, cis diol introduction to compound **19** proceeded presumably from less-hindered side opposite to the 5-acetoxyl group to give solely (1*R*,3*S*,4*S*,5*S*,6*S*,8*R*,-9*R*)-5-acetoxy-8,9-isopropylidenedioxy-7-oxabicyclo-[4.3.0]nonane-3,4-diol (**20**). The possibility of formation of other stereoisomer possessing (1*R*,3*R*,4*R*,5*S*,6*S*,-8*R*,9*R*)-configuration, however, could not be excluded. To confirm the structure of **21**, we examined the sol-



Scheme 2.

volysis of (1*R*,3*S*,4*S*,5*R*,6*S*,8*R*,9*R*)-4,5-epoxy-8,9-isopropylidenedioxy-7-oxabicyclo[4.3.0]nonan-3-ol (**22**). The solvolysis of **22** in aqueous solvent in the presence of sodium acetate was expected to give compound **21** via diaxial opening of epoxy ring by hydroxide ion and acetylation of the solvolytic product. The synthesis of **22** was carried out as follows. Epoxidation of an inseparable mixture of **2** and **2'** with *m*-chloroperbenzoic acid (MCPBA) in refluxing dichloromethane gave two products **22** and **22'** in 50 and 16% yield, respectively. The ^{1}H NMR spectrum of **22'**, which was derived from a minor allyl alcohol **2'**, was identical with that of authentic sample.[3] The ^{1}H NMR spectrum of **22** was apparently different from that of another possible epoxy alcohol possessing (3*S*,4*R*,5*S*)-configuration, which was prepared from **1** by (1) epoxidation and (2) sodium borohydride reduction.[3] The structure of **22** was confirmed. In epoxidation of **2** and **2'**, hydroxyl groups governed the direction of attack of the peroxy acid.[12] As expected, the solvolysis of **22** and successive acetylation gave compound **21**, which was identical with the compound derived from **19**, in 79% yield, and the structure of **21** was thus confirmed. The compound **20** seems to be a promising precursor for synthesizing pseudo-β-L-altropyranose and pseudo-α-D-glucopyranose.[13]

Experimental

General. Reactions were performed at room temperature unless otherwise stated. Evaporation was done under a reduced pressure at below 40 °C with a bath. Melting points were determined with a Mitamura Riken micro mp apparatus. Specific rotation was measured by a Jasco DIP-4 polarimeter with a 10 mm cell. Column chromatography was performed with Kieselgel 60 (Merck), and thin-layer chromatography (TLC) by a glass plate coated with Kieselgel 60 GF_{254} (Merck), followed by UV light detection and charring with sulfuric acid. IR spectra were recorded with a Hitachi 225 spectrometer by the KBr method or with a Jasco A-202 spectrometer by the $CHCl_3$ method. ^{1}H NMR spectra were recorded with a Varian EM-390 (90 MHz) 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 benzophenone.

Mixture of (1*R*,3*S*,6*R*,8*R*,9*R*)- and (1*R*,3*R*,6*R*,8*R*,9*R*)-8,9-Isopropylidenedioxy-7-oxabicyclo[4.3.0]non-4-en-3-ol, (2) and (2'). To a solution of (1*R*,6*R*,8*R*,9*R*)-8,9-isopropylidenedioxy-7-oxabicyclo[4.3.0]non-4-en-3-one (**1**)[3] (1.20 g, 5.70 mmol) in dichloromethane (20 ml) was added with stirring DIBAL-H (1.5 mol dm^{-3} in toluene, 6.08 ml, 9.12 mmol) at −78 °C under an argon atmosphere. The mixture was stirred at the same temperature for 1 h, diluted with water (50 ml), and warmed to room temperature. The resulting insoluble materials were filtered with Celite pad, and the filtrate was condensed by evaporation. The residue was partitioned between dichloromethane (60 ml) and water (50 ml), and the aqueous layer was extracted with dichloromethane (60 ml×2). The organic layer was dried on Na_2SO_4 and condensed. The residue was chromatographed with silica gel (100 g, ethyl acetate-hexane=1 : 4), and the fraction corresponding to R_f 0.17 (ethyl acetate-hexane=1 : 2) was evaporated to give inseparable mixed crystals of **2** and **2'** (830 mg, 69% yield), mp 99—101.5 °C. IR ν_{max}^{KBr} 3500, 3000, 2950, 2900, 2845, 1450, 1400, 1385, 1375, 1315, 1265, 1240, 1210 cm^{-1}; ^{1}H NMR δ=1.33, 1.50 (3H×2, each s, $C(CH_3)_2$), 1.60—2.13 (3H, m, H-2,2', OH), 2.27—2.60 (1H, m, H-1), 4.07—4.50 (2H, m, H-3,6), 4.58 (1H, t, *J*=4.5 Hz, H-9), 5.87—5.97 (1H, m, H-4 or 5), 5.83 (1H, d, *J*=4.5 Hz, H-8), 6.00—6.33 (1H, m, H-4 or 5). Found: C, 62.51; H, 7.51%. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60%.

(1*R*,3*S*,6*R*,8*R*,9*R*)- and (1*R*,3*R*,6*R*,8*R*,9*R*)-3-(*t*-Butyldimethylsilyloxy)-8,9-isopropylidenedioxy-7-oxabicyclo[4.3.0]-non-4-ene, (3) and (3'). To a solution of inseparable mixture of **2** and **2'** (24.8 mg, 0.12 mmol) in DMF (1 ml) were added *t*-butylchlorodimethylsilane (158.7 mg, 1.09 mmol) and imidazole (68.1 mg, 1.03 mmol) with stirring. The mixture was stirred at 70 °C for 72 h, and diluted with ethyl acetate (15 ml). The solution was washed with water (15 ml×3), and the organic layer was dried on Na_2SO_4 and condensed by evaporation. The residue was chromatographed with silica gel (4 g, ethyl acetate-hexane=1 : 50). The fraction corresponding to R_f 0.71 (ethyl acetate-hexane=1 : 4) was evaporated to give **3'** (3.4 mg, 9%) as a colorless syrup, and the fraction corresponding to R_f 0.60 was evaporated to give **3** (23.5 mg, 62% yield) as a colorless syrup. **3**: $[\alpha]_D^{25}$ −14.6° (*c* 1.14, $CHCl_3$); IR ν_{max}^{KBr} 2990, 2960, 2940, 2880, 1460, 1380, 1375, 1260, 1215 cm^{-1}; ^{1}H NMR δ=0.08 (6H, s, $OSiC(CH_3)_3(C\underline{H}_3)_2$), 0.90 (9H, s, $OSiC(C\underline{H}_3)_3(CH_3)_2$), 1.31, 1.49 (3H×2, each s, $C(CH_3)_2$), 1.60—1.78 (2H, m, H-2,2'), 2.18—2.37 (1H, m, H-1), 4.35—4.47 (2H, m, H-3,6), 4.54 (1H, t, *J*=3.5 Hz, H-9), 5.45—5.58 (1H, m, H-4 or 5), 5.81 (1H, d, *J*=3.5 Hz, H-8), 5.94—6.17 (1H, m, H-5 or 4). **3'**: ^{1}H NMR δ=0.08 (6H, s, $OSiC(CH_3)_3(C\underline{H}_3)_2$), 0.88 (9H, s, $OSiC(C\underline{H}_3)_3(CH_3)_2$), 1.31, 1.48 (3H×2, each s, $C(CH_3)_2$), 1.87—1.97 (3H, m, H-1, 2,2'), 4.03—4.39 (2H, m, H-3,6), 4.60 (1H, t, *J*=3.5 Hz, H-9), 5.47—5.65 (1H, m, H-4 or 5), 5.72 (1H, d, *J*=3.5 Hz, H-8), 6.03—6.22 (1H, m, H-5 or 4).

Mixture of (1*R*,3*S*,6*R*,8*R*,9*R*)- and (1*R*,3*R*,6*R*,8*R*,9*R*)-3-Acetoxy-8,9-isopropylidenedioxy-7-oxabicyclo[4.3.0]non-4-ene, (4) and (4'). An inseparable mixture of **2** and **2'** (596 mg, 2.81 mmol) was acetylated with acetic anhydride (6 ml) in pyridine (6 ml) for 4 h and the mixture was evaporated. The residue was chromatographed with silica gel (20 g, ethyl acetate-hexane=1 : 8), and the fraction corresponding to R_f 0.50 (ethyl acetate-hexane=1 : 2) was evaporated to give an inseparable mixed crystals of **4** and **4'** (683 mg, 96% yield), mp 63—66 °C°; IR ν_{max}^{KBr} 3000, 2980, 2965, 2940, 2840, 1735, 1370, 1325, 1300, 1265, 1240, 1210 cm^{-1}; ^{1}H NMR δ=1.35, 1.50 (3H×2, each s, $C(CH_3)_2$), 1.60—2.00 (2H, m, H-2, 2'), 2.05 (3H, s, $OCOCH_3$), 2.33—2.60 (1H, m, H-1), 4.10—4.50 (1H, m, H-6), 4.58 (1H, t, *J*=4.5 Hz, H-9), 5.30—5.70 (2H, m, H-3, H-4 or 5), 5.87 (1H, d, *J*=4.5 Hz, H-8), 6.13—6.43 (1H, m, H-5 or 4). Found: C, 61.55; H, 7.07%. Calcd for $C_{13}H_{18}O_5$: C, 61.40; H, 7.13%.

(1*R*,3*S*,4*R*,5*S*,6*S*,8*R*,9*R*)- and (1*R*,3*R*,4*S*,5*R*,6*S*,8*R*,9*R*)-3-Acetoxy-8,9-isopropylidenedioxy-7-oxabicyclo[4.3.0]nonane-4,5-diol, (5) and (5'). To a solution of the inseparable mixture of **4** and **4'** (675.8 mg, 2.66 mmol) in *t*-butyl alcohol (15 ml) were added osmium tetraoxide in *t*-butyl alcohol (0.02

mol dm^{-3} solution, 2.66 ml, 0.053 mmol) and aqueous hydrogen peroxide (35wt%, 1.5 ml) with stirring. The solution was stirred in dark for 38 h and evaporated. The residue was chromatographed with silica gel (50 g, ethyl acetate-hexane=2 : 3). The fraction corresponding to R_f 0.10 (ethyl acetate-hexane=1 : 1) was evaporated to give crystals of **5′** (49.5 mg, 6% yield). The fraction corresponding to R_f 0.06 was evaporated to give crystals of **5** (406.3 mg, 53% yield). **5**: Mp 154—155 °C; $[\alpha]_D^{21}$ +71.5° (*c* 1.57, $CHCl_3$); IR ν_{max}^{KBr} 3450, 2990, 2980, 2940, 2880, 1710, 1445, 1390, 1375, 1365, 1265, 1250, 1210 cm^{-1}; ^{1}H NMR δ=1.32, 1.50 (3H×2, each s, $C(CH_3)_2$), 1.95—2.40 (3H, m, H-1,2, 2′), 2.06 (3H, s, $OCOCH_3$), 3.20—3.78 (4H, m, H-4 or 5, 6, 2×OH), 4.32—4.50 (1H, m, H-5 or 4), 4.59 (1H, t, *J*=3 Hz, H-9), 4.99 (1H, dt, *J*=11 and 5 Hz, H-3), 5.88 (1H, d, *J*=3 Hz, H-8). **5′**: Mp 191—193 °C; $[\alpha]_D^{22}$ −7.9° (*c* 1.29, $CHCl_3$); IR ν_{max}^{KBr} 3450, 3300, 2980, 2930, 2890, 1730, 1450, 1370, 1350, 1330, 1305, 1250, 1220 cm^{-1}; ^{1}H NMR δ=1.32, 1.52 (3H×2, each s, $C(CH_3)_2$), 1.67—2.00 (3H, m, H-1, 2, 2′), 2.05 (3H, s, $OCOCH_3$), 2.70—3.20 (1H, br s, OH), 3.75—4.15 (4H, m, H-4, 5, 6, OH), 4.58 (1H, t, *J*=3.5 Hz, H-9), 5.22 (1H, q, *J*=3 Hz, H-3), 5.85 (1H, d, *J*=3.5 Hz, H-8).

Tri-*O*-acetyl Derivatives 6 and 6′ of 5 and 5′. Compounds **5** and **5′** were acetylated with acetic anhydride in pyridine. **6**: (96% yield): TLC R_f 0.61 (ethyl acetate-hexane=1 : 1); mp 66—67 °C; $[\alpha]_D^{23}$ +41.8° (*c* 0.97, $CHCl_3$); IR ν_{max}^{KBr} 2980, 2940, 1740, 1375, 1230, 1165, 1130, 1105 cm^{-1}; ^{1}H NMR δ=1.32, 1.50 (3H×2, each s, $C(CH_3)_2$), 2.00, 2.03, 2.12 (3H×3, each s, 3×$OCOCH_3$), 2.10—2.40 (3H, m, H-1, 2, 2′), 3.85 (1H, dd, $J_{1,6}$=10.5 Hz and $J_{5,6}$=3 Hz, H-6), 4.57 (1H, t, $J_{1,9}$=$J_{8,9}$=3 Hz, H-9), 4.90—5.20 (2H, m, H-3,5), 5.73—5.90 (2H, m, H-4, 8). Found: C, 54.95; H, 6.41%. Calcd for $C_{17}H_{24}O_9$: C, 54.83; H, 6.50%. **6′** (97% yield): TLC R_f 0.66 (ethyl acetate-hexane=1 : 1); mp 140—142 °C; $[\alpha]_D^{23}$ −25.5° (*c* 0.64, $CHCl_3$); IR ν_{max}^{KBr} 3000, 2960, 2940, 2900, 1750, 1735, 1435, 1375, 1305, 1285, 1275, 1250, 1235, 1220 cm^{-1}; ^{1}H NMR δ=1.32, 1.53 (3H×2, each s, $C(CH_3)_2$), 1.77—2.20 (3H, m, H-1, 2, 2′), 2.00, 2.10 (3H and 6H, each s, 3×$OCOCH_3$), 4.02 (1H, t, $J_{1,6}$=$J_{5,6}$=9.5 Hz, H-6), 4.58 (1H, t, $J_{1,9}$=$J_{8,9}$=3.5 Hz, H-9), 5.00—5.30 (2H, m, H-3, 5), 5.35 (1H, t, $J_{3,4}$=$J_{4,5}$=3 Hz, H-4), 5.85 (1H, d, $J_{8,9}$=3.5 Hz, H-8). Found: C, 54.97; H, 6.42%. Calcd for $C_{17}H_{24}O_9$: C, 54.83; H, 6.50%.

(1*R*,3*S*,4*R*,5*S*,6*S*,8*R*,9*R*)-3,4,5-Tris(benzyloxy)-8,9-isopropylidenedioxy-7-oxabicyclo[4.3.0]nonane (8). To a solution of **5** (302.5 mg, 1.05 mmol) in methanol (5 ml) was added sodium methoxide in methanol (1 mol dm^{-3} solution, 1.57 ml, 1.57 mmol) at 0 °C with stirring. The mixture was stirred at 0 °C for 30 min and neutralized by addition of Amberlite IR 120B (H^+). After removal of the resin by filtration, the filtrate was evaporated to give crude (1*R*,3*S*,4*R*,5*S*,6*S*,8*R*,9*R*)-8,9-isopropylidenedioxy-7-oxabicyclo[4.3.0]-nonane-3,4,5-triol (**7**) which was *O*-benzylated without purification. Sodium hydride (60% emulsion in mineral oil, 630 mg, 15.8 mmol) was washed with hexane (1 ml×2), dried, and suspended in DMF (5 ml). To the suspension was added a DMF (10 ml) solution of crude **7** and the mixture was stirred for 10 min. Benzyl bromide (1.87 ml, 15.8 mmol) was added. After the mixture was stirred for 12 h, ethanol (1 ml) was added and evaporated. The residue was dissolved in water (80 ml) and extracted with dichloromethane (80 ml×3). The extract was dried on Na_2SO_4 and evaporated. The residue was chromatographed with silica gel (90 g, ethyl acetate-hexane=1 : 15). The fraction corresponding to R_f 0.46 (ethyl acetate-hexane=1 : 3) was evaporated to give **8** (473.8 mg, 88% yield) as a colorless syrup, $[\alpha]_D^{21}$ +36.7° (*c* 1.15, $CHCl_3$); IR $\nu_{max}^{CHCl_3}$ 3060, 3000, 2930, 2880, 1490, 1455, 1385, 1375, 1360, 1305, 1260, 1200 cm^{-1}; ^{1}H NMR δ=1.28, 1.45 (3H×2, each s, $C(CH_3)_2$), 1.67—2.33 (3H, m, H-1, 2, 2′), 3.88 (1H, dd, *J*=9.5 and 3 Hz, H-6), 3.53—4.00 (2H, m, H-3, 4), 4.23 (1H, t, *J*=3 Hz, H-5), 4.52 (1H, t, *J*=4.5 Hz, H-9), 4.58—4.83 (6H, m, 3×$OC\underline{H}_2C_6H_5$), 5.83 (1H, d, *J*=4.5 Hz, H-8), 7.13—7.52 (15H, m, 3×$OCH_2C_6\underline{H}_5$). Found: *m/z* 516.2522. Calcd for $C_{32}H_{36}O_6$: M, 516.2510.

(1*R*)-1-[(1*S*,2*S*,3*S*,4*R*,5*S*)-3,4,5-Tris(benzyloxy)-2-hydroxycyclohexyl]-1,2-ethanediol (9). A solution of **8** (161 mg, 0.31 mmol) in a mixture of 80% aqueous acetic acid (32 ml) and dioxane (1.5 ml) was refluxed for 30 min and evaporated. The residue was dissolved in ethanol (4 ml) and sodium borohydride (24 mg, 0.64 mmol) was added. After stirring for 19 h, 35% aqueous hydrogen peroxide (1 ml) was added and stirred for further 15 min. The solution was neutralized with 1 mol dm^{-3} HCl and saturated aqueous sodium sulfite (1 ml) was added. The solution was diluted with water (20 ml) and extracted with dichloromethane (20 ml×3). The extract was dried on Na_2SO_4 and evaporated. The residue was chromatographed with silica gel (12 g, ethanol-toluene=1 : 25), and the fraction corresponding to R_f 0.26 (ethanol-toluene=1 : 7) was evaporated to give **9** (84 mg, 56% yield) as a colorless syrup, $[\alpha]_D^{22}$ +4.4° (*c* 1.09, $CHCl_3$); IR $\nu_{max}^{CHCl_3}$ 3300, 3050, 2900, 2850, 1600, 1580, 1490, 1400, 1360, 1300, 1200 cm^{-1}; ^{1}H NMR δ=1.67—2.17 (3H, m, H-1, 6, 6′), 2.83—3.25 (1H, m, 2×OH), 3.35 (1H, dd, *J*=10 and 3 Hz, H-2), 3.45—4.23 (7H, m, H-3, 4, 5, $C\underline{H}(OH)C\underline{H}_2OH$, OH), 4.57—5.15 (6H, m, 3×$OC\underline{H}_2C_6H_5$), 7.28—7.47 (15H, m, 3×$OCH_2C_6\underline{H}_5$). Found: *m/z* 479.2407. Calcd for $C_{29}H_{35}O_6$: M+H, 479.2430.

(1*S*,2*S*,3*S*,4*R*,5*S*)-2-Acetoxy-1-acetoxymethyl-3,4,5-tris(benzyloxy)cyclohexane (10). To a solution of **9** (77 mg, 0.16 mmol) in methanol (2 ml) was added an aqueous solution (0.5 ml) of sodium periodate (38 mg, 0.18 mmol) at 0 °C with stirring. The mixture was stirred at 0 °C for 2 h and evaporated. The residue was dissolved in water (10 ml) and extracted with dichloromethane (25 ml×5). The extract was dried on Na_2SO_4 and evaporated to give crude (1*R*,2*S*,3*S*,4*R*,-5*S*)-3,4,5-tris(benzyloxy)-2-hydroxycyclohexanecarbaldehyde, which was subjected to next step without purification. The residue was dissolved in ethanol (2 ml) and sodium borohydride (12 mg, 0.32 mmol) was added. The mixture was stirred for 1 h and 35% aqueous hydrogen peroxide (0.5 ml) was added, and stirred for 15 min. The solution was neutralized with 1 mol dm^{-3} HCl and saturated sodium sulfite (0.5 ml) was added. The solution was diluted with water (60 ml) and extracted with dichloromethane (60 ml×3). The extract was dried on Na_2SO_4 and evaporated. The residue (TLC R_f 0.37, ethanol-toluene=1 : 7) was acetylated with acetic anhydride (1 ml) in pyridine (1 ml) for 14 h. The mixture was evaporated and the residue was chromatographed with silica gel (5 g, ethyl acetate-hexane=1 : 5). The fraction corresponding to R_f 0.72 (ethanol-toluene=1 : 10) was evaporated to give **10** (73 mg, 85% yield) as a colorless syrup, $[\alpha]_D^{18}$ −40.2° (*c* 1.00, $CHCl_3$); IR $\nu_{max}^{CHCl_3}$ 3000, 2950, 2900, 2870, 1730, 1495, 1450, 1370, 1245, 1205 cm^{-1}; ^{1}H NMR δ=1.23—1.58 (2H, m, H-6, 6′), 1.97, 2.00 (3H×2, each s, 2×$OCOCH_3$), 2.08—2.45 (1H, m, H-1), 3.43 (1H, dd, $J_{3,4}$=3 Hz and $J_{4,5}$=9 Hz, H-4), 3.83—4.24 (4H, m, H-3,5, $C\underline{H}_2OAc$), 4.57—4.92 (7H, m, H-2, 3×$OC\underline{H}_2C_6H_5$), 7.29—7.47 (15H, m, 3×$OCH_2C_6\underline{H}_5$). Found: *m/z* 533.2538. Calcd for $C_{32}H_{37}O_7$: M+H, 533.2537.

(1*S*,2*S*,3*S*,4*R*,5*S*)-2,3,4,5-Tetraacetoxy-1-(acetoxymethyl)-

cyclohexane, Pentaacetate of Pseudo-β-L-allopyranose (11). A solution of **10** (53.5 mg, 0.10 mmol) in methanol (2 ml) was hydrogenolyzed in the presence of palladium-black in the Parr apparatus for 14 h. The catalyst was removed by filtration and washed with methanol. The mixture of filtrate and washing methanol was evaporated to give crude *O*-debenzylated product, which was acetylated with acetic anhydride (1 ml) in pyridine (1 ml) for 46 h. The mixture was evaporated and the residue was chromatographed with silica gel (1 g, ethyl acetate-hexane=1 : 4). The fraction corresponding to R_f 0.29 (ethyl acetate-hexane=1 : 2) was evaporated to give crystals of **11** (30.5 mg, 79% yield). **11**: Mp 135—136 °C; $[\alpha]_D^{18}$ +3.7° (*c* 1.41, $CHCl_3$); IR ν_{max}^{KBr} 1750, 1740, 1425, 1375, 1225, 1095, 1075 cm^{-1}; ^1H NMR δ=1.10—2.60 (3H, m, H-1, 6, 6′), 2.00, 2.03, 2.05, 2.14 (6H, 3H, 3H, and 3H, each s, 5×$OCOCH_3$), 4.03—4.08 (2H, m, CH_2OAc), 4.91 (1H, dd, *J*=10 and 3 Hz, H-2 or 4), 5.03—5.43 (2H, m, H-4 or 2, 5), 5.59 (1H, t, *J*=3 Hz, H-3). The ^1H NMR spectrum of **11** was identical with that of authentic DL-**11**.[8] Found: C, 52.63; H, 6.15%. Calcd for $C_{17}H_{24}O_{10}$: C, 52.57; H, 6.23%.

(3*S*,4*R*,5*S*)-3,4,5-Tris(benzyloxy)-1-cyclohexene-1-methanol (13). Compound **9** (245 mg, 0.51 mmol) was converted to a glycol-cleaved compound as described in the preparation of **10**. The crude residue extracted with dichloromethane was dissolved in pyridine (10 ml) and methanesulfonyl chloride (0.32 ml, 4.1 mmol) was added. The mixture was stirred for 14 h and evaporated. The residue was partitioned between dichloromethane (60 ml) and water (30 ml). The aqueous layer was extracted with dichloromethane (60 ml×2). The organic layer was dried on Na_2SO_4 and evaporated to give crude (3*S*,4*R*,5*S*)-3,4,5-tris(benzyloxy)-1-cyclohexenecarbaldehyde (**12**) (256 mg). To a solution of crude **12** in THF (4 ml) was added a suspension of lithium aluminium hydride (39 mg, 1.0 mmol) in THF (4 ml) at 0 °C with stirring. The mixture was stirred at 0 °C for 4 h and ethyl acetate (1 ml) was added. The resulting solids were removed with Celite pad. The filtrate was evaporated and the residue was chromatographed with silica gel (10 g, ethyl acetate-hexane=1 : 4). The fraction corresponding to R_f 0.18 (ethyl acetate-hexane=1 : 2) was evaporated to give **13** (81 mg, 37% yield) as a colorless syrup, $[\alpha]_D^{21}$ +61.7° (*c* 0.85, $CHCl_3$); IR $\nu_{max}^{CHCl_3}$ 3580, 3000, 2910, 2860, 1490, 1450, 1360, 1140 cm^{-1}; ^1H NMR δ=1.20—1.63 (1H, OH), 1.90—2.65 (2H, m, H-6, 6′), 3.63—4.27 (5H, m, H-3, 4, 5, CH_2OH), 4.63—4.72 (6H, m, 3×$OCH_2C_6H_5$), 5.67—5.83 (1H, m, H-2), 7.35 (15H, s, 3×$OCH_2C_6H_5$). Found: *m/z* 430.2135. Calcd for $C_{28}H_{30}O_4$: M, 430.2141.

(1*R*,2*R*,3*S*,4*R*,5*S*)-2-Acetoxy-1-acetoxymethyl-3,4,5-tris(benzyloxy)cyclohexane (14). To a solution of **13** (81 mg, 0.19 mmol) in THF (2 ml) was added borane-THF complex (1 mol dm^{-3} in THF, 0.66 ml, 0.66 mmol) at 0 °C under an argon atmosphere with stirring. The mixture was stirred at 0 °C for 20 min, and at room temperature for 2 h. To the mixture were added water (1.8 ml), 3 mol dm^{-3} aqueous NaOH (0.6 ml), and hydrogen peroxide (35 wt% in water, 0.96 ml), successively. The mixture was stirred for 2 h and 1 mol dm^{-3} HCl was added for neutralization. The solution was evaporated, and the residue was dissolved in water (30 ml), extracted with dichloromethane (30 ml×3). The extract was dried on Na_2SO_4 and evaporated. The residue was acetylated with acetic anhydride (2 ml) in pyridine (2 ml) for 12 h. The mixture was evaporated and the residue was chromatographed with silica gel (7 g, ethyl acetate-hexane=1 : 10). The fraction corresponding to R_f 0.73 (ethyl acetate-hexane=1 : 2) was evaporated to give **14** (46 mg, 47% yield) as a colorless syrup, $[\alpha]_D^{19}$ +7.0° (*c* 0.97, $CHCl_3$); IR $\nu_{max}^{CHCl_3}$ 3000, 2920, 2860, 1730, 1490, 1450, 1365, 1240 cm^{-1}; ^1H NMR δ=1.75—2.10 (3H, m, H-1, 6, 6′), 2.00, 2.02 (3H×2, each s, 2×$OCOCH_3$), 3.60—4.07 (5H, m, H-3, 4, 5, CH_2OAc), 4.37—4.73 (6H, m, 3×$OCH_2C_6H_5$), 5.36 (1H, t, $J_{1,2}=J_{2,3}$=10 Hz, H-2), 7.17—7.47 (15H, m, 3×$OCH_2C_6H_5$). Found: *m/z* 532.2448. Calcd for $C_{32}H_{36}O_7$: M, 532.2458.

(1*R*,2*R*,3*S*,4*R*,5*S*)-2,3,4,5-Tetraacetoxy-1-(acetoxymethyl)cyclohexane, Pentaacetate of Pseudo-α-D-mannopyranose (15). A solution of **14** (44.5 mg, 0.08 mmol) in methanol (2 ml) was hydrogenolyzed in the presence of palladium black in the Parr apparatus for 45 h. After the catalyst was removed, the filtrate was evaporated. The residue was chromatographed with silica gel (2 g, chloroform-methanol=15 : 1), and the fraction corresponding to R_f 0.42 (chloroform-methanol=8 : 1) was evaporated. The colorless syrup was acetylated with acetic anhydride (0.5 ml) in pyridine (0.5 ml) for 2 h. The mixture was evaporated, and the residue was chromatographed with silica gel (1 g, ethyl acetate-hexane=1 : 4). The fraction corresponding to R_f 0.30 (ethyl acetate-hexane=1 : 2) was evaporated to give crystals of **15** (18 mg, 56% yield). **15**: Mp 80—81 °C; $[\alpha]_D^{19}$ +27.8° (*c* 0.84, $CHCl_3$); IR $\nu_{max}^{CHCl_3}$ 2950, 1740, 1430, 1370, 1220 cm^{-1}; ^1H NMR δ=1.50—2.70 (3H, m, H-1, 6, 6′), 1.97, 2.03, 2.05, 2.13 (3H, 3H, 3H, and 6H, each s, 5×$OCOCH_3$), 3.87—4.27 (2H, m, CH_2OAc), 5.03—5.40 (4H, m, H-2, 3, 4, 5). The ^1H NMR spectrum of **15** was identical with that of authentic DL-**15**.[10] Found: C, 52.79; H, 6.14%. Calcd for $C_{17}H_{24}O_{10}$: C, 52.57; H, 6.23%.

(1*R*,5*R*,6*S*,8*R*,9*R*)-8,9-Isopropylidenedioxy-7-oxabicyclo[4.3.0]non-3-en-5-ol (17). To a solution of (1*R*,4*S*,5*S*,6*S*,-8*R*,9*R*)-4,5-epoxy-8,9-isopropylidenedioxy-7-oxabicyclo-[4.3.0]nonan-3-one (**16**)[3] (373 mg, 1.65 mmol) in ethanol (54 ml) were added hydrazine hydrate (0.40 ml, 8.26 mmol) and acetic acid (0.47 ml, 8.26 mmol) with stirring. The mixture was stirred for 2.5 min, and added to a saturated aqueous $NaHCO_3$ solution (170 ml). The aqueous solution was extracted with chloroform (170 ml×5). The combined extract was dried on Na_2SO_4 and evaporated. The residue was chromatographed with silica gel (13 g, ethyl acetate-hexane=1 : 3), and the fraction corresponding to R_f 0.44 (ethyl acetate-hexane=1 : 1) was evaporated to give **17** (258 mg, 74% yield), mp 95—98 °C; $[\alpha]_D^{22.5}$ −136.4° (*c* 1.00, $CHCl_3$); IR $\nu_{max}^{CHCl_3}$ 3490, 3000, 2900, 1635, 1460, 1440, 1420, 1380, 1320, 1305, 1250 cm^{-1}; ^1H NMR δ=1.33, 1.50 (3H×2, each s, $C(CH_3)_2$), 1.80—2.50 (4H, m, H-1, 2, 2′, OH), 3.72 (1H, dd, δ=10.5 and 4.5 Hz, H-6), 4.43 (1H, t, *J*=4.5 Hz, H-5 or 9), 4.61 (1H, t, *J*=4.5 Hz, H-9 or 5), 5.70—6.10 (3H, m, H-3, 4, 8). Found: C, 62.07; H, 7.54%. Cacld for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60%.

(1*S*,6*S*,8*R*,9*R*)-8,9-Isopropylidenedioxy-7-oxabicyclo[4.3.0]non-3-en-5-one (18). To a solution of **17** (128.5 mg, 0.61 mmol) in dichloromethane (12 ml) were added PCC (521 mg, 2.42 mmol) and molecular sieves (4A powder, 150 mg) with stirring. The mixture was stirred for 1.5 h and evaporated. The residue charged on a silica-gel column (10 g) was eluted with ether to give crystals of **18** (110.4 mg, 87% yield; TLC R_f 0.57, ethyl acetate-hexane=3 : 2), mp 96—98 °C; $[\alpha]_D^{24}$ −141.0° (*c* 0.70, $CHCl_3$); IR $\nu_{max}^{CHCl_3}$ 2975, 2925, 2825, 1700, 1595, 1445, 1425, 1370, 1320, 1300, 1240, 1210 cm^{-1}; ^1H NMR δ=1.35, 1.52 (3H×2, each s, $C(CH_3)_2$), 2.00—2.50 (1H, m,

H-1), 2.55—2.80 (2H, m, H-2, 2'), 4.45 (1H, d, J=12 Hz, H-6), 4.69 (1H, t, J=4.5 Hz, H-9), 5.88 (1H, d, J=4.5 Hz, H-8), 5.98 (1H, d, J=12 Hz, H-4), 6.91 (1H, dt, J=12 and 4.5 Hz, H-3). Found: C, 62.96; H, 6.72%. Calcd for $C_{11}H_{14}O_4$: C, 62.85; H, 6.71%.

(1*R*,5*R*,6*S*,8*R*,9*R*)-5-Acetoxy-8,9-isopropylidenedioxy-7-oxabicyclo[4.3.0]non-3-ene (19). Acetylation of **17** (162 mg, 0.76 mmol) with acetic anhydride (5 ml) in pyridine (5 ml) for 14 h, and chromatographic purification with silica gel (4 g, ethyl acetate-hexane=1 : 3) gave **19** (191 mg, 98% yield), TLC R_f 0.47 (ethyl acetate-hexane=1 : 2); mp 121—122 °C; $[\alpha]_D^{24}$ −262.1° (c 0.62, $CHCl_3$); IR $\nu_{max}^{CHCl_3}$ 3040, 2975, 2925, 2875, 1730, 1630, 1450, 1370, 1330, 1290, 1250 cm^{-1}; ^1H NMR δ=1.33, 1.46 (3H×2, each s, $C(CH_3)_2$), 2.03 (3H, s, $OCOCH_3$), 2.10—2.50 (3H, m, H-1, 2, 2'), 3.86 (1H, dd, J=12 and 4.5 Hz, H-6), 4.60 (1H, t, J=4.5 Hz, H-9), 5.50 (1H, t, J=4.5 Hz, H-5), 5.70—6.20 (3H, m, H-3, 4, 8). Found: C, 61.16; H, 7.11%. Calcd for $C_{13}H_{18}O_5$: C, 61.40; H, 7.13%.

(1*R*,3*S*,4*S*,5*S*,6*S*,8*R*,9*R*)-5-Acetoxy-8,9-isopropylidenedioxy-7-oxabicyclo[4.3.0]nonane-3,4-diol (20). To a solution of **19** (190 mg, 0.74 mmol) in t-butyl alcohol (4 ml) were added osmium tetraoxide in t-butyl alcohol (0.02 mol dm^{-3} solution, 0.37 ml, 0.007 mmol) and hydrogen peroxide (35% in water, 0.26 ml) with stirring. The mixture was stirred for 88 h in dark. The mixture was evaporated and the residue was chromatographed with silica gel (15 g, ethyl acetate-hexane=1 : 2). The fraction corresponding to R_f 0.37 (ethanol-toluene=1 : 6) was evaporated to give crystals of **20** (75 mg, 35% yield), mp 174—175 °C; $[\alpha]_D^{22}$ −0.19 ° (c 0.90, MeOH); IR ν_{max}^{KBr} 3500, 3450, 2990, 1725, 1375, 1255 cm^{-1}; ^1H NMR δ=1.31, 1.52 (3H×2, each s, $C(CH_3)_2$), 1.70—2.10 (5H, m, H-1, 2, 2',2×OH), 2.07 (3H, s, $OCOCH_3$), 3.66—4.35 (3H, m, H-3, 4, 6), 4.56 (1H, t, J=4.5 Hz, H-9), 5.43 (1H, t, J=3 Hz, H-5), 5.81 (1H, d, J=4.5 Hz, H-8). Found: C, 54.31; H, 6.83%. Calcd for $C_{13}H_{20}O_7$: C, 54.15; H, 6.99%.

(1*R*,3*S*,4*S*,5*S*,6*S*,8*R*,9*R*)-3,4,5-Triacetoxy-8,9-isopropylidenedioxy-7-oxabicyclo[4.3.0]nonane (21). Acetylation of **20** (23 mg, 0.08 mmol) with acetic anhydride (1 ml) in pyridine (1 ml), and chromatographic purification with silica gel (2 g, ethyl acetate-hexane=1 : 3) gave crystals of **21** (27 mg, 90% yield, TLC R_f 0.71 (ethanol-toluene=1 : 6); mp 135—137 °C; $[\alpha]_D^{22}$ +28.5° (c 0.94, $CHCl_3$); IR $\nu_{max}^{CHCl_3}$ 2990, 2930, 1745, 1370, 1250 cm^{-1}; ^1H NMR δ=1.30, 1.52 (3H×2, each s, $C(CH_3)_2$), 1.80—2.40 (3H, m, H-1, 2, 2'), 1.99, 2.10 (3H and 6H, each s, 3×$OCOCH_3$), 4.05 (1H, dd, J=10.5 and 3 Hz, H-6), 4.58 (1H, t, J=4.5 Hz, H-9), 4.90—5.56 (3H, m, H-3,4,5), 5.83 (1H, d, J=4.5 Hz, H-8). Found: C, 55.12; H, 6.50%. Calcd for $C_{17}H_{24}O_9$: C, 54.83; H, 6.50%.

(1*R*,3*S*,4*S*,5*R*,6*S*,8*R*,9*R*)- and (1*R*,3*R*,4*R*,5*S*,6*S*,8*R*,9*R*)-4,5-Epoxy-8,9-isopropylidenedioxy-7-oxabicyclo[4.3.0]nonan-3-ol, (22) and (22'). A solution of inseparable mixture of **2** and **2'** (106 mg, 0.50 mmol) in dichloromethane (4 ml) containing MCPBA (429 mg, 2.5 mmol) was refluxed for 41 h. The solution diluted with water (20 ml) was extracted with dichloromethane (20 ml×6). The combined extract was washed with saturated aqueous sodium sulfite (30 ml), dried on Na_2SO_4, and evaporated. The residue was chromatographed with silica gel (13 g, ethyl acetate-hexane=1 : 7). The fraction corresponding to R_f 0.29 (ethyl acetate-hexane=2 : 1) was evaporated to give **22'**[3] (18 mg, 16% yield), which was identical with authentic sample in TLC, mp, and ^1H NMR. The fraction corresponding to R_f 0.23 was evaporated to give crystals of **22** (57 mg, 50% yield), mp 159—161 °C; $[\alpha]_D^{21}$ −21.0° (c 1.00, $CHCl_3$); IR $\nu_{max}^{CHCl_3}$ 3560, 3000, 2850, 1460, 1380, 1300, 1265, 1255, 1215 cm^{-1}; ^1H NMR δ=1.30, 1.50 (3H×2, each s, $C(CH_3)_2$), 1.12—2.24 (3H, m, H-1, 2, 2'), 2.49—2.75 (1H, br, OH), 3.32 (1H, t, J=3 Hz, H-5), 3.58—3.83 (2H, m, H-4,6), 4.04—4.32 (1H, m, H-3), 4.51 (1H, t, J=4 Hz, H-9), 5.85 (1H, d, J=4 Hz, H-8). Found: C, 57.52; H, 6.90%. Calcd for $C_{11}H_{16}O_5$: C, 57.88; H, 7.07%.

Solvolysis of 22 and Successive Acetylation. Compound **21** from **22**. A solution of **22** (36 mg, 0.16 mmol) in a mixture of water and 2-methoxyethanol (3 : 10 v/v, 5 ml) in the presence of sodium acetate (39 mg, 0.48 mmol) was refluxed for 47 h and evaporated. The residue was acetylated with acetic anhydride (1.3 ml) in pyridine (1.3 ml) for 2 h. After the mixture was condensed by evaporation, the residue was partitioned between dichloromethane (10 ml) and water (10 ml). The aqueous layer was extracted with dichloromethane (10 ml×2). The organic layer was dried on Na_2SO_4 and evaporated. The residue was chromatographed with silica gel (5 g, ethyl acetate-hexane=1 : 4 to 1 : 3), and the fraction corresponding to R_f 0.59 (ethanol-toluene=1 : 6) was evaporated to give **21** (46 mg, 79%), which was identical with the compound prepared from **19** in TLC, mp, $[\alpha]_D$, and ^1H NMR.

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