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Note

A novel synthesis of 4-deoxy-D-*lyxo*-hexose ("4-deoxy-D-mannose") from 1,6-anhydro-3,4-dideoxy-β-D-*glycero*-hex-3-enopyranose-2-ulose (levoglucosenone)

Katsuya Matsumoto *, Takashi Ebata, Koshi Koseki, Koji Okano, Hiroshi Kawakami and Hajime Matsushita

Life Science Research Laboratory, Japan Tobacco Inc., 6–2 Umegaoka, Midori-ku, Yokohama, Kanagawa 227 (Japan)

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Replacement of natural sugars by 4-deoxy-D-*lyxo*-hexose ("4-deoxy-D-mannose", **8**) as the component parts of saccharides may endow compounds with new functions or biological activities. In previous studies, syntheses of **8** gave low overall yields or required many steps[1–4]. Thus a simplified synthetic route to **8** giving larger yields is needed.

For our purpose, levoglucosenone (1,6-anhydro-3,4-dideoxy-β-D-*glycero*-hex-3-enopyranos-2-ulose, **1**) [†], which is readily available by the acidic pyrolysis of cellulose[5], seemed to be an ideal starting material. We have previously reported the novel syntheses of D-altrosan (1,6-anhydro-β-D-altropyranose), D-altrose, D-allosan (1,6-anhydro-β-D-allopyranose), D-allose, and 1,6:3,4-dianhydro-β-D-talopyranose (**3**) from **1** as a common building block[6,7].

Compound **3** is easily and stereoselectively obtained in high yield from **1** in two steps[7]. We tried a synthesis of **8** via the cleavage of the oxirane ring of **3** with a reductant. This method is presented in Scheme 1.

The reduction of the carbonyl group of **1** with lithium aluminum hydride stereoselectively gave 1,6-anhydro-3,4-dideoxy-β-D-*threo*-hex-3-enopyranose (**2**) in a 70.3% yield[5,6]. The *trans*-iodoacetoxylation of **2** with iodine and silver acetate in acetic acid, followed by the treatment with ammonia water in methanol, stereoselectively gave **3** in a 93.8% yield[7]. The reductive cleavage of the oxirane ring of **3**

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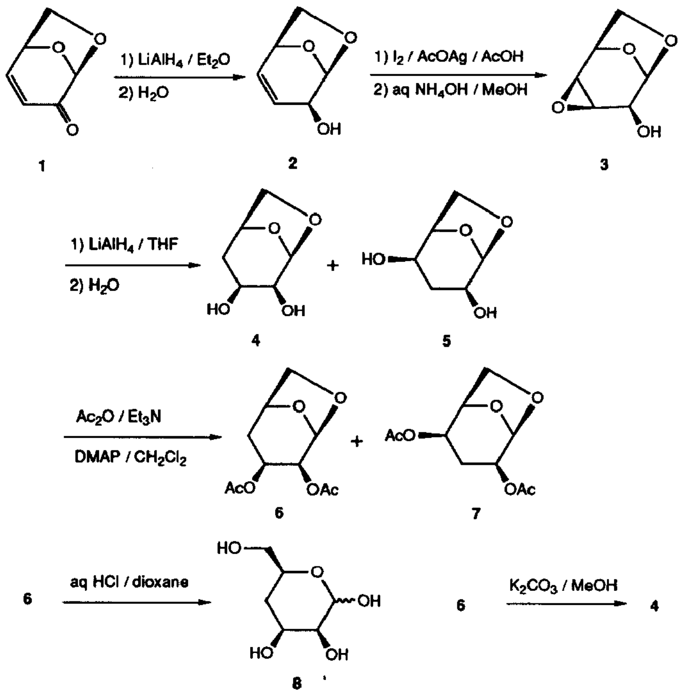
* Corresponding author.

[†] Levoglucosenone (**1**) is available from Yuki Gosei Kogyo Co., Ltd; Hirakawa-cho CH BLDG. 3–24 Hirakawa-cho 2 chome, Chiyoda-ku, Tokyo 102, Japan.

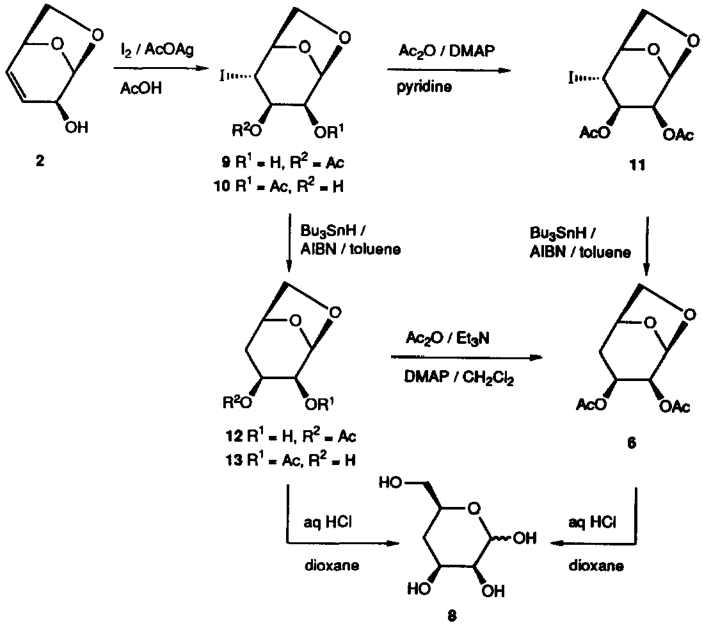


Scheme 1. Method 1.

with lithium aluminum hydride gave the mixture of 1,6-anhydro-4-deoxy-β-D-*lyxo*-hexopyranose (**4**) as a major product and 1,6-anhydro-3-deoxy-β-D-*lyxo*-hexopyranose (**5**) as a minor product. The mixture of **4** and **5** could not be separated by column chromatography. The *O*-acetylation of the mixture with acetic anhydride, triethylamine, and a catalytic amount of 4-dimethylaminopyridine in dichloromethane, gave each of the corresponding diacetates (**6** and **7**). Pure 2,3-di-*O*-acetyl-1,6-anhydro-4-deoxy-β-D-*lyxo*-hexopyranose (**6**) was obtained easily by column chromatography (in an 80.8% yield from **3**). The hydrolysis of the 1,6-anhydro-bond and two *O*-acetyl-protecting groups at C-2 and C-3 of **6** with hydrochloric acid gave **8** in a 71.7% yield. Treatment of **6** with potassium carbonate in methanol gave the 1,6-anhydro derivative **4** in a 90.8% yield.

The above synthesis of **8** from **1** via **3** (method 1) afforded a high yield in short steps (38.2% overall yield in five steps from **1**), compared with conventional methods. However, only the 4-deoxy-product **4** could not be obtained by cleavage of the epoxide **3**. Trnka and Černý[4] also synthesized **3** from 1,6-anhydro-β-D-mannopyranose, and then obtained **4** via the cleavage of the oxirane ring of **3** by hydrogenation on Raney nickel, with the formation of **5** and 1,6-anhydro-3,4-dideoxy-β-D-*threo*-hexopyranose as by-products. We therefore attempted the alternative synthesis of **8** from **1**, which would show higher stereoselectivity (method 2).

In our synthesis of the epoxide **3** from **2**, we have found that the introduction of the iodine atom took place at C-4 with high regio- and stereo-selectivities, which



Scheme 2. Method 2.

resulted in formations of iodoacetate derivatives **9** and **10** in 97.1% yield[7]. Therefore, utilization of compounds **9** and **10** for the synthesis of **8** was examined (method 2). This method is shown in Scheme 2.

The free-radical reduction of the 4-iodo group of the mixture of **9** and **10** with tributyltin hydride afforded the mixture of 2- or 3-*O*-acetyl-1,6-anhydro-4-deoxy-β-D-*lyxo*-hexopyranoses **12** and **13** which could not be separated by column chromatography. The hydrolysis of the mixture of **12** and **13** with hydrochloric acid gave **8** in a 78.2% yield (53.4% overall yield, four steps from **1**).

Since avoiding the use of mixtures as intermediates (of **9** and **10**, or **12** and **13**), in spite of increasing the number of steps, we attempted syntheses of **2** via diacetate **11** or **6**, respectively. The pathway via the order of the iodomonoacetate mixture (of **9** and **10**), iododiacetate **11**, which was induced by the acetylation of the mixture of **9** and **10**, and **6**, which was induced by the free-radical reduction of **11**, gave **8** in five steps in a 38.8% overall yield from **1**. The pathway via the order of the iodomonoacetate mixture (of **9** and **10**), the monoacetate mixture (of **12** and **13**), and **6**, which was induced by the acetylation of the mixture of **12** and **13**, gave **8** in five steps in a 47.3% overall yield from **1**.

In conclusion, we have developed an easy method for preparing 4-deoxy-D-*lyxo*-hexose (**8**) streoselectively in four steps giving a 53.4% overall yield from levoglucosenone (**1**) via a *trans*-iodoacetate intermediate. The structure of **8** is suitable as a starting material for syntheses of various saccharides.

EXPERIMENTAL

General methods.—All melting points are uncorrected. Optical rotations were measured with a JASCO DIP-370 polarimeter. IR spectra were measured on a JASCO FTIR-5000 spectrophotometer. ^1H NMR spectra were recorded at 300 MHz and ^{13}C NMR spectra at 75 MHz, with Me_4Si as an internal standard on a Bruker AC 300P spectrometer. Column chromatography was performed on Silica Gel 60 (70–230 mesh, E. Merck No. 7734).

*Method 1 (via epoxidation). 1,6:3,4-Dianhydro-β-*D*-talopyranose* (**3**).—To a stirred and mixed solution of 128 mg (1.00 mmol) of **2** (refs. 5 and 6) and 334 mg (2.00 mmol) of silver acetate in 4.6 mL of AcOH was slowly added 267 mg (1.05 mmol) of iodine at room temperature. The mixture was stirred for 5 h at room temperature under N_2 (until the iodine was consumed). Then 40 mL of aq 25% ammonia and 40 mL of MeOH were added to the mixture, followed by stirring at room temperature overnight. The precipitate was filtered off and washed with water, and the filtrate was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (1:1 → 1:3 hexane–EtOAc) to afford 135 mg (93.8%) of **3**: mp 74.0–75.2°C; $[\alpha]_D^{24}$ $-49.7°$ (c 1.44, H_2O) [lit.[8], mp 73–74°C; $[\alpha]_D$ $-49.5°$ (c 1.44, H_2O)]; IR (KBr): 3440 (br), 1427 (w), 1408 (w), 1346 (w), 1309 (w), 1259 (w), 1149 (m), 1096 (w), 1065 (s), 1025 (w), 998 (m), 975 (s), 917 (s), 870 (w), 843 (w), 816 (m), 754 (w), 698 (m), 621 (m), 588 (br), 516 (m), 474 (m), 451 (w), and 416 cm^{-1} (m); ^1H NMR ($CDCl_3$): δ 5.30 (d, 1 H, J 3.8 Hz, H-1), 4.82 (dd, 1 H, J 4.7, 4.7 Hz, H-5), 3.95 (d, 1 H, J 6.6 Hz, H-6), 3.83–3.76 (m, 2 H, H-2, H-4), 3.56 (dd, 1 H, J 6.6, 4.7 Hz, H-6′), 3.34 (ddd, 1 H, J 3.9, 3.9, 1.0 Hz, H-3), 2.41 (d, 1 H, J 12.2 Hz, OH); ^{13}C NMR ($CDCl_3$) δ 98.2 (C-1), 72.1 (C-5), 68.9 (C-2), 64.3 (C-6), 57.6 (C-4), 50.6 (C-3). Anal. Calcd for $C_6H_8O_4$: C, 50.00; H, 5.60. Found: C, 49.98; H, 5.64.

The reduction of **3**; *2,3-di-O-acetyl-1,6-anhydro-4-deoxy-β-*D-lyxo-*hexopyranose* (**6**).—A solution of 288 mg (2.00 mmol) of **3** in 4 mL of dry THF was added dropwise to 152 mg (4.40 mmol) of $LiAlH_4$ in 8 mL of dry THF cooled with ice, and stirred for 24 h at room temperature under N_2. Lithium aluminum hydride was then decomposed by careful addition of 0.4 mL of water. The mixture was diluted with MeOH, filtered through a Celite pad, and the residue washed with MeOH. The filtrate was evaporated under reduced pressure to give a yellow oil. To the residue was added 6.0 mL (63.6 mmol) of Ac_2O, 8.9 mL (63.6 mmol) of Et_3N, a catalytic amount of 4-dimethylaminopyridine, and 30 mL of dry CH_2Cl_2. The mixture was stirred overnight at room temperature under N_2 and then refluxed for 2 h. After cooling to room temperature, the mixture was poured into satd aq $NaHCO_3$ and extracted with $CHCl_3$. The organic layer was dried (anhyd $MgSO_4$), and the solvent was distilled off under reduced pressure. The separation of two products from the residue by column chromatography on silica gel (3:1 → 1:1 hexane–EtOAc) afforded 28 mg (6.1%) of **7** as the first fraction and 372 mg (80.8%) of **6** as the second fraction. Compounds **6** and **7** were recrystallized from hexane–Et_2O, respectively.

2,4-Di-*O*-acetyl-1,6-anhydro-3-deoxy-β-D-*lyxo*-hexopyranose (**7**): mp 112.0–113.0°C; $[\alpha]_D^{23}$ −67.5° (*c* 0.16, $CHCl_3$); IR (KBr): 1729 (s), 1489 (w), 1462 (w), 1439 (w), 1379 (m), 1365 (m), 1253 (s), 1152 (m), 1135 (m), 1048 (s), 1033 (s), 955 (w), 919 (w), 897 (m), 870 (w), 847 (w), 797 (w), 683 (w), 648 (w), 605 (w), 596 (w), 559 (w), 530 (w), 499 (w), and 422 cm^{-1} (m); ^1H NMR ($CDCl_3$): δ 5.41 (br, 1 H, H-1), 5.05–4.98 (m, 1 H, H-4), 4.79 (ddd, 1 H, *J* 10.7, 6.1, 1.6 Hz, H-2), 4.53 (dd, 1 H, *J* 5.0, 5.0 Hz, H-5), 4.16 (d, 1 H, *J* 7.9 Hz, H-6), 3.82 (dd, 1 H, *J* 7.9, 5.0 Hz, H-6′), 2.40 (ddddd, 1 H, *J* 12.3, 6.1, 6.1, 1.0, 1.0 Hz, H-3), 2.08 (s, 3 H, OAc), 2.06 (s, 3 H, OAc′), 1.69 (ddd, 1 H, *J* 12.3, 10.7, 10.7 Hz, H-3′). Anal. Calcd for $C_{10}H_{14}O_6$: C, 52.17; H, 6.13. Found: C, 52.08; H, 6.14.

2,3-Di-*O*-acetyl-1,6-anhydro-4-deoxy-β-D-*lyxo*-hexopyranose (**6**): mp 68.0–69.0°C; $[\alpha]_D^{26}$ −83.1° (*c* 0.59, $CHCl_3$) [lit.[2], oil, $[\alpha]_D^{20}$ −66.0° (*c* 0.6, $CHCl_3$)]; IR (KBr): 1742 (s), 1377 (m), 1253 (s), 1209 (m), 1141 (m), 1120 (m), 1075 (m), 1033 (m), 977 (m), 890 (m), 845 (m), 822 (m), 721 (w), 659 (w), 632 (w), 601 (w), 584 (w), 526 (m), 472 (w), 458 (w) and 435 cm^{-1} (m); ^1H NMR ($CDCl_3$): δ 5.43 (dd, 1 H, *J* 5.0, 5.0 Hz, H-3), 5.39 (s, 1 H, H-1), 4.90 (dd, 1 H, *J* 5.0, 1.7 Hz, H-2), 4.57 (dd, 1 H, *J* 4.4, 4.4 Hz, H-5), 4.26 (d, 1 H, *J* 7.0 Hz, H-6), 3.85 (m, 1 H, H-6′), 2.34 (dddd, 1 H, *J* 15.5, 5.0, 4.4, 1.7 Hz, H-4), 2.13 (s, 3 H, OAc), 2.07 (s, 3 H, OAc′), 1.92 (d, 1 H, *J* 15.5 Hz, H-4′). Anal. Calcd for $C_{10}H_{14}O_6$: C, 52.17; H, 6.13. Found: C, 52.01; H, 6.20.

*4-Deoxy-*D-lyxo-*hexose* (**8**) *via the acid hydrolysis of* **6**.—A solution of 1.02 g (4.41 mmol) of **6** in 30 mL of 1 mol · dm^{-3} HCl and 15 mL of dioxane was stirred for 8 h at ca. 90–100°C under N_2. After cooling to room temperature, the mixture was passed over Amberlite IRA-410 (OH^-). Evaporation of the mixture under reduced pressure afforded 0.52 g (71.7%) of **8** as a colorless oil of the anomeric mixture (the α : β anomer ratio determined by ^{13}C NMR spectral analysis of the mixture was 1.5 : 1): $[\alpha]_D^{24}$ +13.2° (*c* 1.61, CH_3OH) [lit.[2], $[\alpha]_D^{20}$ +17.7° (*c* 1.7, MeOH)]; IR (neat): 3400 (br), 1640 (w), 1386 (br), 1243 (m), 1040 (br), 930 (w), 862 (w), and 772 cm^{-1} (w); ^1H NMR (D_2O), α anomer: δ 5.20 (br, 1 H, H-1), 4.12–3.99 (m, 2 H, H-3, H-5), 3.75 (br, 1 H, H-2), 3.68–3.55 (m, 2 H, H-6, H-6′), 1.72–1.43 (m, 2 H, H-4, H-4′), β anomer: δ 4.74 (br, 1 H, H-1), 3.89 (ddd, 1 H, *J* 12.0, 5.1, 3.0 Hz, H-3), 3.81 (br, 1 H, H-2), 3.68–3.55 (m, 3 H, H-5, H-6, H-6′); ^{13}C NMR (D_2O) δ, α anomer: 95.4 (C-1), 69.7 (C-5), 69.5 (C-2), 65.5 (C-3), 65.0 (C-6), 29.9 (C-4); β anomer: 94.8 (C-1), 73.4 (C-5), 70.7 (C-2), 68.8 (C-3), 64.7 (C-6), 29.3 (C-4).

*1,6-Anhydro-4-deoxy-β-*D-lyxo-*hexopyranose* (**4**) *via the base hydrolysis of* **6**.—A solution of 497 mg (2.16 mmol) of **6** and 1.50 g (10.9 mmol) of K_2CO_3 in 374 mL of MeOH was stirred for 1 h at room temperature. The mixture was evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel (1 : 2 → 1 : 4 CH_2Cl_2–Me_2CO) to give 287 mg (90.8%) of **4**. This was recrystallized from EtOH–hexane: mp 128–140°C; $[\alpha]_D^{26}$ −89.3° (*c* 0.68, H_2O), $[\alpha]_D^{24}$ −99.9° (*c* 0.92, $CHCl_3$) [lit.[2], mp 65°C, $[\alpha]_D^{20}$ −66.2° (*c* 0.9, $CHCl_3$); lit.[3], mp 91–110°C, $[\alpha]_D^{22}$ −87° (*c* 0.66, H_2O); lit.[4], mp 85–100°C, $[\alpha]_D$ −89° (*c* 0.66, H_2O)]; IR (KBr): 3440 (br), 1479 (w), 1429 (m), 1342 (m), 1294 (w), 1247 (w), 1218 (w), 1193 (w), 1135 (m), 1118 (m), 1077 (m), 1019 (m), 973 (m), 899 (m), 899 (w), 876 (m), 864 (m), 814 (w), 797 (m), 717 (m), 605 (w), 509 (m), and 414 cm^{-1} (m); ^{1}H NMR ($CDCl_3$): δ 5.37 (br, 1 H, H-1), 4.52 (dd, 1 H, J 4.3 and 4.3 Hz, H-5), 4.23 (d, 1 H, J 6.9 Hz, H-6), 4.12 (ddd, 1 H, J 5.3, 4.4 and 4.3 Hz, H-3), 3.75 (ddd, 1 H, J 6.9, 4.3, and 1.5 Hz, H-6′), 3.65–3.60 (m, 1 H, H-2), 2.96 (d, 1 H, J 8.8 Hz, 2-OH), 2.82 (d, 1 H, J 5.3 Hz, 3-OH), 2.20 (dddd, 1 H, J 15.1, 4.3, 4.3, and 1.5 Hz, H-4), 2.03 (d, 1 H, J 15.1 Hz, H-4′); ^{13}C NMR (CD_3OD) δ 103.8, 74.1, 70.9, 69.6, 67.7, 37.1. Anal. Calcd for $C_6H_{10}O_4$: C, 49.31; H, 6.90. Found: C, 49.17; H, 7.03.

Method 2 (via the iodoacetoxylation and free-radical reduction). (a) trans-*Iodoacetoxylation upon* **2**.

*3-O-Acetyl-1,6-anhydro-4-deoxy-4-iodo-β-*D*-mannopyranose* (**9**) *and 2-O-acetyl-1,6-anhydro-4-deoxy-4-iodo-β-*D*-mannopyranose* (**10**)—To a stirred and mixed solution of 128 mg (1.00 mmol) of **2** and 334 mg (2.00 mmol) of silver acetate in 4.6 mL of AcOH was slowly added 267 mg (1.05 mmol) of iodine at room temperature. The mixture was stirred for 5 h at room temperature under N_2. Sodium (200 mg) iodide was added to the mixture, and then the mixture was poured into aq $NaHCO_3$ (7.10 g of $NaHCO_3$ in 100 mL of water). The resulting precipitate was filtered off and washed with MeOH and water. The filtrate was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (1:1 hexane–EtOAc) to afford 305 mg (97.1%) of the mixture of **9** and **10** as a colorless oil. The ratio of **9**:**10** was 57:43 as determined by ^{1}H NMR spectral analysis of the mixture.

3-*O*-Acetyl-1,6-anhydro-4-deoxy-4-iodo-β-D-mannopyranose (**9**): ^{1}H NMR ($CDCl_3$): δ 5.45 (br, 1 H, H-1), 5.35 (ddd, 1 H, J 5.5, 2.7, 1.3 Hz, H-3), 4.63 (d, 1 H, J 5.5 Hz, H-5), 4.27 (br, 1 H, H-4), 4.20 (ddd, 1 H, J 11.6, 5.5, 1.9 Hz, H-2), 4.11 (dd, 1 H, J 7.9, 0.7 Hz, H-6), 3.82–3.76 (m, 1 H, H-6), 2.39 (d, 1 H, J 11.6 Hz, OH), 2.16 (s, 3 H, OAc).

2-*O*-Acetyl-1,6-anhydro-4-deoxy-4-iodo-β-D-mannopyranose (**10**): ^{1}H NMR ($CDCl_3$): δ 5.53 (br, 1 H, H-1), 5.20 (dd, 1 H, J 4.8, 1.6 Hz, H-2), 4.72 (d, 1 H, J 4.8 Hz, H-5), 4.48 (ddd, 1 H, J 5.0, 5.0, 1.6 Hz, H-3), 4.41–4.39 (m, 2 H, H-4, H-6), 3.82–3.76 (m, 1 H, H-6′), 3.23 (d, 1 H, J 5.3 Hz, OH), 2.18 (s, 3 H, OAc).

*2,3-di-O-acetyl-1,6-anhydro-4-deoxy-4-iodo-β-*D*-mannopyranose* (**11**) *via acetylation of* **9** *and* **10**.—A solution of 314 mg of a mixture of **9** and **10**, 0.19 mL of Ac_2O, 0.32 mL of pyridine, and a catalytic amount of 4-dimethylaminopyridine in 10 mL of CH_2Cl_2 was stirred for 4 h at room temperature under N_2. The mixture was poured into ice–water containing $NaHCO_3$ and extracted three times with CH_2Cl_2. The organic layer was washed with satd $CuSO_4$ (twice), followed with water (twice), and then dried (anhyd $MgSO_4$). The solvent was distilled off under reduced pressure. The residue was purified by column chromatography on silica gel (1:1 hexane–EtOAc) to afford 313 mg (87.9%) of **11** that was recrystallized from hexane–Et_2O–CH_2Cl_2: mp 95.5–96.1°C; $[\alpha]_D^{26}$ -187.2° (c 1.03, $CHCl_3$); IR (KBr): 1750 (s), 1373 (m), 1236 (s), 1143 (m), 1110 (w), 1069 (s), 982 (m), 897 (m), 837 (w), 721 (w), 687 (w), 663 (w), 615 (w), 592 (w), 522 (w), and 460 cm^{-1} (w); ^{1}H

NMR ($CDCl_3$): δ 5.53 (dd, 1 H, *J* 5.1, 1.4 Hz, H-3), 5.49 (br, 1 H, H-1), 5.36 (dd, 1 H, *J* 5.1, 1.6 Hz, H-2), 4.69 (dd, 1 H, *J* 5.4, 0.6 Hz, H-5), 4.29 (dd, 1 H, *J* 7.8, 0.6 Hz, H-6), 4.25 (br, 1 H, H-4), 3.84 (dd, 1 H, *J* 7.8, 5.4 Hz, H-6′), 2.15 (s, 3 H, OAc), 2.08 (s, 3 H, OAc′); ^{13}C NMR ($CDCl_3$): δ 170.0 (C=O), 169.8 (C=O), 100.2 (C-1), 78.1 (C-5), 73.1 (C-3), 68.5 (C-6), 66.0 (C-2), 23.9 (C-4), 21.2 (CH_3), 21.0 (CH_3). Anal. Calcd for $C_{10}H_{13}IO_6$: C, 33.73; H, 3.68; I, 35.64. Found: C, 33.67; H, 3.56; I, 35.29.

(b) Free-radical reduction.

*3-O-Acetyl-1,6-anhydro-4-deoxy-β-*D-lyxo*-hexopyranose* (**12**) *and 2-O-acetyl-1,6-anhydro-4-deoxy-β-*D-lyxo*-hexopyranose* (**13**); *free-radical reduction of* **9** *and* **10**.—To a solution of 551 mg (1.75 mmol) of **9** and **10** in 13 mL of toluene was added 0.58 mL (2.16 mmol) of tributyltin hydride at room temperature under Ar, followed by addition of a catalytic amount of 2,2′-azo-bis-*iso*-butyronitrile. The mixture was refluxed for 1 h. After cooling, the mixture was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (2 : 1 → 1 : 2 hexane–EtOAc) to quantitively give 343 mg of a mixture of **12** and **13**.

3-*O*-Acetyl-1,6-anhydro-4-deoxy-β-D-*lyxo*-hexopyranose (**12**): ^1H NMR ($CDCl_3$): δ 5.32 (br, 1 H, H-1), 5.21 (br, 1 H, H-3), 4.46 (dd, 1 H, *J* 4.4, 4.3 Hz, H-5), 4.02 (d, 1 H, *J* 7.0 Hz, H-6), 3.77–3.73 (m, 1 H, H-6′), 3.67 (dd, 1 H, *J* 11.3, 5.7 Hz, H-2), 2.44 (d, 1 H, *J* 11.3 Hz, OH), 2.21 (ddd, 1 H, *J* 15.8, 4.3, 4.2 Hz, H-4), 2.10 (s, 3 H, OAc), 1.90 (d, 1 H, *J* 15.8 Hz, H-4′).

2-*O*-Acetyl-1,6-anhydro-4-deoxy-β-D-*lyxo*-hexopyranose (**13**): ^1H NMR ($CDCl_3$): δ 5.40 (br, 1 H, H-1), 4.71 (d, 1 H, *J* 4.7 Hz, H-2), 4.52 (dd, 1 H, *J* 4.3, 4.3 Hz, H-5), 4.31 (d, 1 H, *J* 6.8 Hz, H-6), 4.21 (br, 1 H, H-3), 3.77–3.73 (m, 1 H, H-6′), 2.68 (d, 1 H, *J* 4.5 Hz, OH), 2.25–2.17 (m, 1 H, H-4), 2.14 (s, 3 H, OAc), 2.01 (d, 1 H, *J* 15.5 Hz, H-4′).

*2,3-Di-O-acetyl-1,6-anhydro-4-deoxy-β-*D-lyxo*-hexopyranose* (**6**) *via the acetylation of* **12** *and* **13**.—A solution of 143 mg (0.76 mmol) of a mixture of **12** and **13**, 0.16 mL of Ac_2O, 0.23 mL of Et_3N, and a catalytic amount of 4-dimethylaminopyridine in 3 mL of CH_2Cl_2 was stirred at room temperature overnight under N_2. The mixture was poured into the ice–water containing $NaHCO_3$ and extracted three times with $CHCl_3$. The organic layer was washed with dil HCl (once), satd aq $NaHCO_3$ (once), and water (twice). Then it was dried (anhyd $MgSO_4$). The solvent was distilled off under reduced pressure. The residue was purified by column chromatography on silica gel (1 : 1 hexane–EtOAc) to afford 169 mg (96.6%) of **6**. The analytical and spectral data of **6** thus obtained were in agreement with those reported or those of **6** obtained by method 1.

*2,3-Di-O-acetyl-1,6-anhydro-4-deoxy-β-*D-lyxo*-hexopyranose* (**6**) *via free-radical reduction of* **11**.—To a solution of 712 mg (2.00 mmol) of **11** in 17 mL of toluene was added 0.65 mL (2.40 mmol) of tributyltin hydride at room temperature under Ar, followed by addition of a catalytic amount of 2,2′-azo-bis-*iso*-butyronitrile. The mixture was refluxed for 1 h. After cooling, the mixture was evaporated under reduced pressure. The residue was poured into water and extracted three times with CH_2Cl_2. The organic layer was washed with satd KF (once), satd aq $NaHCO_3$ (once), and water (once). Then it was dried (anhyd $MgSO_4$). The solvent was distilled off under reduced pressure. The residue was purified by column chromatography on silica gel (2:1 hexane–EtOAc) to give 415 mg (90.2%) of **6**. The analytical and spectral data of **6** thus obtained were in agreement with those reported or those of **6** obtained by method 1.

*(c) 4-Deoxy-*D-lyxo*-hexose* (**8**) *via the acid hydrolysis of* **12** *and* **13**.—A solution of 343 mg (1.82 mmol) of **12** and **13** in 10 mL of 1 mol · dm^{-3} HCl and 5 mL of dioxane was stirred for 8 h at ca. 90–100°C under N_2. After cooling to room temperature, the mixture was passed over Amberlite IRA-410 (OH^-). The evaporation of the mixture under reduced pressure afforded 234 mg (78.2%) of **8** as a colorless oil of the anomeric mixture. The analytical and spectral data of **8** thus obtained were in agreement with those reported or those of **8** obtained by method 1.

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