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Synthesis of 6-deoxy-L-idose and L-acovenose from 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose

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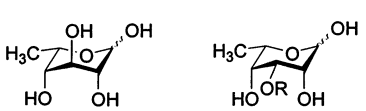
Abstract

A practical route toward the synthesis of 6-deoxy-L-idose and L-acovenose from 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose is described. Key steps include the stereoselective hydrogenation of 6-deoxy-1,2:3,5-di-*O*-isopropylidene-α-D-*xylo*-hex-5-enofuranose, regioselective protection of 6-deoxy-1,2-*O*-isopropylidene-β-L-idofuranose at O-5, and epimerisation of 6-deoxy-5-*O*-*tert*-butyldimethylsilyl-1,2-*O*-isopropylidene-β-L-idofuranose at C-3.

Keywords: L-Acovenose; 6-Deoxy-L-idose; 6-Deoxy-L-talose

1. Introduction

6-Deoxy-L-*ido* and 6-deoxy-L-*talo* sugars are components of numerous biologically active terpenoid glycosides, antibiotics and glycopeptides.[1] For example, some diterpene glycosides isolated from *Aster spathulifolius maxim*[2] contain 6-deoxy-L-idopyranose **1**[3] as a constituent. The 6-deoxy-L-talopyranose **2**[4] is found in talopeptin,[5] the glycopeptidolipid antigens of *Mycobacterium avium*,[6] serotype-specific polysaccharide antigens of *Actinobacillus actinomycetemcomitans*,[7] and O45, O45-related as well as O66 antigens of *Escherichia coli*.[8] Finally, the antibacterial antibiotics, acovenosides[9] and maduralide,[10] have 6-deoxy-3-*O*-methyl-L-talopyranose [L-acovenose (**3**)][11] as the sugar subunit. Given the importance of 6-deoxy-L-hexoses in the field of glycobiology, and the fact that these rare L-form sugars are not readily accessible from natural sources, we have developed a practical route toward their synthesis. Our approach is based on the stereoselective hydrogenation of 6-deoxy-1,2:3,5-di-*O*-isopropylidene-α-D-*xylo*-hex-5-enofuranose to afford 6-deoxy-1,2:3,5-di-*O*-isopropylidene-β-L-idofuranose, which is further converted into the 6-deoxy-β-L-talofuranosyl sugars via epimerisation at C-3.



2. Results and discussion

Synthesis of 6-deoxy-L-idose.—The only difference between D-glucose and L-idose is the stereochemistry at the C-5 position. Most approaches for the synthesis of L-ido sugars

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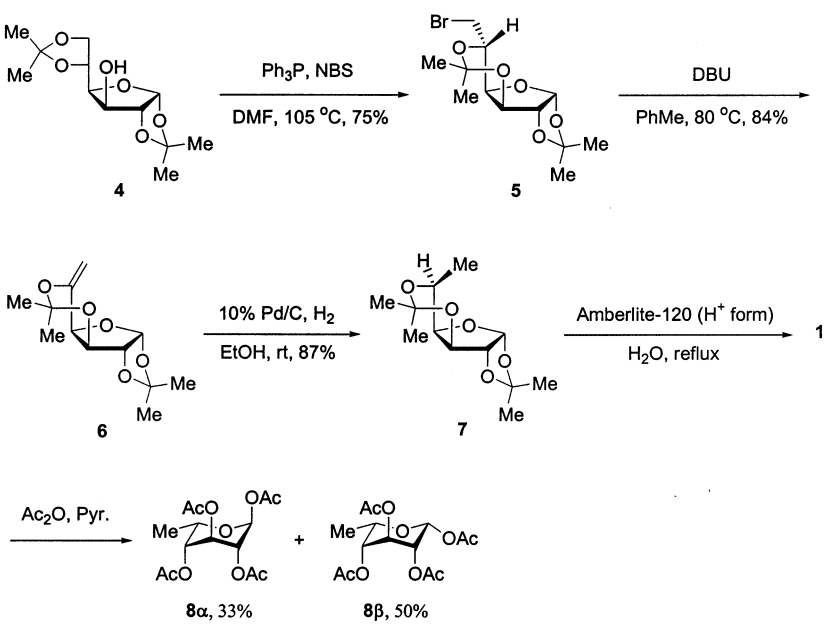
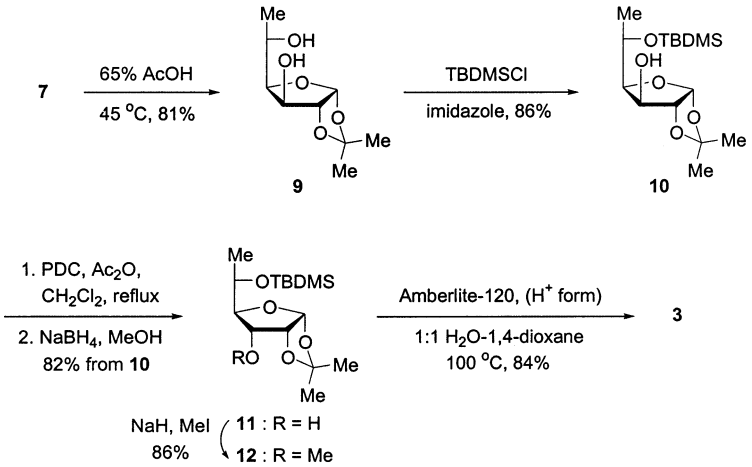
begin with D-gluco compounds and involve the selective inversion of configuration at C-5.[3a] A short synthesis of 6-deoxy-L-idose (**1**) from the cheap and commercially available 1,2:3,5-di-*O*-isopropylidene-α-D-glucofuranose (**4**) is outlined in Scheme 1. 6-Bromo-6-deoxy-1,2:3,5-di-*O*-isopropylidene-α-D-glucofuranose (**5**), generated from **4** with triphenylphosphine and *N*-bromosuccinimide employing a two-step isopropylidene rearrangement and regioselective bromination at C-6,[12] was treated with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in toluene at 80 °C to provide the enol ether (**6**) (84%). In contrast, a one-pot synthesis via direct addition of excess DBU into the reaction mixture of Mitsunobu-type bromination at 105 °C only led to **6** in 12% yield. Stereoselective hydrogenation in ethanol using 10% palladium-on-charcoal as the catalyst furnished 6-deoxy-1,2:3,5-di-*O*-isopropylidene-β-L-idofuranose (**7**) as a single isomer in 87% yield. The configuration was determined by its NOESY spectrum, which illustrates that H-5 has a nuclear Overhauser enhancement with H-3, showing that the methyl group at C-5 orients toward the β-face. The high stereoselectivity is perhaps induced by the steric hindrance caused by the cis-fused ring junction and the addition of a hydrogen molecule with the double bond favoured from α-face. Since 6-deoxy-L-idose (**1**) was unstable and slowly rearranged to 6-deoxy-L-sorbose,[3d] hydrolysis of **7** at reflux temperature for 24 h in the presence of Amberlite-120 (H^+) resin gave the desired target molecule **1**, which was directly subjected to per-O-acetylation to afford the tetraacetates **8α** and **8β** in 33% and 50% yields, respectively.

Synthesis of L-*acovenose*.—With the key synthon **7** in hand, the synthesis of L-acovenose (**3**) was carried out (Scheme 2). Selective hydrolysis of **7** in 65% aqueous HOAc at 45 °C for 10 h led to the diol (**9**) in 81% yield. Regioselective silylation with *tert*-butylchlorodimethylsilane and imidazole at O-5 furnished the alcohol (**10**) in 86% yield. The regiochemistry of **10** was determined through its ^1H NMR and ^1H–^1H COSY spectra, which show that H-3 ($\delta = 4.20$, $J_{3,OH} = 3.7$ Hz) has a correlation with the proton of free hydroxyl. Oxidation of **10** with pyridinium dichromate and Ac_2O, followed by reduction with sodium borohydride, provided the 6-deoxy-L-talofuranosyl sugar (**11**) in 82% overall yield. This product was treated with sodium hydride and iodomethane to give the 3-*O*-methyl adduct **12** (86%). Hydrolysis in acidic media afforded the expected L-acovenose (**3**) in 84% yield. The ^1H and ^{13}C NMR data for **3** matched those reported.[11a]



Scheme 1.



Scheme 2.

In summary, we have successfully developed an efficient and convenient route toward the synthesis of 6-deoxy-L-idopyranosyl tetraacetate and L-acovenose from 1,2:3,5-di-*O*-isopropylidene-α-D-glucofuranose in five and nine steps in 45 and 23% overall yields, respectively.

3. Experimental

General methods.—Solvents were purified and dried from a safe purification system.[13] Flash chromatography[14] was carried out as recommended with Silica Gel 60 (230–400 mesh, E. Merck). TLC was performed on pre-coated glass plates of Silica Gel 60 F254 (0.25 mm, E. Merck); detection was executed by spraying with a solution of $Ce(NH_4)_2(NO_3)_6$, $(NH_4)_6Mo_7O_{24}$, as well as H_2SO_4 in water and subsequent heating on a hotplate. Melting points were determined with a Büchi B-540 apparatus and are uncorrected. Optical rotations were measured with a JASCO DIP-370 polarimeter at ~25 °C. ^1H and ^{13}C NMR spectra were recorded with Bruker AC 300 and AMX 400 MHz instruments. Chemical shifts are in ppm from Me_4Si, generated from the $CHCl_3$ lock signal at δ 7.26. Mass spectra were obtained with a VG 70-250S mass spectrometer in the EI and FAB modes. IR spectra were taken with a Perkin–Elmer Paragon 1000 FTIR spectrometer. Elemental analyses were carried out with a Perkin–Elmer 2400CHN instrument.

6-Deoxy-1,2:3,5-di-O-isopropylidene-α-D-xylo-hex-5-enofuranose (**6**).—To a solution of **5**[12] (3.23 g, 10.0 mmol) in toluene (20 mL) was added DBU (3.1 mL, 20.0 mmol) at rt, and the mixture was warmed at 80 °C for 12 h. After cooling to rt, the resulting solution was filtered, and the solid was washed with hexane. The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (1:16 EtOAc–hexane) to afford **6** (2.03 g, 84%) as a colourless oil: $[\alpha]_D^{25}$ 163.7° (*c* 1.0, $CHCl_3$); IR ($CHCl_3$): 2988, 1660, 1375, 1082, 1017 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.98 (d, $J_{1,2}$ 3.7 Hz, 1 H, H-1), 4.76 (d, $J_{6a,6b}$ 0.6 Hz, 1 H, H-6a), 4.69 (d, 1 H, H-6b), 4.56 (d, 1 H, H-2), 4.37 (d, $J_{3,4}$ 2.3, Hz, 1 H, H-3), 4.34 (d, 1 H, H-4), 1.52 (s, 3 H, Me), 1.47 (s, 3 H, Me), 1.40 (s, 3 H, Me), 1.33 (s, 3 H, Me); ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.31 (C), 111.80 (C), 105.20 (CH), 101.37 (CH_2), 100.53 (C), 84.27 (CH), 74.66 (CH), 72.34 (CH), 28.01 (CH_3), 26.72 (CH_3), 26.11 (CH_3), 21.90 (CH_3); HRFABMS: Calc. for $C_{12}H_{18}O_5$ (M^+) 242.1154; Found: *m/z* 242.1152. Anal. Calc. for $C_{12}H_{18}O_5$: C, 59.49; H, 7.49. Found: C, 59.19; H, 7.38%.

6-Deoxy-1,2:3,5-di-O-isopropylidene-β-L-idofuranose (**7**).—To a solution of **6** (1.66 g, 6.81 mmol) in EtOH (30 mL) was added a catalytic amount of 10% Pd/C (160 mg). Argon was bubbled through the reaction, and a hydrogen balloon was attached. After stirring at rt for 14 h, the mixture was filtered through Celite, and the reaction bottle was washed with EtOH (2 × 10 mL). The filtrate was con-

centrated in vacuo, and the residue was purified by flash chromatography (1:20 EtOAc–hexane) to afford **7** as a colourless oil (1.46 g, 87%): $[\alpha]_D^{25}$ +15.4° (*c* 1.0, $CHCl_3$); IR ($CHCl_3$): 2990, 2938, 1374, 1204, 1164, 1090, 1016 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.89 (d, $J_{1,2}$ 3.6 Hz, 1 H, H-1), 4.43 (d, 1 H, H-2), 4.12 (d, $J_{3,4}$ 1.5 Hz, 1 H, H-3), 4.07 (dq, $J_{5,6}$ 6.5 Hz, 1 H, H-5), 3.78 (t, $J_{4,5}$ 1.5 Hz, 1 H, H-4), 1.42 (s, 3 H, Me), 1.37 (s, 3 H, Me), 1.32 (s, 3 H, Me), 1.27 (d, 3 H, Me-6), 1.25 (s, 3 H, Me); ^{13}C NMR (75 MHz, $CDCl_3$): δ 111.44 (C), 104.86 (CH), 97.90 (C), 84.19 (CH), 73.85 (CH), 73.69 (CH), 64.48 (CH), 29.30 (CH_3), 26.62 (CH_3), 26.07 (CH_3), 19.09 (CH_3), 17.56 (CH_3); HRFABMS: Calc. for $C_{12}H_{21}O_5$ (MH^+) 245.1388; Found: *m*/*z* 245.1381. Anal. Calc. for $C_{12}H_{20}O_5$: C, 59.00; H, 8.25. Found: C, 59.07; H, 8.20%.

1,2,3,4-Tetra-O-*acetyl-6-deoxy-*L*-idopyranose (***8α** *and* **8β**).—A mixture of **7** (1.40 g, 5.73 mmol), Amberlite-120 resin (H^+ form, 0.5 g) and water (10 mL) was refluxed for 24 h. After cooling to rt, the resin was filtered and washed with water. The filtrate was co-evaporated with EtOH and toluene under reduced pressure to obtain a faint yellow oily residue. This crude 6-deoxy-L-idose was dissolved in pyridine (8 mL) and cooled to 0 C. Acetic anhydride (4 mL) was slowly added to the mixture, and the ice bath was removed. After stirring at rt for 8 h, the solution was cooled in an ice bath, MeOH (4 mL) was slowly added, and the mixture was kept stirring for 0.5 h. The resulting solution was concentrated at reduced pressure, then diluted with EtOAc (20 mL), and the whole mixture was sequentially washed with 1 N HCl, satd $NaHCO_3$, and brine. The organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by flash chromatography (1:2 EtOAc–hexane) to afford **8α** (0.63 g, 33%) and **8β** (0.94g, 50%). **8α**: $[\alpha]_D^{25}$ −61.3° (*c* 1.0, $CHCl_3$); IR ($CHCl_3$): 2989, 1751, 1438, 1372, 1223, 1053 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 6.00 (d, $J_{1,2}$ 2.8 Hz, 1 H, H-1), 5.03 (t, $J_{3,4}$ 4.8 Hz, 1 H, H-3), 4.88 (dd, $J_{2,3}$ 4.8 Hz, 1 H, H-2), 4.83 (dd, $J_{4,5}$ 2.5 Hz, 1 H, H-4), 4.35 (dq, $J_{5,6}$ 6.6 Hz, 1 H, H-5), 2.10 (s, 3 H, Ac), 2.07 (s, 3 H, Ac), 2.06 (s, 3 H, Ac), 2.06 (s, 3 H, Ac), 1.19 (d, 3 H, Me-6); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.80 (C), 168.99 (C), 168.83 (C), 168.58 (C), 90.78 (CH), 68.88 (CH), 67.42 (CH), 66.44 (CH), 64.80 (CH), 20.73 (CH_3), 20.53 (CH_3), 15.29 (CH_3). Anal. Calc. for $C_{14}H_{20}O_9$: C, 50.60; H, 6.07. Found: C, 50.37; H, 5.90%. **8β**: $[\alpha]_D^{25}$ +16.9° (*c* 1.0, $CHCl_3$); IR ($CHCl_3$): 2989, 1751, 1432, 1371, 1221, 1052, 645 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 6.03 (d, $J_{1,2}$ 2.1 Hz, 1 H, H-1), 5.18 (t, $J_{3,4}$ 4.3 Hz, 1 H, H-3), 4.96 (dd, $J_{2,3}$ 4.3 Hz, 1 H, H-2), 4.76 (dd, $J_{4,5}$ 2.6 Hz, 1 H, H-4), 4.22 (dq, $J_{5,6}$ 6.6 Hz, 1 H, H-5), 2.11 (s, 3 H, Ac), 2.10 (s, 3 H, Ac), 2.10 (s, 3 H, Ac), 2.08 (s, 3 H, Ac), 1.26 (d, 3 H, Me-6); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.56 (C), 169.35 (C), 168.61 (C), 168.41 (C), 89.91 (CH), 70.37 (CH), 67.95 (CH), 67.53 (CH), 65.99 (CH), 20.66 (CH_3), 20.52 (CH_3), 20.49 (CH_3), 20.42 (CH_3), 15.98 (CH_3). Anal. Calc. for $C_{14}H_{20}O_9$: C, 50.60; H, 6.07. Found: C, 50.30; H, 5.89%.

*6-Deoxy-1,2-*O-*isopropylidene-β-*L*-idofuranose (***9**).—Compound **7** (0.60 g, 2.4 mmol) was dissolved in 65% aq HOAc (5 mL), and the mixture was stirred at 40 °C for 10 h. After cooling to rt, the solution was co-evaporated with EtOH and toluene at reduced pressure, and the residue was purified by flash chromatography (1:1 EtOAc–hexane) to afford **9** (0.41 g, 81%): $[\alpha]_D^{25}$ −15.5° (*c* 1.0, $CHCl_3$): mp 89–90 °C; IR ($CHCl_3$): 3441, 2985, 1458, 1376, 1217, 1070, 792 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.98 (d, $J_{1,2}$ 3.6 Hz, 1 H, H-1), 4.52 (d, 1 H, H-2), 4.25 (dd, $J_{3,4}$ 2.9, $J_{3,OH}$ 3.3 Hz, 1 H, H-3), 4.24–4.17 (ddq, $J_{5,6}$ 6.5, $J_{5,OH}$ 7.9 Hz, 1 H, H-5), 3.99 (t, $J_{4,5}$ 2.9 Hz, 1 H, H-4), 3.98 (d, 1 H, OH-3), 2.35 (d, 1 H, OH-5), 1.49 (s, 3 H, Me), 1.37 (d, 3 H, Me-6), 1.32 (s, 3 H, Me); ^{13}C NMR (75 MHz, $CDCl_3$): δ 111.75 (C), 104.70 (CH), 85.62 (CH), 82.07 (CH), 76.48 (CH), 67.07 (CH), 26.74 (CH_3), 26.14 (CH_3), 20.66 (CH_3); HRFABMS: Calc. for $C_9H_{17}O_5$ (MH^+) 205.1075; Found: *m*/*z* 205.1070.

*5-*O-tert-*Butyldimethylsilyl-6-deoxy-1,2-*O-*isopropylidene-β-*L*-idofuranose (***10**).—To a solution of **9** (0.19 g, 0.93 mmol) in DMF (1 mL) was consecutively added imidazole (0.18 g, 2.7 mmol) and *tert*-butylchlorodimethylsilane (0.15 g, 1.0 mmol) at rt under nitrogen. After 2 days, the mixture was diluted with

EtOAc (15 mL), and the resulting solution was sequentially washed with cold water, 0.1 N HCl, satd $NaHCO_3$ and brine. The organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by flash chromatography (1:2 EtOAc–hexane) to afford **10** (0.26 g, 86%): $[\alpha]_D^{25}$ +6.5° (*c* 1.0, $CHCl_3$); mp 77–78 °C; IR ($CHCl_3$): 3461, 2931, 1463, 1374, 833 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.95 (d, $J_{1,2}$ 3.7 Hz, 1 H, H-1), 4.46 (d, 1 H, H-2), 4.31 (dq, $J_{5,6}$ 6.4 Hz, 1 H, H-5), 4.20 (dd, $J_{3,4}$ 2.7, $J_{3,OH}$ 3.7 Hz, 1 H, H-3), 3.93 (dd, $J_{4,5}$ 4.0 Hz, 1 H, H-4), 3.80 (d, 1 H, OH-3), 1.48 (s, 3 H, Me), 1.35 (d, 3 H, Me-6), 1.31 (s, 3 H, Me), 0.90 (s, 9H, *t*-Bu), 0.14 (s, 3 H, Si–Me) 0.13 (s, 3 H, Si–Me); ^{13}C NMR (100 MHz, $CDCl_3$): δ 111.37 (C), 104.62 (CH), 85.32 (CH), 82.01 (CH), 76.46 (CH), 69.04 (CH), 26.72 (CH_3), 26.19 (CH_3), 25.76 (CH_3), 21.20 (CH_3), 17.99 (C), −3.94 (CH_3), −4.66 (CH_3); HRFABMS: Calc. for $C_{15}H_{31}O_5Si$ (MH^+) 319.1940; found: *m*/*z* 319.1935. Anal. Calc. for $C_{15}H_{30}O_5Si$: C, 56.57; H, 9.49. Found: C, 56.32; H, 9.66%.

5-O-tert-*Butyldimethylsilyl*-*6*-*deoxy*-*1,2*-O-*isopropylidene*-*β*-*L*-*talofuranose* (**11**).—To a solution of **10** (0.22 g, 0.69 mmol) in CH_2Cl_2 (1 mL) was sequentially added pyridinium dichromate (0.20 g, 0.51 mmol) and Ac_2O (0.20 mL, 2.1 mmol) under nitrogen. The mixture was refluxed for 3 h, then filtered through Celite. The filtrate was concentrated in vacuo to afford the ketone as a pale yellow oil. The crude ketone was dissolved in MeOH (1 mL), and $NaBH_4$ (35 mg, 0.92 mmol) was added. After stirring for 0.5 h, the reaction was quenched with brine (5 mL), and the mixture extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by flash chromatography (1:5 EtOAc–hexane) to afford **11** (0.18 g, 82%) as a colourless oil: $[\alpha]_D^{25}$ +38.8° (*c* 1.0, $CHCl_3$); IR ($CHCl_3$): 3504, 2932, 1463, 1254, 1061, 835 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.78 (d, $J_{1,2}$ 3.8 Hz, 1 H, H-1), 4.54 (dd, $J_{2,3}$ 5.3 Hz, 1 H, H-2), 4.00 (dq, $J_{5,6}$ 6.4 Hz, 1 H, H-5), 3.91 (ddd, $J_{3,4}$ 8.2, $J_{3,OH}$ 8.9 Hz, 1 H, H-3), 3.64 (dd, $J_{4,5}$ 3.7 Hz, 1 H, H-4), 2.38 (d, 1 H, OH-3), 1.54 (s, 3 H, Me), 1.35 (s, 3 H, Me), 1.23 (d, 3 H, Me-6), 0.87 (s, 9H, *t*-Bu), 0.07 (s, 3 H, Si–Me), 0.06 (s, 3 H, Si–Me); ^{13}C NMR (75 MHz, $CDCl_3$): δ 112.51 (C), 104.05 (CH), 84.07 (CH), 78.93 (CH), 71.35 (CH), 67.54 (CH), 26.59 (CH_3), 25.84 (CH_3), 19.65 (CH_3), 18.16 (C), −4.51 (CH_3), −4.76 (CH_3). Anal. Calc. for $C_{15}H_{30}O_5Si$: C, 56.57; H, 9.49. Found: C, 56.66; H, 9.67.

5-O-tert-*Butyldimethylsilyl*-*6*-*deoxy*-*1,2*-O-*isopropylidene*-*3*-O-*methyl*-*β*-*L*-*talofuranose* (**12**).—To a solution of **11** (50 mg, 0.15 mmol) in DMF (1 mL) was added 60% NaH (6.8 mg, 0.17 mmol) at 0 °C under nitrogen. After 20 min, iodomethane (30 μL, 0.47 mmol) was added to the solution, and the mixture was kept stirring for another 3 h. The reaction was quenched with water (2 mL), and the resulting solution was extracted with EtOAc (3 × 3 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by flash chromatography (1:9 EtOAc–hexane) to afford **12** (45 mg, 86%). $[\alpha]_D^{25}$ +78.3° (*c* 1.0, $CHCl_3$); IR ($CHCl_3$): 2930, 1463, 1373, 1273, 1080, 835 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.74 (d, $J_{1,2}$ 3.6 Hz, 1 H, H-1), 4.63 (t, $J_{2,3}$ 3.6 Hz, 1 H, H-2), 3.92 (dq, $J_{5,6}$ 6.4 Hz, 1 H, H-5), 3.79 (dd, $J_{4,5}$ 2.6 Hz, 1 H, H-4), 3.61 (dd, $J_{3,4}$ 8.6 Hz, 1 H, H-3), 3.44 (s, 3 H, OMe), 1.33 (s, 3 H, Me), 1.23 (s, 3 H, Me), 1.23 (d, 3 H, Me-6), 0.88 (s, 9H, *t*-Bu), 0.06 (s, 3 H, Si–Me) 0.06 (s, 3 H, Si–Me); ^{13}C NMR (100 MHz, $CDCl_3$): δ 112.73 (C), 104.04 (CH), 82.48 (CH), 80.06 (CH), 77.28 (CH), 66.70 (CH), 57.85 (CH_3), 26.82 (CH_3), 26.58 (CH_3), 25.90 (CH_3), 20.29 (CH_3), 18.16 (C), −3.96 (CH_3), −4.64 (CH_3); HRFABMS: Calc. for $C_{16}H_{33}O_5Si$ (MH^+) 333.2097; Found: *m*/*z* 333.2082. Anal. Calc. for $C_{16}H_{32}O_5Si$: C, 57.79; H, 9.70. Found: C, 57.52; H, 9.83%.

L-*Acovenose* (**3**).—A mixture of **12** (50 mg, 0.15 mmol), Amberlite-120 resin (H^+ form, 100 mg), 1,4-dioxane (1 mL) and water (1 mL) was stirred at 100 °C for 12 h. After cooling to rt, the resin was filtered and washed with water. The filtrate was concentrated under reduced pressure and freeze-dried to afford **3** (31 mg, 84%). ^1H and ^{13}C NMR spectra were identical to those reported.[11a]

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