deuteriated analogue): ^{1}H NMR (D_2O) δ 1.04 (m, 2 H, 2-H_R, 3-H_RH_S), 1.18 (m, 1 H, 3-H_RH_S); MS, m/e 103 $(MH)^+$.

(1*S*,2*R*)-1-Amino[2-^{2}H]cyclopropane-1-carboxylic Acid (14a). The title [^{2}H]ACC **14a** was obtained in 50% de at C-1 [or **14a** and **14b** (3:1)] in a manner similar to that for **12a** from 0.1 g (0.37 mmol) of the compound **10a** (de at C-6 50%) by hydrolysis with hydrochloric acid in 48% yield: mp 228-230 °C (water/methanol) (lit.[22] mp 229-231 °C for the nondeuteriated analogue); NMR (D_2O) δ 1.04 (m, 1 H, 3-H_RH_S), 1.19 (m, 2 H, 2-H_S, 3-H_RH_S); MS, m/e 103 $(MH)^+$.

(22) Rich, D. H.; Tam, J. P. *Synthesis* **1978**, 46.

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Syntheses of (1*S*,2*S*,3*S*,4*R*)- and (1*R*,2*R*,3*S*,4*R*)-2,3,4-Trihydroxycyclopentane-1-methanol, Carbocyclic Analogues of α-L-Arabinofuranose and β-D-Ribofuranose[1]

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The title compounds, two carbocyclic analogues of aldopentofuranoses, were synthesized from D-glucose. The key cyclopentane ring formation was achieved under the glycol cleavage reaction of methyl 3-*O*-benzyl-5,6-dideoxy-6-*C*-(methoxycarbonyl)-D-*xylo*-hepto-1,4-furanuronate, which was prepared by a seven-step sequence from D-glucose. The diastereomeric mixture of dimethyl 2-acetoxy-4-(formyloxy)-3-(benzyloxy)cyclopentane-1,1-dicarboxylates was converted into the title compounds through demethoxycarbonylation, Dibal-H reduction, hydroboration of thus formed 1-cyclopentene-1-methanol followed by oxidative workup, and deprotection.

We reported recently the synthesis of enantiomerically pure 2,3,4,5-tetrahydroxycyclohexane-1-methanol and 2,3,4-trihydroxycyclopentane-1-methanol.[2] These polyoxygenated six- and five-membered compounds can be regarded as carbocyclic analogues of carbohydrates. Access to the five-membered carbocycles opens an alternative synthetic approach toward carbocyclic nucleoside antibiotics, which have aroused much interest in recent years owing to their significant antitumor and antimicrobial activities.[3] Our synthesis of these carbocycles relies on the intramolecular aldol cyclization of carbohydrate-derived precursors. Herein, we report syntheses of (1*S*,2*S*,3*S*,4*R*)- and (1*R*,2*R*,3*S*,4*R*)-2,3,4-trihydroxycyclopentane-1-methanol (**1** and **2**, respectively) from D-glucose. The present syntheses are based on a similar approach reported previously.[2f] Compounds **1** and **2** are pseudo-α-L-arabinofuranose and pseudo-β-D-ribofuranose, respectively.[4]

Glycol cleavage of 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose (**3**)[5] with $NaIO_4$ and successive Knoevenagel condensation of the resulting 1,5-dialdofuranose **4** with dimethyl malonate in a mixture of pyridine and acetic anhydride gave α,β-unsaturated diester **5**. 1,4-Conjugate addition of hydride to **5** with $NaBH_4$ gave the saturated diester **6** in an overall yield of 41% from **3**. The isopropylidene group in **6** was then hydrolyzed with aqueous HCl to give **7** as an anomeric mixture. Hydrolysis of the ester groups also occurred partly under these conditions. Unfortunately, we could not find optimal conditions for selective hydrolysis of the isopropylidene group. The glycol in **7** was cleaved with $NaIO_4$ in aqueous MeOH solution. Under the glycol cleavage conditions, the intermediate **8** cyclized spontaneously in an intramolecular aldol fashion. The resulting diastereomeric mixture of the cyclized products **9** and **9′** were acetylated to give **10** and **10′** in a combined yield of 30.5% from **6** (7% of **6** was also recovered at this stage). By careful chromatography on a silica gel column, pure **10** and **10′** were separated in an approximately 5 to 1 ratio. The configurations of the newly introduced asymmetric carbons (C-2) in **10** and **10′** (therefore those in **9** and **9′**) are tentatively assigned as depicted based on ^{1}H NMR (400 MHz) spectra analyses. H-2 of the major isomer **10** appears at δ 5.93 as a doublet with $J_{2,3}$ = 3.4 Hz, while that of **10′** appears at δ 6.01 as a doublet with $J_{2,3}$ = 4.4 Hz. These data indicate that relationship of H-2 and H-3 are trans for **10** and cis for **10′**, respectively.[6] We did not carry out any further experiments for confirmation of the structures of **10** and **10′**. The

(1) This work was presented at the 56th National Meeting of the Chemical Society of Japan, Tokyo, April 1-4 1988; Abstract 3XID12.

(2) (a) Suami, T.; Tadano, K.; Kameda, Y.; Iimura, Y. *Chem. Lett.* **1984**, 1919; *J. Carbohydr. Chem.* **1987**, *6*, 231. (b) Suami, T.; Tadano, K.; Ueno, Y.; Fukabori, C. *Chem. Lett.* **1985**, 1557. (c) Tadano, K.; Ueno, Y.; Fukabori, C.; Hotta, Y.; Suami, T. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1727. (d) Tadano, K.; Maeda, H.; Hoshino, M.; Iimura, Y.; Suami, T. *Chem. Lett.* **1986**, 1081; *J. Org. Chem.* **1987**, *52*, 1946. (e) Tadano, K.; Fukabori, C.; Miyazaki, M.; Kimura, H.; Suami, T. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 2189. (f) Tadano, K.; Kimura, H.; Hoshino, M.; Ogawa, S.; Suami, T. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3673. (g) Tadano, K.; Hoshino, M.; Ogawa, S.; Suami, T. *Tetrahedron Lett.* **1987**, *28*, 2741; *J. Org. Chem.* **1988**, *53*, 1427.

(3) Suhadolnik, R. J. *Nucleoside Antibiotics*; Wiley: New York, 1970; pp 236-245, and for related papers, see ref 2g.

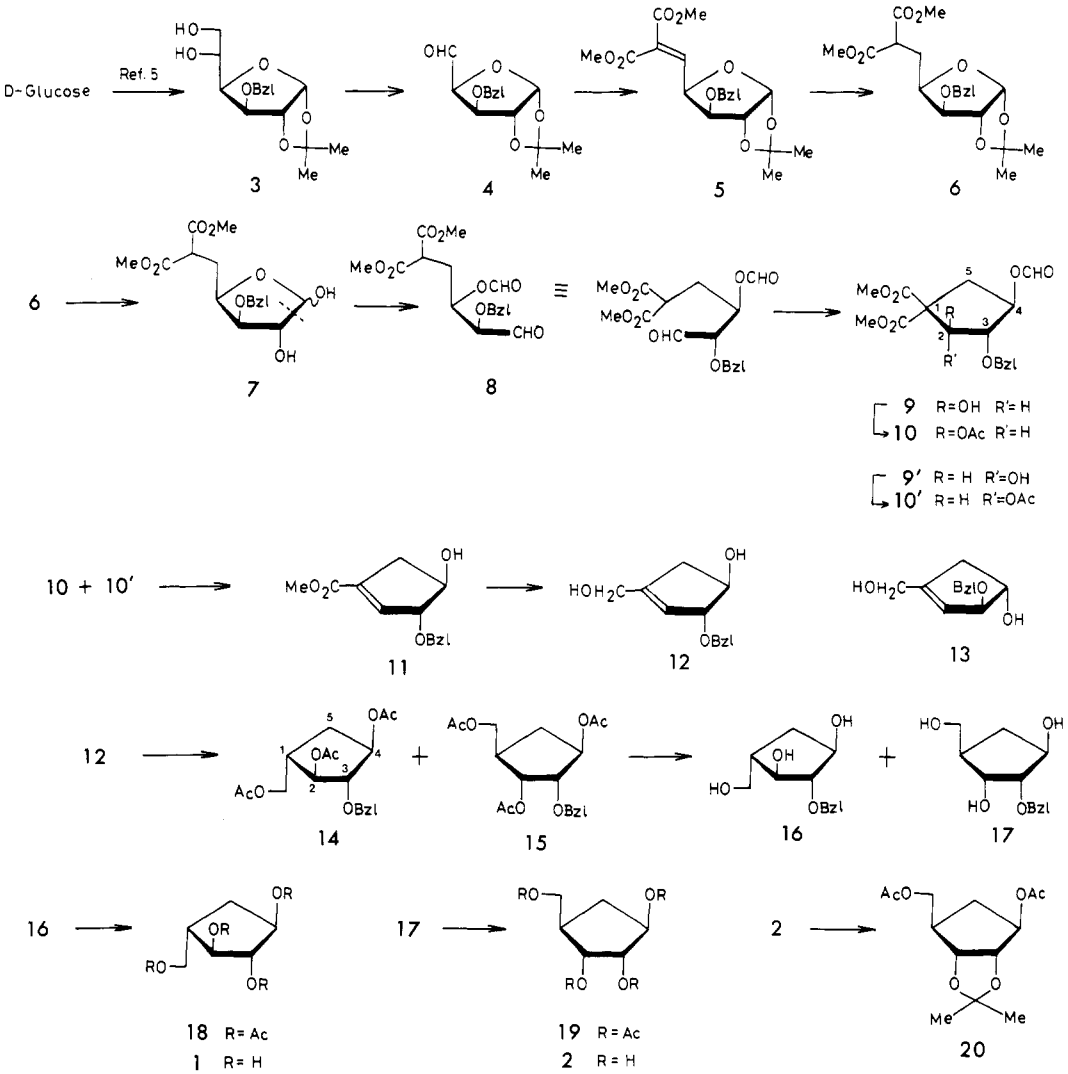
(4) Compounds **1**, **2**, and **14-20** are considered to be carbocyclic analogues of carbohydrates, which are frequently designated as pseudosugars.

(5) Whistler, R. L.; Lake, W. C.; In *Methods in Carbohydrate Chemistry*; Whistler, R. L., BeMiller, J. N., Eds.; Academic Press: New York, 1972; Vol. VI, p 286.

(6) For ^{1}H NMR spectral interpretation of five-membered compounds, see: Jackman, L. M.; Sternhell, S. *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, 2nd ed.; Pergamon Press: Oxford, 1969; p 287.

0022-3263/89/1954-0276$01.50/0

Scheme I



mixture of **10** and **10′** was thermally demethoxycarbonylated in aqueous DMSO in the presence of NaCl,[7] and the product was successively deformylated to give **11** in 65% yield. Under the demethoxycarbonylation conditions, β-elimination of the acetoxyl groups also took place. Reduction of **11** with diisobutylaluminum hydride (Dibal-H) at 0 °C gave 1-cyclopentene-1-methanol **12** in 93% yield. We previously synthesized the enantiomer of **12** (i.e. **13**) in an enantiomerically pure form.[2f] The IR and ^{1}H NMR spectra of **12** and **13** are completely identical, and the specific rotation values of **12** [$[\alpha]^{24}_D$ −102.8° (*c* 1.08, $CHCl_3$)] and **13** [$[\alpha]^{25}_D$ +100.0° (*c* 0.99, $CHCl_3$)][2f] reveal that they are enantiomers. Hydroboration of **12** with BH_3–THF followed by H_2O_2 oxidation and successive acetylation provided protected forms of 2,3,4-trihydroxycyclopentane-1-methanols, **14** and **15**, as an inseparable mixture. This diastereomeric mixture of **14** and **15** was then deacetylated to give **16** and **17** in 39% and 24% yields, respectively, after silica gel chromatographic separation. These results show that the attack of borane to **12** proceeded somewhat preferentially from the β-side of the cyclopentene ring. Hydrogenolytic debenzylation in the presence of 10% Pd on charcoal of **16** followed by acetylation gave pseudo-α-L-arabinofuranose tetraacetate (**18**) quantitatively. Deacetylation of **18** with sodium methoxide gave pseudo-α-L-arabinofuranose (**1**) as a coloress oil in 95% yield. Similarly, **17** was converted into the tetraacetate **19** (95%) and the unprotected form (**2**) (98%) of pseudo-β-D-ribofuranose. The structures of **1** and **2** were confirmed as follows. Under the usual isopropylidenation conditions, **1** failed to react and was recovered quantitatively. On the other hand, **2** was converted into 2,3-*O*-isopropylidene derivative **20** in 82% yield by the same conditions employed for **1** followed by acetylation. From these results, it is clear that the 2,3-diol of **1** is trans oriented and that of **2** has a cis relationship. Therefore, compounds **1** and **2** are (1*S*,2*S*,3*S*,4*R*)- and (1*R*,2*R*,3*S*,4*R*)-2,3,4-trihydroxycyclopentane-1-methanol.

Experimental Section

General Procedures. Reactions were carried out at room temperature unless otherwise described. Melting points are uncorrected. Specific rotations were measured in $CHCl_3$ solution with a 10-mm cell. Column chromatography was performed with silica gel (Katayama Chemicals, K070), and thin-layer chromatography (TLC) with a glass plate coated with Kieselgel 60 GF_{254} (Merck). ^{1}H NMR spectra at 90 and 400 MHz were recorded in $CDCl_3$ (90 MHz) and CD_3OD (400 MHz) solutions. ^{13}C NMR spectra were measured at 100 MHz in CD_3OD solution.

Dichloromethane (CH_2Cl_2) and *N*,*N*-dimethylformamide (DMF) were dried over CaH_2 and then distilled. Pyridine was distilled over NaOH. Tetrahydrofuran (THF) was distilled over $LiAlH_4$ and then Na/benzophenone.

Methyl 3-*O*-Benzyl-5,6-dideoxy-1,2-*O*-isopropylidene-6-*C*-(methoxycarbonyl)-α-D-*xylo*-hepto-1,4-furanuronate (6).

(7) Krapcho, A. P.; Jahngen, E. G. E., Jr.; Lovey, A. J.; Short, F. W. *Tetrahedron Lett.* **1974**, 1091.

To a stirred solution of **3**[5] (2.94 g, 9.5 mmol) in MeOH (50 mL) was added an aqueous solution (25 mL) of $NaIO_4$ (4.04 g, 18.9 mmol) at 0 °C. After being stirred for 30 min, the resulting solids were removed by filtration and washed with MeOH. The combined filtrate and washing were concentrated in vacuo. The residue was dissolved in water (50 mL) and extracted with CH_2Cl_2 (150 mL × 4). The combined extracts were dried (Na_2SO_4) and concentrated in vacuo to give **4**, which was directly used in the next step. To a solution of **4** in pyridine (20 mL) were added freshly distilled dimethyl malonate (3.25 mL, 28.4 mmol) and acetic anhydride (15 mL). After being stirred for 41 h, the mixture was diluted with AcOEt (300 mL). This was washed with water (150 mL × 4), saturated aqueous $NaHCO_3$ solution (100 mL × 2), saturated aqueous NaCl solution (150 mL × 3), and water (150 mL), successively. The organic layer was dried (Na_2SO_4) and concentrated in vacuo to give **5** (4.74 g), which was used in the next step. In a small-scale experiment, **5** was purified by silica gel chromatography (AcOEt/hexane, 1:9); **5** as a colorless oil: TLC R_f 0.55 (AcOEt/hexane, 1:3); ^1H NMR (90 MHz) δ 1.26, 1.44 (each s, each 3 H, $C(CH_3)_2$), 3.73, 3.79 (each s, each 3 H, 2 $COOCH_3$), 4.14 (d, 1 H, J = 3 Hz, H-3), 4.40–4.66 (m, 3 H, $OCH_2C_6H_5$, H-2), 5.04 (dd, 1 H, J = 3 and 6 Hz, H-4), 5.95 (d, 1 H, J = 4.5 Hz, H-1), 7.07 (d, 1 H, J = 6 Hz, H-5), 7.28 (s, 5 H, $OCH_2C_6H_5$).

To a stirred solution of **5** (4.74 g) in MeOH (40 mL) was added $NaBH_4$ (0.43 g, 11.4 mmol) at 0 °C. After being stirred at 0 °C for 40 min, Amberlite IR-120 (H^+) was added for neutralization. The resin was removed and washed with MeOH. The combined filtrate and washing were concentrated in vacuo. The residue was chromatographed on silica gel (AcOEt/hexane, 1:15), and the fractions corresponding to R_f 0.64 (AcOEt/hexane, 1:2) were concentrated in vacuo to give **6** (1.52 g, 41%) as white crystals, mp 85–86 °C: $[\alpha]^{29}_D$ −36.5° (c 1.26); IR ν_{max}^{KBr} 2960, 1755, 1730 cm^{-1}; ^1H NMR (90 MHz) δ 1.29, 1.44 (each s, each 3 H, $C(CH_3)_2$), 2.13–2.41 (m, 2 H, H-5,5′), 3.70 (s, 6 H, 2 $COOCH_3$), 3.43–3.72 (m, 1 H, H-6), 3.79 (d, 1 H, J = 3 Hz, H-3), 4.03–4.25 (m, 1 H, H-4), 4.46, 4.67 (each d, each 1 H, J = 12 Hz, $OCH_2C_6H_5$), 4.55 (d, 1 H, J = 4 Hz, H-2), 5.85 (d, 1 H, J = 4 Hz, H-1), 7.32 (s, 5 H, $OCH_2C_6H_5$). Anal. Calcd for $C_{20}H_{26}O_6$: C, 60.90; H, 6.65. Found: C, 60.82; H, 6.51.

Dimethyl (2*S*,3*S*,4*R*)- and (2*R*,3*S*,4*R*)-2-Acetoxy-3-(benzyloxy)-4-(formyloxy)cyclopentane-1,1-dicarboxylate (10 and 10′). A solution of **6** (3.00 g, 7.6 mmol) in a mixture of 12 M HCl solution (44 mL), water (680 mL), and 1,4-dioxane (300 mL) was stirred for 2 days. Then, a mixture of 12 M HCl (22 mL), water (330 mL), and 1,4-dioxane (146 mL) was added, and the mixture was stirred for an additional 2 days. The mixture was neutralized by addition of solid $NaHCO_3$ (ca. 72 g). This was extracted with AcOEt (1 L × 4), and the combined extracts were dried (Na_2SO_4) and then concentrated in vacuo to give **7** (2.10 g; TLC R_f 0.39, AcOEt/hexane, 2:1) as a colorless oil. To a solution of **7** (2.10 g) in MeOH (700 mL) was added an aqueous solution (90 mL) of $NaIO_4$ (16.3 g, 76.1 mmol) at 0 °C. The solution was stirred for 2.5 h, after which 8.1 g (38.1 mmol) of $NaIO_4$ in water (45 mL) was added. The mixture was stirred for 1.5 h more, and the resulting solids were removed by filtration and washed with MeOH. The combined filtrate and washing were concentrated in vacuo. The residue was partitioned between AcOEt (600 mL) and water (600 mL). The aqueous phase was extracted with AcOEt (600 mL × 3). The combined extracts were dried (Na_2SO_4) and concentrated in vacuo to give a mixture of **9** and **9′** (2.10 g) as a colorless oil. The mixture of **9** and **9′** was acetylated with acetic anhydride (150 mL) in pyridine (150 mL) for 2 h, and the mixture was concentrated in vacuo. The residue was chromatographed on silica gel (AcOEt/hexane, 1:8), and the combined fractions corresponding to R_f 0.42 (for **10′**) and R_f 0.38 (for **10**) (AcOEt/hexane, 1:2) were concentrated in vacuo to give the mixture of **10** and **10′** (915 mg, 30.5%) as a colorless oil. Compound **6** (197 mg, 7%) was also recovered (TLC R_f 0.64). The mixture of **10** and **10′** was used in the next step without separation. In a small-scale experiment, the 5 to 1 mixture of **10** and **10′** was separated by silica gel chromatography. **10**: $[\alpha]^{21}_D$ −52.1° (c 1.02); IR ν_{max}^{neat} 2960, 1740, 1460, 1440, 1375 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.04 (s, 3 H, $OCOCH_3$), 2.55 (dd, 1 H, J = 6.8 and 14.6 Hz, H-5), 2.97 (dd, 1 H, J = 7.8 and 14.6 Hz, H-5′), 3.70, 3.73 (each s, each 3 H, 2 $COOCH_3$), 4.00 (dd, 1 H, J = 3.4 and 3.4 Hz, H-3), 4.59, 4.69 (each d, each 1 H, J = 11.7 Hz, $OCH_2C_6H_5$), 5.16 (ddd, 1 H, J = 3.4, 6.8 and 7.8 Hz, H-4), 5.93 (d, 1 H, J = 3.4 Hz, H-2), 7.26–7.35 (m, 5 H, $OCH_2C_6H_5$), 8.00 (s, 1 H, OCHO). Anal. Calcd for $C_{19}H_{22}O_9$: C, 57.86; H, 5.62. Found: C, 58.15; H, 5.68. **10′**: $[\alpha]^{21}_D$ −11.0° (c 0.89); IR ν_{max}^{neat} 2975, 1760, 1745, 1460, 1380 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.95 (dd, 1 H, J = 5.4 and 15.1 Hz, H-5), 2.04 (s, 3 H, $OCOCH_3$), 3.36 (dd, 1 H, J = 9.3 and 15.1 Hz, H-5′), 3.72, 3.75 (each s, each 3 H, 2 $COOCH_3$), 4.20 (dd, 1 H, J = 4.4 and 7.0 Hz, H-3), 4.51, 4.67 (each d, each 1 H, J = 11.2 Hz, $OCH_2C_6H_5$), 5.26 (ddd, 1 H, J = 5.4, 7.0 and 9.3 Hz, H-4), 6.01 (d, 1 H, J = 4.4 Hz, H-2), 7.27–7.36 (m, 5 H, $OCH_2C_6H_5$), 8.00 (s, 1 H, OCHO). Anal. Calcd for $C_{19}H_{22}O_9$: C, 57.86; H, 5.62. Found: C, 58.16; H, 5.67.

Methyl (3*R*,4*R*)-3-(Benzyloxy)-4-hydroxy-1-cyclopentene-1-carboxylate (11). A stirred solution of the mixture of **10** and **10′** (1.07 g, 2.7 mmol) in a mixture of DMSO (100 mL) and water (4 mL) containing NaCl (480 mg) was heated from 125 to 155 °C for 3 h. Then, the solution was heated at 155 °C for 6.5 h. After being cooled to room temperature, the solution was diluted with MeOH (100 mL), and sodium methoxide in MeOH (1 M, 8.2 mL, 8.2 mmol) was added. After being stirred for 1.5 h, the mixture was neutralized by addition of Amberlite IR-120 (H^+). The resin was removed and washed with MeOH. The combined filtrate and washing were concentrated in vacuo. The residue was diluted with AcOEt (100 mL) and washed with water (100 mL × 5). The combined aqueous phases were extracted with CH_2Cl_2 (500 mL × 4). The combined organic phases were dried (Na_2SO_4) and concentrated in vacuo. The residue was chromatographed on silica gel (AcOEt/toluene, 1:12), and the fractions corresponding to R_f 0.59 (AcOEt/toluene, 1:5) were concentrated in vacuo to give **11** (440 mg, 65%) as a colorless oil. **11**: $[\alpha]^{26}_D$ −123.4° (c 0.88); IR ν_{max}^{neat} 3450, 2960, 1720, 1630, 1490, 1450 cm^{-1}; ^1H NMR (90 MHz) δ 1.95–2.52 (m, 2 H, H-5, OH), 2.80–3.15 (m, 1 H, H-5′), 3.71 (s, 3 H, $COOCH_3$), 4.24–4.52 (m, 2 H, H-3, H-4), 4.59 (s, 2 H, $OCH_2C_6H_5$), 6.59 (dd, 1 H, J = 1.5 and 3.5 Hz, H-2), 7.27 (s, 5 H, $OCH_2C_6H_5$); high-resolution mass spectra, calcd for $C_{14}H_{16}O_4$ m/z 248.1047, found (M) 248.1033.

(3*R*,4*R*)-3-(Benzyloxy)-4-hydroxy-1-cyclopentene-1-methanol (12). The reaction was carried out under an argon atmosphere. To a solution of **11** (429 mg, 1.7 mmol) in CH_2Cl_2 (50 mL) was added Dibal-H (1.5 M solution in toluene, 11.5 mL, 17.3 mmol) at 0 °C. After being stirred at 0 °C for 1.5 h, more Dibal-H (5.8 mL) was added, and the mixture was stirred for 2 h more. Water (5.5 mL) was then added, and the resulting solids were removed by filtration. The solids were extracted repeatedly with AcOEt (200 mL × 6). The filtrate was diluted with CH_2Cl_2 (100 mL) and washed with water (100 mL). The combined organic phases were dried (Na_2SO_4) and concentrated in vacuo. The residue was chromatographed on silica gel (AcOEt/hexane, 5:6), and the fractions corresponding to R_f 0.41 (EtOH/toluene, 1:5) were concentrated in vacuo to give **12** (353 mg, 93%) as a colorless oil, $[\alpha]^{24}_D$ −102.8° (c 1.08). The spectra (IR, 90 MHz ^1H NMR, and MS) and TLC behavior of **12** were identical with those of **13** reported previously.[2f]

(1*S*,2*S*,3*S*,4*R*)- and (1*R*,2*R*,3*S*,4*R*)-3-(Benzyloxy)-2,4-dihydroxycyclopentane-1-methanol (16 and 17). The reaction was carried out under an argon atmosphere. To a stirred solution of **12** (326 mg, 1.48 mmol) in THF (30 mL) was added BH_3–THF (1 M solution in THF, 29.6 mmol) at 0 °C. After being stirred at 0 °C for 2 h, the solution was diluted with water (20 mL) and made basic with 3 M aqueous NaOH solution (35 mL). The solution was warmed to room temperature, and 35% H_2O_2 solution (37 mL) was added. The solution was stirred for 3 h. To the solution was added saturated aqueous Na_2SO_3 solution (37 mL). The resulting solids were removed by filtration, and the filtrate was concentrated in vacuo. The residue was placed on a short silica gel column, and the column was eluted with EtOH. The ethanolic eluate (ca. 700 mL) was concentrated in vacuo. The residue was acetylated with acetic anhydride (15 mL) in pyridine (15 mL) for 15 h. The mixture was diluted with water (50 mL), and extracted with CH_2Cl_2 (100 mL × 3). The extracts were dried (Na_2SO_4) and concentrated in vacuo. The residue was chromatographed on silica gel (AcOEt/toluene, 1:11), and the fractions corresponding to R_f 0.69 (EtOH/toluene, 1:5) were concentrated in vacuo to give an inseparable mixture of **14** and **15** (383 mg) as a colorless oil. To a solution of the mixture of **14** and **15** (383 mg) in MeOH (15 mL) was added sodium methoxide in MeOH

(1 M, 3.2 mL, 3.2 mmol). After being stirred at 0 °C for 3 h, the solution was neutralized by addition of Amberlite IR-120 (H^+). The resin was removed and washed with MeOH. The combined filtrate and washing were concentrated in vacuo. The residue was chromatographed on silica gel ($CHCl_3$/MeOH, 30:1). The fractions corresponding to R_f 0.25 (EtOH/toluene, 1:5) were concentrated to give **17** (86 mg, 24%) as a colorless oil. The fractions corresponding to R_f 0.23 were concentrated in vacuo to give **16** (136 mg, 39%) as white crystals, mp 105–106.5 °C. **16**: $[\alpha]^{21}_D$ −32.4° (c 0.96, MeOH); IR ν_{max}^{KBr} 3380, 2940, 2900 cm^{-1}; ^1H NMR (400 MHz, CD_3OD) δ 1.73–1.87 (m, 2 H, H-5, H-5′), 2.07–2.17 (m centered at δ 2.11, H-1), 3.51 (dd, 1 H, J = 6.5 and 11.0 Hz, CH_2OH), 3.63–3.75 (m, 3 H, H-2, H-3, CH_2OH), 4.02 (ddd, 1 H, J = 4.9, 4.9, and 7.3 Hz, H-4), 4.72 (s, 2 H, $OCH_2C_6H_5$), 7.23–7.40 (m, 5 H, $OCH_2C_6H_5$). Anal. Calcd for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61. Found: C, 65.47; H, 7.52. **17**: $[\alpha]^{21}_D$ −12.1° (c 0.92, MeOH); ^1H NMR (400 MHz, CD_3OD) δ 1.20–1.28 (m centered at δ 2.14, 1 H, H-5), 2.04–2.10 (m centered at δ 2.06, 1 H, H-1), 2.18–2.26 (m centered at δ 2.22, 1 H, H-5′), 3.50–3.66 (m, 3 H, H-3, CH_2OH), 3.95 (dd, 1 H, J = 5.4 and 5.4 Hz, H-2), 4.16 (dd, J = 6.8 and 12.2 Hz, H-4), 4.64, 4.70 (each d, each 1 H, J = 12.0 Hz, $OCH_2C_6H_5$), 7.23–7.41 (m, 5 H, $OCH_2C_6H_5$); high-resolution mass spectra, calcd for $C_{13}H_{18}O_4$ m/z 238.1203, found (M) 238.1187.

(1*S*,2*S*,3*S*,4*R*)-2,3,4-Triacetoxy-1-(acetoxymethyl)cyclopentane (18). A solution of **16** (117 mg, 0.49 mmol) in EtOH (10 mL) was hydrogenolyzed in the presence of 10% Pd on charcoal (234 mg) under 1 atm of hydrogen for 15 h. The catalyst was removed by filtration through a Celite pad, and the filtrate was concentrated in vacuo. The residue was acetylated with acetic anhydride (3 mL) in pyridine (3 mL) for 15 h. The mixture was concentrated in vacuo, and the residue was chromatographed on silica gel (AcOEt/hexane, 1:6). The fractions corresponding to R_f 0.72 (AcOEt/hexane, 1:1) were concentrated in vacuo to give **18** (155 mg, quantitative) as a colorless oil: $[\alpha]^{21}_D$ −46.9° (c 0.72); IR ν_{max}^{neat} 2950, 1750, 1440 cm^{-1}; ^1H NMR (90 MHz) δ 1.91–2.01 (m, 3 H, H-1, H-5, H-5′), 2.05 (s, 12 H, 4 $OCOCH_3$), 4.05 (d, 2 H, J = 6 Hz, CH_2OAc), 4.87–5.30 (m, 3 H, H-2, H-3, H-4). Anal. Calcd for $C_{14}H_{20}O_8$: C, 53.16; H, 6.37. Found: C, 53.34; H, 6.33.

(1*R*,2*R*,3*S*,4*R*)-2,3,4-Triacetoxy-1-(acetoxymethyl)cyclopentane (19). Compound **17** (68 mg, 0.28 mmol) was hydrogenolyzed in the presence of 10% Pd on charcoal (204 mg) as described in the case of **18**. After acetylation of the products and chromatographic purification (AcOEt/hexane, 1:6), 84 mg (95%) of **19** was obtained as a colorless oil. **19**: TLC R_f 0.72 (AcOEt/hexane, 1:1); $[\alpha]^{21}_D$ −5.3° (c 0.79); IR ν_{max}^{neat} 2975, 1750, 1440, 1380 cm^{-1}; ^1H NMR (90 MHz) δ 2.09, 2.10 (each s, 3 H and 9 H, 4 $OCOCH_3$), 2.40–2.81 (m, 3 H, H-1, H-5, H-5′), 4.28 (d, 2 H, J = 6 Hz, CH_2OAc), 5.20–5.60 (m, 3 H, H-2, H-3, H-4). Anal. Calcd for $C_{14}H_{20}O_8$: C, 53.16; H, 6.37. Found: C, 53.28; H, 6.33.

(1*S*,2*S*,3*S*,4*R*)-2,3,4-Trihydroxycyclopentane-1-methanol, Pseudo-α-L-arabinofuranose (1). A solution of **18** (60 mg, 0.19 mmol) in MeOH (5 mL) containing sodium methoxide in MeOH (1 M, 0.57 mL, 0.57 mmol) was stirred at 0 °C for 2.5 h. The solution was neutralized with Amberlite IR-120 (H^+). The resin was removed and washed with MeOH, and the combined filtrate and washing were concentrated in vacuo. The residue was chromatographed on silica gel ($CHCl_3$/MeOH, 9:1 to 8:1), and the fractions corresponding to R_f 0.41 ($CHCl_3$/MeOH, 2:1) were concentrated in vacuo to give **1** (27 mg, 95%) as a colorless oil: $[\alpha]^{16}_D$ −40.5° (c 0.84, MeOH); ^1H NMR (400 MHz, CD_3OD) δ 1.69–1.88 (m, 2 H, H-5, H-5′), 2.00–2.08 (m, 1 H, H-1), 3.47–3.67 (m, 4 H, H-2, H-3, CH_2OH), 3.81 (ddd, 1 H, J = 6.4, 6.4, and 8.3 Hz, H-4); ^{13}C NMR (100 MHz, CD_3OD) δ 33.02, 44.90, 64.50, 75.45, 78.53, 85.56; high-resolution mass spectrum calcd for $C_6H_{13}O_4$ m/z 149.0812, found (M + H) 149.0795.

(1*R*,2*R*,3*S*,4*R*)-2,3,4-Trihydroxycyclopentane-1-methanol, Pseudo-β-D-ribofuranose (2). By the analogous procedure described in the preparation of **1**, **19** (59 mg) was deacetylated to give **2** (27 mg, 98%) after silica gel chromatography ($CHCl_3$/MeOH, 2:1) as a colorless oil: TLC R_f 0.46 ($CHCl_3$/MeOH, 2:1); $[\alpha]^{16}_D$ +6.6° (c 1.00, MeOH); ^1H NMR (400 MHz, CD_3OD) δ 1.21–1.28 (m, 1 H, H-5), 1.99–2.08 (m, 1 H, H-1), 2.18–2.25 (m, 1 H, H-5′), 3.54 (dd, 1 H, J = 6.3 and 10.7 Hz, CH_2OH), 3.63 (dd, 1 H, J = 5.6 and 10.7 Hz, CH_2OH), 3.68 (dd, 1 H, J = 4.9 and 5.4 Hz, H-3), 3.85 (dd, 1 H, J = 5.4 and 5.4 Hz, H-2), 3.98 (ddd, 1 H, J = 4.4, 4.9 and 6.6 Hz, H-4); ^{13}C NMR (100 MHz, CD_3OD) δ 33.69, 45.98, 65.30, 74.52, 76.64, 79.59; high-resolution mass spectrum calcd for $C_6H_{13}O_4$ m/z 149.0812, found (M + H) 149.0798.

(1*R*,2*R*,3*S*,4*R*)-4-Acetoxy-1-(acetoxymethyl)-2,3-(isopropylidenedioxy)cyclopentane (20). To a solution of **2** (5 mg, 0.04 mmol) in DMF (0.5 mL) were added 2,2-dimethoxypropane (0.03 mL) and camphorsulfonic acid (2 mg). After being stirred for 6 h, the mixture was neutralized with saturated aqueous $NaHCO_3$ and concentrated in vacuo. The residue was acetylated with acetic anhydride (0.5 mL) in pyridine (0.5 mL) for 2 h. After concentration of the mixture, the residue was chromatographed on silica gel (AcOEt/hexane, 1:10). The fractions corresponding to R_f 0.62 (AcOEt/hexane, 2:3) were concentrated in vacuo to give **20** (7.5 mg, 82%) as a colorless oil: $[\alpha]^{24}_D$ −20.1° (c 0.33); IR ν_{max}^{neat} 3000, 2950, 1750, 1380 cm^{-1}; ^1H NMR (400 MHz) δ 1.30, 1.46 (each s, each 3 H, $C(CH_3)_2$), 1.59–1.65 (m, 1 H, H-5), 2.05, 2.08 (each s, each 3 H, 2 $OCOCH_3$), 2.33–2.40 (m, 1 H, H-5′), 2.45–2.52 (m, 1 H, H-1), 4.01–4.09 (m, 2 H, CH_2OAc), 4.52–4.56 (m, 2 H, H-2, H-3), 5.06–5.08 (m, 1 H, H-4). Anal. Calcd for $C_{13}H_{20}O_6$: C, 57.34; H, 7.40. Found: C, 57.42; H, 7.71.

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Registry No. **1**, 118013-55-1; **2**, 118013-56-2; **3**, 22529-61-9; **4**, 23558-05-6; **5**, 117918-35-1; **6**, 117918-36-2; α-**7**, 117918-37-3; β-**7**, 117918-42-0; **9**, 117918-38-4; **9′**, 118013-63-1; **10**, 117940-39-3; **10′**, 118014-53-2; **11**, 117918-39-5; **12**, 118013-57-3; **14**, 118013-58-4; **15**, 118013-59-5; **16**, 117918-40-8; **17**, 118013-60-8; **18**, 118013-61-9; **19**, 118013-62-0; **20**, 117918-41-9; $CH_2(COOMe)_2$, 108-59-8.

α-Acylamino Radical Cyclizations: Application to the Synthesis of a Tetracyclic Substructure of Gelsemine

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Syntheses of gelsemine substructures **2** and **3** are described. Free-radical precursors **14**, **18**, **35**, and **38** were prepared, and their behavior upon treatment with tri-*n*-butyltin hydride and AIBN was examined. The radical derived from **14** afforded reduction product **15**, whereas the radicals derived from **18**, **35**, and **38** gave cyclization products **23**, **37**, and **39**, respectively. Aspects of these free-radical cyclizations as well as the conversion of **23** and **37** to **2** and **3**, respectively, are presented.

Gelsemine (**1**) is an oxindole alkaloid that has eluded synthesis since its structure was reported nearly 30 years ago.[1-3] This has not, however, been due to a lack of effort. In fact, numerous studies that have been reported in the

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