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Note

Radical reactions on carbohydrate acetals: use of a furanoid glycal for the synthesis of *cis*-fused bicyclic acetals ☆

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Since a large and growing number of natural products have been shown to contain fused cyclic acetals, such as furo[2,3-*b*]furans, as part structures [1] and since many of them have a variety of activities (e.g., antitumor, antimicrobial, and insect antifeedant), interest has rapidly grown and resulted in several strategies for the construction [2] of these systems. Herein, we describe a protocol, utilising an intramolecular radical cyclisation [3] of α-halogeno acetals [4] of chiral templates derived from the furanoid glycal **1**, for the synthesis of fused bicyclic acetals **8–11**.

The required furanoid glycal, 1,4-anhydro-2-deoxy-5,6-*O*-isopropylidene-D-*arabino*-hex-1-enitol (**1**) [5] was prepared from D-mannose. Reaction of **1** with *tert*-butyldimethylsilyl chloride in the presence of imidazole in *N*,*N*-dimethylformamide afforded **2** in 83% yield. In the ^{1}H NMR (200 MHz) spectrum of **2**, H-1 and H-2 resonated at δ 6.55 (d, $J_{1,2}$ 2.5 Hz) and 5.1 (t), respectively. Treatment of **2** with *N*-bromosuccinimide [6] in the presence of 10 equivalents of the propargylic and allylic alcohols 2-propyn-1-ol, 2-methyl-3-butyn-2-ol, 2-propen-1-ol, and 2-methyl-2-propen-1-ol resulted in the stereoselective formation of 1,2-*trans*-β-D-glycosides [7], viz., 2-propynyl 2-bromo-3-*O*-*tert*-butyldimethylsilyl-2-deoxy-5,6-*O*-isopropylidene-β-D-glucofuranoside (**3**), 1,1-dimethyl-2-propynyl 2-bromo-3-*O*-*tert*-butyldimethylsilyl-2-deoxy-5,6-*O*-isopropylidene-β-D-glucofuranoside (**4**), allyl 2-bromo-3-*O*-*tert*-butyldimethylsilyl-2-deoxy-5,6-*O*-isopropylidene-β-D-glucofuranoside (**5**), and 2-methyl-2-propenyl 2-bromo-3-*O*-*tert*-butyldimethylsilyl-2-deoxy-5,6-*O*-isopropylidene-β-D-glucofuranoside (**6**), respectively, in good

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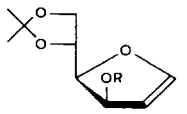
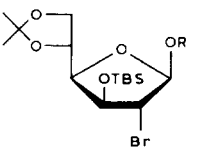


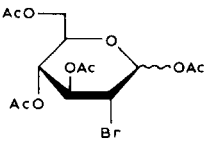
1 R = H

2 R = t-BuMe$_2$Si (TBS)

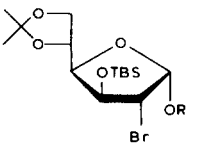


3 R = $-CH_2C\equiv CH$, 5 R = $-CH_2CH=CH_2$

4 R = $-CMe_2C\equiv CH$, 6 R = $-CH_2CMe=CH_2$

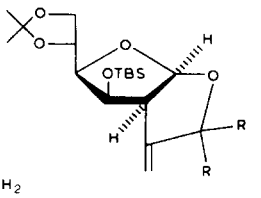


7



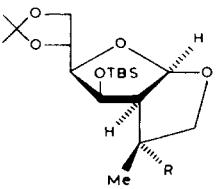
3a R = $-CH_2C\equiv CH$, 5a R = $-CH_2CH=CH_2$

4a R = $-CMe_2C\equiv CH$, 6a R = $-CH_2CMe=CH_2$



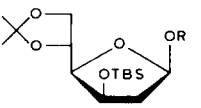
8 R = H

9 R = Me



10 R = H

11 R = Me



12 R = $-CH_2CH=CH_2$

13 R = $-CH_2CMe=CH_2$

14 R = $-CH_2CH_2CH_3$

yields. Unlike the haloetherification of *arabino*-hexopyranoid glycals [6] which results in the formation of α-mannopyranosides, electrophilic addition to furanoid glycals affords β-glycosides [7].

The structures of the major glycosides **3–6** were established as β-D-glucofuranosides from their negative optical rotations and from their ^{1}H NMR spectra in which the H-1 signals appeared as singlets [8]. The corresponding minor products **3a**, **5a**, and **6a** showed positive optical rotations and $J_{1,2}$ 4 Hz, consistent with α-D-glucofuranosides. This aspect was conclusively solved by chemical reactions on **5** and **5a**. Hydrolysis of **5** with toluene-*p*-sulfonic acid monohydrate in dichloromethane followed by acetylation with Ac_2O in pyridine gave 1,3,4,6-tetra-*O*-acetyl-2-bromo-2-deoxy-α,β-D-glucopyranose (**7**). The ^{1}H NMR spectrum of **7** indicated the absence of allylic protons and protons derived from the silyl group. Further, H-1 appeared at δ 5.8 (d, $J_{1,2}$ 9 Hz) and 6.35 (d, $J_{1,2}$ 3 Hz) for the β and α anomers, respectively. Similarly, **5a** on hydrolysis and acetylation afforded a compound which had ^{1}H NMR data identical with those of **7** obtained from **5**, indicating that **5** and **5a** are β and α anomers having the *gluco* configuration at C-2. This experiment established the β-D-*gluco* configuration for **3–6**

and α-D-*gluco* configuration for **3a–6a**, which is critically important for the further determination of the stereochemistry of the cyclisation products **8–11**. In the case of the β-glucoside **4**, the ^{1}H NMR spectrum of the corresponding α-glucoside **4a** was not observed.

The crucial regio- and stereo-selective C–C bond formation by intramolecular radical cyclisation [3] of 5-hexenyl radicals on the carbohydrate templates **3–6** was efficiently achieved by treatment with a catalytic amount of tributylin chloride [9] and α,α′-azobisisobutyronitrile (AIBN) in the presence of sodium cyanoborohydride [10] in *tert*-butyl alcohol at reflux to afford the *cis*-fused bicyclic acetals **8–11** in 30–72% yield by a preferred 5-*exo* mode of cyclisation. The stereochemistry of the newly formed C–C bond is derived [11] from that of the C-1 centre bearing allylic and propargylic appendages.

Furans **8–11** were fully characterised from the ^{1}H NMR spectral analysis, where the resonances for acetylenic and olefinic protons were found to be absent, while H-1 resonated as doublets at δ 5.65 ($J_{1,5}$ 5.4 Hz), 5.6 ($J_{1,5}$ 5.5 Hz), 5.6 ($J_{1,5}$ 6.3 Hz), and 5.8 ($J_{1,5}$ 5.6 Hz), respectively. The assigned configuration at C-1/C-5 and C-1/C-6 in furan **10** as *cis* was based on the observation [12] that, during the course of radical ring closure of cyclic 5-hexenyl radicals, the 1,2- and 1,5-*cis* cyclised products are favoured because of the formation of bicyclo[3.3.0]octane systems.

During the radical cyclisations, the propargylic glycosides **3** and **4** gave **8** and **9** as exclusive products, while the allylic glycosides **5** and **6** gave the expected cyclised products **10** and **11** along with the 2-deoxy compounds **12** and **13**. In the ^{1}H NMR spectrum of **12**, the H-1 signal was merged with olefinic proton signals at δ 5.05–5.35 while H-1 in **13** resonated as a doublet at δ 5.1 ($J_{1,2a}$ 4.8, $J_{1,2b}$ ~ 0 Hz) and H-2 signals appeared at δ 1.9–2.2 as multiplets. Since the H-1 signal in **12** was merged with olefinic protons, it was subjected to catalytic hydrogenation with 5% Pd–C in MeOH to afford propyl 3-O-*tert*-butyldimethylsilyl-2-deoxy-5,6-*O*-isopropylidene-β-D-*arabino*-hexofuranoside (**14**), where the H-1 signal was observed as a doublet at δ 5.05 ($J_{1,2a}$ 5, $J_{1,2b}$ ~ 0 Hz).

These synthetic chiral furan synthons are potentially useful for the synthesis of several natural products.

1. Experimental

General methods.—NMR spectra were recorded for solutions in $CDCl_3$ (internal Me_4Si) with a Varian 200-Gemini spectrometer (^{1}H, 200 MHz). Optical rotations were measured with a Jasco DIP 360 or 370 polarimeter. Silica gel (60–120 and finer than 200 mesh, Acme) was used for column chromatography. TLC was performed on Silica Gel 60 F_{254} (E. Merck) with detection using a solution of 2% phosphomolybdic acid and 1% $Ce_2SO_4 \cdot 4H_2O$ in aq 20% H_2SO_4 at 130°C. All the reactions were carried out in dry solvents under anhydrous conditions unless otherwise stated.

1,4-Anhydro-3-O-tert-*butyldimethylsilyl-2-deoxy-5,6*-O-*isopropylidene*-D-arabino-*hex-1-enitol* (**2**).—A solution of 1,4-anhydro-2-deoxy-5,6-*O*-isopropylidene-D-*arabino*-hex-

1-enitol (**1**; 2 g, 10.7 mmol) and imidazole (2.17 g, 31.8 mmol) in *N,N*-dimethylformamide (5 mL) was treated with *tert*-butyldimethylsilyl chloride (1.6 g, 10.6 mmol) at room temperature. After 12 h, the mixture was quenched with water, and extracted with ether. The ethereal layer was washed with water, dried (Na_2SO_4), and evaporated, and the residue was purified by column chromatography (20:1 light petroleum–EtOAc) to afford **2** (2.7 g, 83%); $[\alpha]_D$ −69.6° (*c* 1, $CHCl_3$); NMR data: ^1H, δ 0.05 (s, 6 H), 0.85 (s, 9 H), 1.14, 1.3 (2 s, 6 H), 3.93 (dd, 1 H, $J_{5,6a}$ 5.4 Hz, H-6a), 4.07 (dd, 1 H, $J_{6a,6b}$ 8.3 Hz, H-6b), 4.34 (ddd, 1 H, $J_{5,6b}$ 4.9 Hz, H-5), 4.45 (dd, 1 H, $J_{4,5}$ 6.3 Hz, H-4), 4.9 (dd, 1 H, $J_{3,4}$ 6.6 Hz, H-3), 5.1 (t, 1 H, H-2), 6.55 (d, 1 H, $J_{1,2}$ 2.5 Hz, H-1). Anal. Calcd for $C_{15}H_{28}O_4Si$: C, 59.95; H, 9.39. Found: C, 59.83; H, 9.33.

*Preparation of the 2-bromo-2-deoxy-β-*D*-glucosides* (**3–6**).—A solution of **2** (1 mmol) and the propargylic/allylic alcohol (10 mmol) in MeCN (5 mL) at 0°C was treated with *N*-bromosuccinimide (1 mmol) and stirred at room temperature for 30–45 min. Acetonitrile was evaporated, the residue taken up in CH_2Cl_2, and the solution washed sequentially with water, aq $Na_2S_2O_3$, and water, and dried (Na_2SO_4). Evaporation of solvent and purification of the residue by column chromatography (Si-gel, Acme, finer than 200 mesh; 50:1 light petroleum–EtOAc) gave the β-D-glucosides **3–6**.

*2-Propynyl 2-bromo-3-*O*-tert-butyldimethylsilyl-2-deoxy-5,6-*O*-isopropylidene-β-*D*-glucofuranoside* (**3**).—Reaction of **2** (0.4 g, 1.33 mmol) with propargyl alcohol (0.744 g, 13.3 mmol) and *N*-bromosuccinimide (0.236 g, 1.33 mmol) for 30 min and chromatographic purification afforded **3** (0.446 g, 77%) as a syrup; $[\alpha]_D$ −41.8° (*c* 1, $CHCl_3$); NMR data: ^1H, δ 0.10, 0.12 (2 s, 6 H), 0.89 (s, 9 H), 1.34, 1.46 (2 s, 6 H), 2.4 (t, 1 H, H-3), 3.90–4.18 (m, 3 H, H-2,6a,6b), 4.2 (d, 2 H, $J_{1',3'}$ 1.98 Hz, 2 H, H-1'a,1'b), 4.28–4.4 (m, 3 H, H-3,4,5), 5.4 (s, 1 H, H-1). Anal. Calcd for $C_{18}H_{31}BrO_5Si$: C, 49.64; H, 7.17. Found: C, 49.57; H, 7.09.

Eluted second was 2-propynyl 2-bromo-3-*O*-*tert*-butyldimethylsilyl-2-deoxy-5,6-*O*-isopropylidene-α-D-glucofuranoside (**3a**; 0.047 g, 8.1%) as a syrup; $[\alpha]_D$ +63.9° (*c* 0.25, $CHCl_3$); NMR data: ^1H, δ 0.09, 0.13 (2 s, 6 H), 0.85 (s, 9 H), 1.29, 1.38 (2 s, 6 H), 2.4 (t, 1 H, H-3), 3.8–4.1 (m, 3 H, H-2,6a,6b), 4.16–5.05 (m, 5 H, H-1'a,1'b,3,4,5), 5.3 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1).

*1,1-Dimethyl-2-propynyl 2-bromo-3-*O*-tert-butyldimethylsilyl-2-deoxy-5,6-*O*-isopropylidene-β-*D*-glucofuranoside* (**4**).—Reaction of **2** (0.4 g, 1.33 mmol) with 2-methyl-3-butyn-2-ol (1.12 g, 13.3 mmol) and *N*-bromosuccinimide (0.236 g, 1.33 mmol) for 30 min gave **4** (0.45 g, 73%) as a syrup; $[\alpha]_D$ −30.2° (*c* 1, $CHCl_3$); NMR data: ^1H, δ 0.12, 0.14 (2 s, 6 H), 0.92 (s, 9 H), 1.34, 1.41, 1.49, 1.52 (4 s, 12 H), 2.48 (s, 1 H, H-3'), 3.92 (s, 1 H, H-2), 3.95–4.15 (m, 2 H, H-6a,6b), 4.20–4.45 (m, 3 H, H-3,4,5), 5.4 (s, 1 H, H-1). Anal. Calcd for $C_{20}H_{35}BrO_5Si$: C, 51.82; H, 7.61. Found: C, 51.79; H, 7.52.

*Allyl 2-bromo-3-*O*-tert-butyldimethylsilyl-2-deoxy-5,6-*O*-isopropylidene-β-*D*-glucofuranoside* (**5**).—Reaction of **2** (0.4 g, 1.33 mmol) with allyl alcohol (0.773 g, 13.3 mmol) and *N*-bromosuccinimide (0.236 g, 1.33 mmol) for 45 min and chromatographic purification gave **5** (0.45 g, 77.3%) as a syrup; $[\alpha]_D$ −18.5° (*c* 0.5, $CHCl_3$). NMR data: ^1H, δ 0.12, 0.14 (2 s, 6 H), 0.92 (s, 9 H), 1.33, 1.41 (2 s, 6 H), 3.93 (s, 1 H, H-2), 3.80–4.45 (m, 7 H, H-3,4,5,6a,6b,1'a,1'b), 5.25 (s, 1 H, H-1), 5.1–5.4 (m, 2 H, olefinic), 5.60–5.75 (m, 1 H, olefinic). Anal. Calcd for $C_{18}H_{33}BrO_5Si$: C, 49.41; H, 7.60. Found: C, 49.32; H, 7.52.

Eluted second was allyl 2-bromo-3-*O*-*tert*-butyldimethylsilyl-2-deoxy-5,6-*O*-isopropylidene-α-D-glucofuranoside (**5a**; 0.052 g, 8.9%) as a syrup; $[\alpha]_D$ +54.6° (*c* 0.5, $CHCl_3$); NMR data: ^1H, δ 0.09, 0.1 (2 s, 6 H), 0.85 (s, 9 H), 1.28, 1.32 (2 s, 6 H), 3.8–4.5 (m, 8 H, H-2,3,4,5,6a,6b,1'a,1'b), 5.08 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1), 5.05–5.35 (m, 2 H, olefinic), 5.7–5.88 (m, 1 H, olefinic).

2-Methyl-2-propenyl 2-bromo-3-O-tert-*butyldimethylsilyl-2-deoxy-5,6*-O-*isopropylidene-β-*D-*glucofuranoside* (**6**).—Reaction of **2** (0.4 g, 1.33 mmol) with 2-methyl-2-propen-1-ol (0.96 g, 13.3 mmol) and *N*-bromosuccinimide (0.236 g, 1.33 mmol) for 30 min and chromatographic purification afforded **6** (0.426 g, 71%) as a syrup; $[\alpha]_D$ −19.1° (*c* 0.5, $CHCl_3$); NMR data: ^1H, δ 0.10, 0.12 (2 s, 6 H), 0.85 (s, 9 H), 1.3, 1.4 (2 s, 6 H), 1.68 (br s, 3 H), 3.82–4.4 (m, 8 H, H-2,3,4,5,6a,6b,1'a,1'b), 4.9, 5.0 (2 s, 2 H, vinylic), 5.2 (s, 1 H, H-1). Anal. Calcd for $C_{19}H_{35}BrO_5Si$: C, 50.54; H, 7.81. Found: C, 50.49; H, 7.75.

Eluted second was 2-methyl-2-propenyl 2-bromo-3-*O*-*tert*-butyldimethylsilyl-2-deoxy-5,6-*O*-isopropylidene-α-D-glucofuranoside (**6a**; 0.052 g, 8.6%) as a syrup; $[\alpha]_D$ +68.3° (*c* 0.5, $CHCl_3$); NMR data: ^1H, δ 0.85 (s, 9 H), 0.9, 1.2 (2 s, 6 H), 1.28, 1.35 (2 s, 6 H), 1.7 (br s, 3 H), 3.8–4.52 (m, 8 H, H-2,3,4,5,6a,6b,1'a,1'b), 5.06 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1).

1,3,4,6-Tetra-O-*acetyl-2-bromo-2-deoxy-α,β-*D-*glucopyranose* (**7**).—A solution of **5** (0.04 g, 0.091 mmol) in CH_2Cl_2 (3 mL) containing $TsOH \cdot H_2O$ (5 mg) was stirred at room temperature for 12 h. The solvent was evaporated and the residue used as such for further reaction.

A solution of the above crude product in pyridine (0.3 mL) at 0°C was treated with Ac_2O (0.15 mL) and left at room temperature for 12 h. The mixture was dissolved in CH_2Cl_2, and the solution washed with water, aq $NaHCO_3$, and water, then dried (Na_2SO_4) and evaporated. The residue obtained was purified by column chromatography (silica gel, 6:1 light petroleum–EtOAc) to afford **7** (0.023 g, 62%); NMR data: ^1H, δ 2.01, 2.02, 2.1, 2.2, 2.4 (5 s, OAc), 3.8–4.4 (m, 4 H), 4.94–5.55 (m, 2 H), 5.8 (d, 0.85 H, $J_{1,2}$ 9 Hz, H-1 of β anomer), 6.35 (d, 0.15 H, $J_{1,2}$ 3 Hz, H-1 of α anomer).

Likewise **5a** (10 mg, 0.022 mmol) on hydrolysis and acetylation for 16 h gave **7** (5.7 mg, 59%).

Radical cyclisation of α-bromo acetals.—A mixture of the α-bromo acetal (1 mmol), tributyltin chloride (0.1 mmol), and $NaCNBH_3$ (2 mmol) in *tert*-butyl alcohol (10 mL) was heated at reflux and treated with AIBN (0.1 mmol) for 12–18 h. The solvent was evaporated and the residue was purified by column chromatography (silica gel, 10:1 light petroleum–EtOAc) to afford the fused bicyclic acetals in good yields.

*(1*R*,3*S*,4*R*,4'*R*,5*S*)-4-*tert*-Butyldimethylsilyloxy-3-(2',2'-dimethyl-1',3'-dioxolan-4'-yl)-6-methylene-2,8-dioxabicyclo[3.3.0]octane* (**8**).—Reaction of **3** (0.3 g, 0.68 mmol) with $NaCNBH_3$ (0.086 g, 1.37 mmol) and tributyltin chloride and AIBN for 14 h afforded **8** (0.176 g, 72%) as a syrup; $[\alpha]_D$ +70° (*c* 0.5, $CHCl_3$); NMR data: ^1H, δ 0.12, 0.13 (2 s, 6 H), 0.94 (s, 9 H), 1.35, 1.39 (2 s, 6 H), 3.28 (t, 1 H, $J_{1,5} = J_{4,5} = 5.4$ Hz, H-5), 3.65 (dd, 1 H, $J_{3,4}$ 4.16, $J_{3,4'}$ 8.0 Hz, H-3), 3.85–4.6 (m, 6 H, H-4,7a,7b,4',5'a,5'b), 5.05, 5.15 (2 br s, 2 H, vinylic), 5.65 (d, 1 H, $J_{1,5}$ 5.4 Hz, H-1). Anal. Calcd for $C_{18}H_{32}O_5Si$: C, 60.64; H, 9.04. Found: C, 60.53; H, 8.95.

*(1*R*,3*S*,4*R*,4'*R*,5*S*)-4-*tert*-Butyldimethylsilyloxy-3-(2',2'-dimethyl-1',3'-dioxolan-4'-

yl)-7,7-dimethyl-6-methylene-2,8-dioxabicyclo[3.3.0]octane (**9**).—Reaction of **4** (0.3 g, 0.647 mmol) and $NaCNBH_3$ (0.081 g, 1.29 mmol) and tributyltin chloride and AIBN for 12 h gave **9** (0.174 g, 70%) as a syrup; $[\alpha]_D$ +56° (*c* 1, $CHCl_3$); NMR data: ^1H, δ 0.12, 0.15 (2 s, 6 H), 0.89 (s, 9 H), 1.32, 1.34, 1.39, 1.47 (4 s, 12 H), 3.4 (t, 1 H, H-5), 3.7 (dd, 1 H, H-3), 3.97 (dd, 1 H, $J_{4',5'a}$ 5.7 Hz, H-5'a), 4.12 (dd, 1 H, $J_{5'a,5'b}$ 8.5, $J_{4',5'b}$ 5.1 Hz, H-5'b), 4.38 (dd, $J_{3,4}$ 5.6, $J_{4,5}$ 5.5 Hz, H-4), 4.53 (dd, 1 H, $J_{3,4'}$ 4.68 Hz, H-4'), 5.0, 5.1 (2 br s, 2 H, vinylic), 5.6 (d, 1 H, $J_{1,5}$ 5.5 Hz, H-1). Anal. Calcd for $C_{20}H_{36}O_5Si$: C, 62.45; H, 9.43. Found: C, 62.41; H, 9.38.

*(1*R,*3*S,*4*R,*4'*R,*5*S,*6*S*)-4*-tert-*Butyldimethylsilyloxy-3-(2',2'-dimethyl-1',3'-dioxolan-4'-yl)-6-methyl-2,8-dioxabicyclo[3.3.0]octane* (**10**).—Reaction of **5** (0.3 g, 0.68 mmol) and $NaCNBH_3$ (0.086 g, 1.37 mmol) for 16 h and chromatographic purification gave, first, allyl 3-*O*-*tert*-butyldimethylsilyl-2-deoxy-5,6-*O*-isopropylidene-β-D-*arabino*-hexofuranoside (**12**; 0.068 g, 28%) as a syrup; $[\alpha]_D$ −63.6° (*c* 1, $CHCl_3$); NMR data: ^1H, δ 0.1 (s, 6 H), 0.85 (s, 9 H), 1.3, 1.4 (2 s, 6 H), 1.90–2.15 (m, 2 H, H-2), 3.8–4.4 (m, 7 H, H-3,4,5,6a,6b,1'a,1'b), 5.1 (d merged with olefinic protons, 1 H, H-1), 5.05–5.35 (m, 2 H, olefinic), 5.60–5.75 (m, 1 H, olefinic). Anal. Calcd for $C_{18}H_{34}O_5Si$: C, 60.29; H, 9.55. Found: C, 60.27; H, 9.49.

Eluted second was **10** (0.127 g, 52%) as a syrup; $[\alpha]_D$ +4.2° (*c* 1, $CHCl_3$); NMR data: ^1H, δ 0.11, 0.13 (2 s, 6 H), 0.92 (s, 9 H), 1.05 (d, 3 H, *J* 7.0 Hz), 1.30, 1.35 (2 s, 6 H), 2.4–2.6 (m, 2 H, H-5,6), 3.45–3.60 (m, 2 H, H-3,5'a), 3.8–4.35 (m, 5 H, H-4,4',5'b,7a,7b), 5.6 (d, 1 H, $J_{1,5}$ 6.3 Hz, H-1). Anal. Calcd for $C_{18}H_{34}O_5Si$: C, 60.29; H, 9.55. Found: C, 60.22; H, 9.51.

*(1*R,*3*S,*4*R,*4'*R,*5*S)*-4*-tert-*Butyldimethylsilyloxy-3-(2',2'-dimethyl-1',3'-dioxolan-4'-yl)-6,6-dimethyl-2,8-dioxabicyclo[3.3.0]octane* (**11**).—Reaction of **6** (0.3 g, 0.66 mmol) with $NaCNBH_3$ (0.083 g, 1.32 mmol) for 16 h and purification first gave 2-methyl-2-propenyl 3-*O*-*tert*-butyldimethylsilyl-2-deoxy-5,6-*O*-isopropylidene-β-D-*arabino*-hexofuranoside (**13**; 0.118 g, 48%) as a syrup; $[\alpha]_D$ −39.7° (*c* 2, $CHCl_3$); NMR data: ^1H, δ 0.1 (s, 6 H), 0.9 (s, 9 H), 1.31, 1.33 (2 s, 6 H), 1.7 (br s, 3 H), 1.90–2.25 (m, 2 H, H-2), 3.8–4.4 (m, 7 H, H-3,4,5,6a,6b,1'a,1'b), 4.87, 4.92 (2 br s, 2 H, vinylic), 5.1 (d, 1 H, $J_{1,2}$ 4.8 Hz, H-1). Anal. Calcd for $C_{19}H_{36}O_5Si$: C, 60.92; H, 9.68. Found: C, 60.87; H, 9.63.

Second eluted was **11** (0.074 g, 30%); $[\alpha]_D$ −17.2° (*c* 0.5, $CHCl_3$); NMR data: ^1H, δ 0.1 (s, 6 H), 0.9 (s, 9 H), 1.1, 1.15, 1.3, 1.4 (4 s, 12 H), 2.25 (d, 1 H, H-5), 3.5 (dd, 2 H, H-7a,7b), 3.7 (dd, 1 H, $J_{3,4'}$ 6.9 Hz, H-3), 3.85–4.2 (m, 3 H, H-4',5'a,5'b), 4.3 (d, 1 H, $J_{3,4}$ 2.8 Hz, H-4), 5.8 (d, 1 H, $J_{1,5}$ 5.6 Hz, H-1). Anal. Calcd for $C_{19}H_{36}O_5Si$: C, 60.92; H, 9.68. Found: C, 60.88; H, 9.59.

Propyl 3-O-tert-*butyldimethylsilyl-2-deoxy-5,6*-O-*isopropylidene*-β-D-arabino-*hexofuranoside* (**14**).—A solution of **12** (0.009 g, 0.025 mmol) in MeOH (3 mL) containing 5% Pd–C was subjected to hydrogenation under atmospheric pressure at room temperature for 4 h. The mixture was filtered and the solvent evaporated to afford **14** (7.5 mg, 83%); $[\alpha]_D$ −39° (*c* 0.025, $CHCl_3$); NMR data: ^1H, δ 0.09 (s, 6 H), 0.9 (s, 9 H), 0.92 (t, merged with singlet, 3 H), 1.32, 1.4 (2 s, 6 H), 1.5–1.65 (m, 2 H), 1.90–2.2. (m, 2 H, H-2), 3.21–3.35 (m, 1 H), 3.56–3.71 (m, 1 H), 3.88–4.1 (m, 3 H, H-5,6a,6b), 4.27–4.42 (m, 2 H, H-3,4), 5.05 (d, 1 H, $J_{1,2}$ 4.8 Hz, H-1).

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