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Note

Synthesis of 3,5-dideoxy-5-iodo-1,2-*O*-isopropylidene-β-L-*lyxo*-hexofuranose derivatives

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The importance of deoxyhalogeno sugars as intermediates in the synthesis of deoxy, azido-deoxy, amino-deoxy, and deoxy-thio derivatives, and their ability to generate radicals, principally from iodinated products, led us to use them as intermediates for the synthesis of prostanoid systems [1], such as in preclavulone and other natural products. In order to extend the synthesis of such systems by radical cyclization [2], a new series of precursors able to generate a secondary radical at C-5, i.e., 3,5-dideoxy-5-iodo-1,2-*O*-isopropylidene-β-L-*lyxo*-hexofuranose derivatives has now been elaborated.

Examples of halogenation reactions at C-5 of hexoses are scarce [3]. Moreover, such reactions on 3-deoxy sugars have not been investigated previously. In a first approach, we have studied the formation of halohydrins by ring opening of 5,6-anhydro-D-*ribo*-hexofuranose derivatives. The regiospecific ring opening of epoxides has been already used for the preparation of C-2 or C-3 halogenated sugars [4]. In general, the reaction to cleave the bond between the less substituted carbon atom and the oxygen atom is termed normal opening, while the other direction is termed abnormal. Our aim was to induce the abnormal opening in 5,6-anhydro-3-deoxy-1,2-*O*-isopropylidene-α-D-*ribo*-hexofuranose [5] **3** in order to obtain halohydrins **4** (Scheme 1).

The epoxide **3** was prepared in two steps (72% overall yield) from the diol **1** [6] via the 2,4,6-trimethylbenzenesulfonate **2**. Several routes for the ring opening of the epoxide have been investigated (Table 1). These methods are reported to offer

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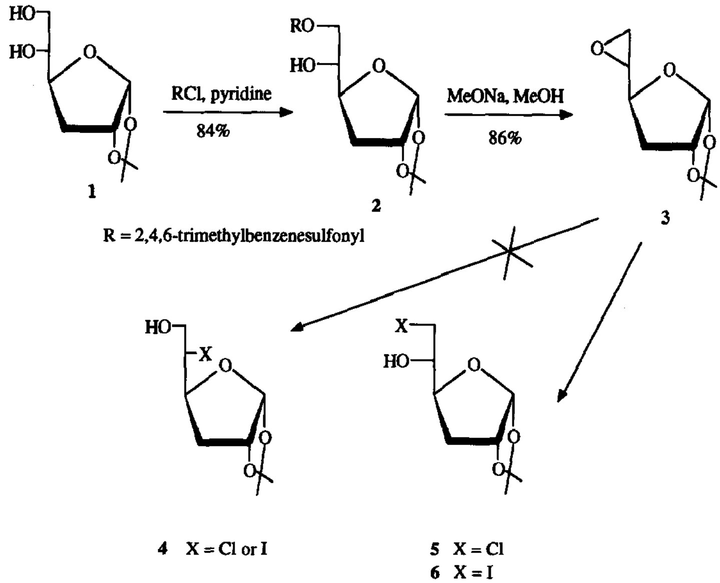


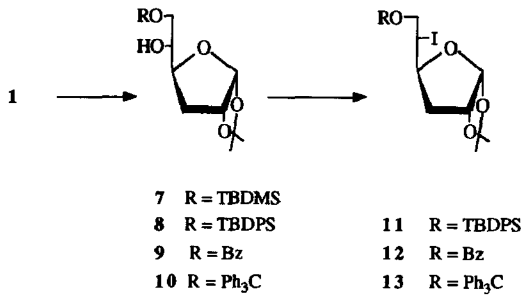
Scheme 1

Table 1
Experimental conditions used in the opening of the 5,6-epoxide in **3**

Experimental conditions	Ref	Results
NO_2Me, $AlCl_3$, 0°C, 2 h	[7]	**5** (6%)
1,2-Dichloroethane, $AlCl_3$, 0°C, 2 h	[7]	**5** (40%)
CH_2Cl_2, $TiCl_4$, DBU, −78°C	[8]	Mixture of tarry products
Toluene, I_2, hexamethyldisilane, −78°C	[9]	**6** (24%)
CH_2Cl_2, Ph_3P, Br_2, BF_3–Et_2O	[10]	Mixture of tarry products

abnormal opening on aliphatic oxiranes [7–9] depending on the salt and the Lewis acid. However, with **3**, they resulted in low yields of the normal opening products **5** and **6** [10], probably because of the difficulty in reaching the C-5 position by S_N2 substitution and also due to the instability of **3** under strong acidic conditions. All NMR data, particularly $\delta_{C\text{-}6}$, are consistent with the location of the halogen substituent at C-6.

Different methods for the direct replacement of OH-5 by halogen in the 6-*O*-protected derivatives **7–10** (Scheme 2), obtained by the selective protection of the primary OH-6 of diol **1** with *tert*-butyldimethylsilyl chloride (TBDMSCl), *tert*-butyldiphenylsilyl chloride (TBDPSCl), benzoyl chloride, and triphenylmethyl chloride [11], respectively, have also been investigated [12–14] (Table 2). The use of Garegg and Samuelsson [15] conditions, triphenylphosphine–iodine–imidazole and xylene as solvent, resulted in the target C-5 halogenated products **11–13** in good yields.



Scheme 2

The ^{13}C NMR spectra for **11–13** showed the expected downfield shift for the resonance of C-5 as compared to the precursor alcohols **8–10**, in agreement with the location of the iodine atom at C-5, while the L-*lyxo* configuration was assigned on the basis of the known S_N2 mechanism of Garegg and Samuelsson [15] halogenation.

1. Experimental

General methods.—TLC was performed on Silica Gel 60 F_{254} (E. Merck) with detection by UV light or anisaldehyde. Flash column chromatography was performed on 60 Å silica (70–200 mesh or 35–70 mesh, E. Merck). Optical rotations were measured at 20°C. ^1H NMR spectra were recorded with Varian EM 360 H and Bruker WH 360 WB spectrometers at 360 MHz. ^{13}C NMR spectra were recorded on a Bruker WP 200 SY spectrometer at 50.3 MHz; $CDCl_3$ was used as solvent, with Me_4Si as internal reference. Elemental analyses were performed by the Service Central d'Analyse du CNRS, Vernaison, France. IR spectra were recorded on a Beckman Acculab 2 apparatus using NaCl cells or KBr disks.

*3-Deoxy-1,2-O-isopropylidene-6-O-(2,4,6-trimethylbenzenesulfonyl)-α-*D-ribo-*hexofuranose* (**2**).—To a solution of 3-deoxy-1,2-*O*-isopropylidene-α-D-*ribo*-hexofuranose [6] (**1**; 1 g, 4.9 mmol) in pyridine (5 mL), was added a solution of 2,4,6-trimethylbenzenesulfonyl chloride (1.6 g, 7.34 mmol) in pyridine (5 mL) at

Table 2
Experimental conditions used for the direct replacement of OH-5 in **7–10**

Starting material	Experimental conditions	Ref	Results
7, **8**	DMF, NBS, Ph_3P	[11]	Decomposition
7, **9**	CH_2Cl_2, CBr_4,DIPHOS	[12]	Tarry products
8, **9**	MeCN, Br_2, Ph_3	[13]	Decomposition
8, **9**	Toluene, PBr_3	[13]	Decomposition
8	Xylene, imidazole, Ph_3P, I_2	[14]	**11** (71%)
9	Xylene, imidazole, Ph_3P, I_2	[14]	**12** (81%)
10	Xylene, imidazole, Ph_3P, I_2	[14]	**13** (75%)

$-15°C$. After 4 days at room temperature, the pyridine was evaporated under reduced pressure and the residue was dissolved in CH_2Cl_2, washed twice with aq 10% HCl, once with water, twice with satd aq $NaHCO_3$, dried (Na_2SO_4), filtered, and evaporated. Purification by column chromatography (1–10% MeOH in CH_2Cl_2) afforded **2** as an oil (1.6 g, 84%); R_f 0.57 (19:1 CH_2Cl_2–MeOH); $[\alpha]_D$ $-4.5°$ (*c* 0.6, $CHCl_3$); ν^{NaCl} 3400 cm^{-1} (OH). ^{1}H NMR: δ 1.27 (s, 3 H, Me), 1.45 (s, 3 H, Me), 1.71–1.80 (ddd, 1 H, $J_{2,3}$ 4.7, $J_{3,4}$ 10.7, $J_{3,3'}$ 13.6 Hz, H-3), 2.04–2.09 (dd, 1 H, $J_{2,3'}$ 0, $J_{3',4}$ 4.5 Hz, H-3′), 2.28 (s, 3 H, Me *p*), 2.59 (s, 6 H, Me *o*), 3.44 (s, 1 H, OH), 3.88 (dd, 1 H, $J_{6,5}$ 6.8, $J_{6,6'}$ 9.8 Hz, H-6), 3.95 (m, 1 H, H-5), 4.05 (dd, 1 H, $J_{5,6'}$ 3.1 Hz, H-6′), 4.10-4.16 (m, 1 H, H-4), 4.69 (t, 1 H, $J_{1,2}$ 4.2 Hz, H-2), 5.7 (d, 1 H, H-1), 6.95 (s, 2 H, Ph); ^{13}C NMR: 143.43, 138.84, 131.85 (Ph), 111.25 (CMe$_2$), 105.24 (C-1), 80.28 (C-2), 77.53 (C-4), 70.07 (C-5, C-6), 34.03 (C-3), 26.72, 26.93 (Me), 22.41, 20.88 (Me, Ar). Anal. Calcd for $C_{18}H_{26}O_7S$: C, 55.9; H, 6.7; O, 29.0. Found: C, 56.2; H, 6.8; O, 28.7.

*5,6-Anhydro-3-deoxy-1,2-O-isopropylidene-α-*D-ribo-*hexofuranose* (**3**).—To a solution of **2** (1.6 g, 4.14 mmol) in dry MeOH (20 mL) at 0°C, was added rapidly NaOMe (270 mg, 4.9 mmol). An orange colour appeared. After 20 h at room temperature, the reaction was quenched by the addition of brine, then extracted with CH_2Cl_2. The organic phase was dried (Na_2SO_4), filtered, and evaporated. The residue was suspended in dry ether, and the sodium trimethylbenzenesulfonate was filtered off. Purification by column chromatography (5–20% EtOAc in cyclohexane) and distillation under reduced pressure afforded **3** as a colourless oil (665 mg, 86%); R_f 0.55 (19:1 CH_2Cl_2–MeOH); bp 110°C, 40 Pa; lit. [5], bp 53°C, 1.35 Pa; $[\alpha]_D$ $-21.4°$ (*c* 2.05, EtOH). The ^{1}H NMR data agreed with those reported in the literature [16]. ^{13}C NMR: 105.39 (C-1), 80.12 (C-2), 77.74 (C-4), 51.50 (C-5), 44.88 (C-6), 34.09 (C-3), 26.63, 26.00 (Me).

*6-Chloro-3,6-dideoxy-1,2-O-isopropylidene-α-*D-ribo-*hexofuranose* (**5**).—To a solution of $AlCl_3$ (100 mg, 0.75 mmol) in 1,2-dichloroethane (1 mL) was added slowly, under stirring at 0°C, a solution of **3** (100 mg, 0.54 mmol) in 1,2-dichloroethane (1 mL). After 30 min, the mixture was poured into concd HCl–ice. The organic phase was washed with water and the aqueous phase was saturated with NaCl and extracted three times with ether. All the organic phases were mixed, dried (Na_2SO_4), filtered, and evaporated. Purification by column chromatography (5% ether in cyclohexane) afforded **5** as an oil (48 mg, 40%); R_f 0.49 (1:1 cyclohexane–EtOAc); $[\alpha]_D$ $-13.6°$ (*c* 1, $CHCl_3$); ν^{NaCl} 3400 cm^{-1} (OH). ^{1}H NMR: δ 1.30 (s, 3 H, Me), 1.49 (s, 3 H, Me), 1.8 (ddd, 1 H, $J_{2,3}$ 4.7, $J_{3,4}$ 10.6, $J_{3,3'}$ 13.4 Hz, H-3), 2.16 (dd, 1 H, $J_{2,3'}$ 0, $J_{3',4}$ 4.5 Hz, H-3′), 2.41 (d, 1 H, $J_{5,OH}$ 4.1 Hz, OH), 3.55 (dd, 1 H, $J_{5,6}$ 7.0, $J_{6,6'}$ 11.3 Hz, H-6), 3.66 (dd, 1 H, $J_{5,6'}$ 4.0 Hz, H-6′), 3.89 (m, 1 H, H-5), 4.22 (td, 1 H, $J_{4,5}$ 10.4 Hz, H-4), 4.73 (t, 1 H, $J_{1,2}$ 4.1 Hz, H-2), 5.78 (d, 1 H, H-1). ^{13}C NMR: 105.55 (C-1), 80.58 (C-2), 78.38 (C-4), 72.41 (C-5), 46.73 (C-6), 34.39 (C-3), 28.88, 28.25 (Me). Anal. Calcd for $C_9H_{15}ClO_4$: C, 48.5; H, 6.8; O, 28.7. Found: C, 48.7; H, 6.9; O, 28.5.

*3,6-Dideoxy-6-iodo-1,2-O-isopropylidene-α-*D-ribo-*hexofuranose* (**6**).—Hexamethyldisilane (79 mg, 0.54 mmol) and iodine (136 mg, 0.54 mmol) were mixed and heated to 65°C to give a homogenous solution. The mixture was refluxed for 90 min to allow Me_3SiI formation, then cooled to −78°C, and a solution of **3** (100 mg, 0.54 mmol) in toluene (2 mL) was added within 30 min. After disappearance of the starting material, the mixture was allowed to reach room temperature and excess iodine was eliminated with 2% aq $NaHSO_3$. Extraction with EtOAc and purification by column chromatography (0.5% MeOH in CH_2Cl_2) afforded **6** as an oil (40 mg, 24%); R_f 0.41 (19:1 CH_2Cl_2–MeOH); $[\alpha]_D$ −11.1° (*c* 1, $CHCl_3$); ν^{NaCl} 3480 cm^{-1} (OH). ^1H NMR: δ 1.32 (s, 3 H, Me), 1.51 (s, 3 H, Me), 1.80 (ddd, 1 H, $J_{2,3}$ 4.7, $J_{3,4}$ 10.6, $J_{3,3'}$ 13.4 Hz, H-3), 2.17 (dd, 1 H, $J_{2,3'}$ 0, $J_{3',4}$ 4.5 Hz, H-3′), 2.25 (d, 1 H, $J_{5,OH}$ 3.72 Hz, OH), 3.22 (dd, 1 H, $J_{5,6}$ 7.6, $J_{6,6'}$ 10.4 Hz, H-6), 3.35 (dd, 1 H, $J_{5,6'}$ 4.1 Hz, H-6′), 3.75 (m, 1 H, H-5), 4.24 (td, 1 H, $J_{5,4}$ 10.3 Hz, H-4), 4.75 (t, 1 H, $J_{1,2}$ 4.1 Hz, H-2), 5.80 (d, 1 H, H-1). ^{13}C NMR: 105.53 (C-1), 80.52 (C-2), 79.61 (C-4), 72.20 (C-5), 33.91 (C-3), 26.88, 26.27 (Me), 9.53 (C-6). Anal. Calcd for $C_9H_{15}IO_4$: C, 34.4; H, 4.8; O, 20.4. Found: C, 34.2; H, 4.9; O, 20.5.

6-O-tert-Butyldimethylsilyl-3-deoxy-1,2-O-isopropylidene-α-D-ribo-hexofuranose (**7**).—*tert*-Butyldimethylsilyl chloride (343 mg, 2.2 mmol) was added dropwise to a solution of 3-deoxy-1,2-*O*-isopropylidene-α-D-*ribo*-hexofuranose (**1**; 300 mg, 1.47 mmol) and imidazole (234 mg, 3.45 mmol) in DMF (12 mL) at 0°C under Ar. The mixture was allowed to reach room temperature. After 2 days, the reaction was quenched by satd aq $NaHCO_3$ and extracted with ether. After evaporation, the residue was purified by column chromatography with 9:1 cyclohexane–EtOAc to give **7** as a solid (340 mg, 73%); R_f 0.62 (1:1 cyclohexane–EtOAc); mp 47°C (from cyclohexane–ether); $[\alpha]_D$ −10.3° (*c* 0.4, $CHCl_3$); ν^{NaCl} 3300 cm^{-1} (OH). ^1H NMR: δ 0.1 (s, 6 H, MeSi), 0.85 (s, 9 H, *t*Bu), 1.28 (s, 3 H, Me), 1.45 (s, 3 H, Me), 1.80 (ddd, 1 H, $J_{3,4}$ 10.6 Hz, H-3), 2.1 (dd, 1 H, $J_{3',4}$ 4.3, $J_{3',3}$ 13.6 Hz, H-3′), 2.45 (s, 1 H, OH), 3.6 (m, 3 H, H-5, H-6, H-6′), 4.18 (td, 1 H, $J_{4,5}$ 5.3 Hz, H-4), 4.71 (t, 1 H, $J_{1,2}$ 4.0, $J_{2,3}$ 4.6 Hz, H-2), 5.72 (d, 1 H, H-1). ^{13}C NMR: 110.98 (CMe_2), 105.20 (C-1), 80.38 (C-2), 78.18 (C-4), 72.23 (C-5), 64.03 (C-6), 34.37 (C-3), 26.56 (Me), 26.01 (Me), 25.69 (*t*Bu), −4.4 ($SiMe_2$). Anal. Calcd for $C_{15}H_{30}O_5Si$: C, 56.6; H, 9.5; O, 18.1. Found: C, 56.5; H, 9.3; O, 18.3.

6-O-tert-Butyldiphenylsilyl-3-deoxy-1,2-O-isopropylidene-α-D-ribo-hexofuranose (**8**).—The same procedure as for **7** was used, but with TBDPSCl (137 mg, 0.5 mmol), diol **1** (100 mg, 0.49 mmol), imidazole (78 mg, 1.15 mmol), and DMF (38 mL). Compound **8** was obtained as a colourless liquid (204 mg, 95%); R_f 0.41 (9:1 CH_2Cl_2–MeOH); $[\alpha]_D$ −16.8° (*c* 1, $CHCl_3$); ν^{NaCl} 3300 cm^{-1} (OH). ^1H NMR: δ 1.07 (s, 9 H, Me), 1.30 (s, 3 H, Me), 1.48 (s, 3 H, Me), 1.81 (ddd, 1 H, $J_{2,3}$ 4.8, $J_{3,4}$ 10.7, $J_{3,3'}$ 13.5 Hz, H-3), 2.08 (dd, 1 H, $J_{2,3'}$ 0, $J_{3',4}$ 4.2 Hz, H-3′), 2.41 (d, 1 H, $J_{5,OH}$ 4.1 Hz, OH), 3.71 (d, 2 H, $J_{5,6} = J_{5,6'} = 5.32$ Hz, H-6, H-6′), 3.86 (td, 1 H, $J_{4,5}$ 4.8 Hz, H-5), 4.28 (td, 1 H, H-4), 4.71 (t, 1 H, $J_{1,2}$ 3.7, H-2), 5.77 (d, 1 H, H-1), 7.34 (m, 6 H, H*o* and H*p*, Ph), 7.65 (m, 4 H, H*m*, Ph). ^{13}C NMR: 135.56, 132.81, 129.81, 127.77 (Ph), 111.40 (CMe_2), 105.48 (C-1), 80.52 (C-2), 76.10 (C-4), 72.00 (C-5), 66.95 (C-6), 39.38 (C-3), 26.68 (*t*Bu, Me), 26.37 (Me). Anal. Calcd for $C_{25}H_{34}O_5Si$: C, 67.8; H, 7.7; O, 11.6. Found: C, 68.0; H, 7.7; O, 11.4.

6-O-Benzoyl-3-deoxy-1,2-O-isopropylidene-α-D-ribo-hexofuranose (**9**).—To a solution of **1** (100 mg, 0.49 mmol) in pyridine (7 mL) at 0°C was added benzoyl chloride (103 mg, 0.73 mmol). After 24 h at room temperature, the pyridine was evaporated under reduced pressure. The residue was dissolved in CH_2Cl_2 and washed with satd aq $NaHCO_3$. The organic phase was then dried (Na_2SO_4), filtered, and evaporated. Purification by flash chromatography afforded **9** as a white solid (45 mg, 80%); R_f 0.72 (9:1 CH_2Cl_2–MeOH); $[\alpha]_D$ −3.9° (*c* 0.4, $CHCl_3$); mp 137–138°C (from 1:1 cyclohexane–$CHCl_3$); ν^{KBr} 3400 (OH), 1650 cm^{-1} (C = O). ^1H NMR: δ 1.32 (s, 3 H, Me), 1.51 (s, 3 H, Me), 1.98 (ddd, 1 H, $J_{2,3}$ 4.7, $J_{3,4}$ 10.5, $J_{3,3'}$ 13.4 Hz, H-3), 2.13 (dd, 1 H, $J_{3',4}$ 4.6 Hz, H-3'), 2.57 (s, 1 H, OH), 4.23 (m, 1 H, H-4), 4.33 (m, 2 H, H-6, H-5), 4.48 (dd, 1 H, $J_{5,6'}$ 3.6, $J_{6,6'}$ 11.6 Hz, H-6'), 4.78 (t, 1 H, $J_{1,2}$ 4.1 Hz, H-2), 5.83 (d, 1 H, H-1), 7.7 (m, 5 H, Ph). ^{13}C NMR: 166.68 (C = O), 133.15, 129.64, 128.35, 128.25 (Ph), 111.33 (*C*Me_2), 105.24 (C-1), 80.58 (C-2), 78.29 (C-4), 70.58 (C-5), 65.88 (C-6), 33.27 (C-3), 26.69, 26.07 (Me). Anal. Calcd for $C_{15}H_{20}O_6$: C, 62.3; H, 6.5; O, 31.1. Found: C, 62.3; H, 6.7; O, 31.0.

*3-Deoxy-1,2-O-isopropylidene-6-O-triphenylmethyl-α-*D-ribo-*hexofuranose* (**10**).— A solution of triphenylmethyl chloride (492 mg, 1.76 mmol) and DBU (312 mg, 2.06 mmol) in dry CH_2Cl_2 (45 mL) at 0°C under N_2 was added dropwise to a solution of **1** (300 mg, 1.47 mmol) in CH_2Cl_2 (30 mL). After 2 days at room temperature, the reaction was quenched with cold water and extracted with CH_2Cl_2. The organic phase was dried (Na_2SO_4), filtered, and evaporated. Purification by column chromatography (cyclohexane and 10–40% ether) afforded **10** as a white amorphous solid (440 mg, 67%); R_f 0.25 (1:1 cyclohexane–ether); $[\alpha]_D$ −14.7° (*c* 0.5, $CHCl_3$); ν^{NaCl} 3400 cm^{-1} (OH); mp 160°C (from cyclohexane–ether). ^1H NMR: δ 1.31 (s, 3 H, Me), 1.50 (s, 3 H, Me), 1.78 (ddd, 1 H, $J_{2,3}$ 4.2, $J_{3,4}$ 10.6, $J_{3,3'}$ 13.5 Hz, H-3), 1.95 (dd, 1 H, $J_{2,3'}$ 0, $J_{3',4}$ 4.6 Hz, H-3'), 2.25 (s, 1 H, OH), 3.2 (ddd, 2 H, H-6, H-6'), 4.04 (q, 1 H, $J_{5,6}$ 4.9, $J_{4,5}$ 10.8 Hz, H-5), 4.29 (td, 1 H, H-4), 4.71 (t, 1 H, $J_{1,2}$ 4.2 Hz, H-2), 5.78 (d, 1 H, H-1), 7.33 (m, 15 H, Ph). ^{13}C NMR: 143.54, 128.47, 127.72, 126.95 (Ph), 111.03 (*C*Me_2), 105.12 (C-1), 86.68 (Ph_3C), 80.42 (C-2), 78.46 (C-4), 70.66 (C-5), 64.55 (C-6), 33.10 (C-3), 26.60, 26.04 (Me). Anal. Calcd for $C_{28}H_{30}O_5$: C, 75.3; H, 6.8; O, 17.9. Found: C, 75.0; H, 6.8; O, 17.8.

*6-O-*tert*-Butyldiphenylsilyl-3,5-dideoxy-5-iodo-1,2-O-isopropylidene-β-*L-lyxo-*hexofuranose* (**11**).—Product **9** (500 mg, 1.13 mmol) was mixed under N_2 with triphenylphosphine (301 mg, 1.14 mmol) and imidazole (154 mg, 2.26 mmol). Xylene (6 mL) was then added and the mixture was heated to 80°C with stirring. Iodine (315 mg, 1.24 mmol) was added slowly and the mixture was stirred at 140°C for 1 h. The hot mixture was poured into a flask containing satd aq $NaHSO_3$ and stirred for 10 min. The organic phase was dried (Na_2SO_4), filtered, and evaporated under reduced pressure. The solid was dissolved in 9:1 hexane–ether, filtered to eliminate Ph_3PO, and evaporated. Purification by column chromatography (10% ether in cyclohexane) afforded **11** as an oil (458 mg, 71%); R_f 0.88 (4:1 cyclohexane–ether); $[\alpha]_D$ −1.1° (*c* 0.4, $CHCl_3$). ^1H NMR: 1.0 (s, 9 H, *t*Bu), 1.25 (s, 3 H, Me), 1.5 (s, 3 H, Me), 1.8 (m, 1 H, H-3), 2.1 (m, 1 H, H-3'), 4.1 (m, 4 H, H-6, H-6', H-4, H-5), 4.7 (t, 1 H, $J_{1,2}$ 4.1, $J_{2,3}$ 4.6 Hz, H-2), 5.8 (d, 1 H, H-1), 7.5 (m, 10 H, Ph). ^{13}C NMR: 135.56, 129.81, 127.77 (Ph), 111.40 (*C*Me_2), 105.48 (C-1), 80.52 (C-2), 76.10 (C-4), 66.95 (C-6), 39.38 (C-3), 39.05 (C-5), 26.68 (*t*Bu, Me), 26.37 (Me). Anal. Calcd for $C_{25}H_{33}IO_4Si$: C, 54.3; H, 6.0; O, 11.6. Found: C, 54.0; H, 6.1; O, 11.8.

*6-O-Benzoyl-3,5-dideoxy-5-iodo-1,2-O-isopropylidene-β-L-*lyxo*-hexofuranose* (**12**). —The same procedure as for *11* was used, starting from **9** (0.857 g, 2.78 mmol), Ph_3P (0.799 g, 2.82 mmol), imidazole (378 mg, 5.56 mmol), xylene (14 mL), and I_2 (0.776 mg, 3.06 mmol). It afforded **12** as a solid (1.011 g, 81%); R_f 0.83 (1:1 cyclohexane–EtOAc); mp 105°C (from cyclohexane–ether); $[\alpha]_D$ −4.4° (*c* 2, $CHCl_3$). ^1H NMR: 1.25 (s, 1 H, Me), 1.45 (s, 1 H, Me), 1.8 (ddd, 1 H, $J_{3,4}$ 9.9 Hz, H-3), 2.2 (dd, 1 H, $J_{2,3'}$ 0, $J_{3',4}$ 4.3, $J_{3,3'}$ 13.4 Hz, H-3′), 3.95 (m, 1 H, H-4), 4.45 (m, 1 H, H-5), 4.5 (t, 1 H, $J_{1,2}$ 4.3, $J_{2,3}$ 4.8 Hz, H-2), 4.8 (m, 2 H, H-6 and H-6′), 5.8 (d, 1 H, H-1), 7.8 (m, 5 H, Ph). ^{13}C NMR: 164.71 (C = O), 133.14, 129.58, 128.32 (Ph), 111.47 (CMe_2), 105.43 (C-1), 80.27 (C-2), 78.89 (C-4), 67.03 (C-6), 38.89 (C-3), 32.67 (C-5), 26.72, 26.14 (Me). Anal. Calcd for $C_{16}H_{19}IO_5$: C, 45.9; H, 4.6; O, 19.1. Found: C, 45.8; H, 4.6; O, 19.1.

*3,5-Dideoxy-5-iodo-1,2-O-isopropylidene-6-O-triphenylmethyl-β-L-*lyxo*-hexofuranose* (**13**).—The same procedure as for **11** was used, starting from **9** (260 mg, 0.58 mmol), Ph_3P (155 mg, 0.59 mmol), imidazole (79 mg, 1.16 mmol), I_2 (163 mg, 0.64 mmol), and xylene (6 mL). Compound **13** was obtained as an oil (243 mg, 75%); R_f 0.71 (4:1 cyclohexane–EtOAc); $[\alpha]_D$ −6.3° (*c* 0.5, $CHCl_3$). ^1H NMR: 1.31 (s, 3 H, Me), 1.5 (s, 3H, Me), 1.9 (m, 2 H, H-3 and H-3′), 3.6 (m, 2 H, H-6 and H-6′), 4.0 (m, 2 H, H-5, H-4), 4.7 (t, 1 H, $J_{1,2}$ 4.1, $J_{2,3}$ 4.7 Hz, H-2), 5.75 (d, 1 H, H-1), 7.4 (m, 15 H, Ph). ^{13}C NMR: 143.64, 128.52, 127.77, 127.04 (Ph), 111.30 (CMe_2), 105.29 (C-1), 87.04 (Ph_3C), 80.40 (C-2), 76.85 (C-4), 66.51 (C-6), 39.03 (C-5), 35.94 (C-3), 26.81, 26.28 (Me). Anal. Calcd for $C_{25}H_{33}IO_4$ Si: C, 60.4; H, 5.2; O, 11.5. Found: C, 60.6; H, 5.5; O, 11.3.

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References

[1] B. Rondot, T. Durand, J.P. Girard, J.C. Rossi, L. Schio, S.P. Khanapure, and J. Rokach, *Tetrahedron Lett.*, 34 (1993) 8245–8248.

[2] D.P. Curran, *Synthesis*, (1988) 417–439.

[3] C.-W. Chiu and R.L. Whistler, *J. Org. Chem.*, 38 (1973) 832–834; S. Hanessian and N.R. Plessas, *ibid.*, 34 (1969) 1053–1058; E.J. Hedgley, O. Mérész, and W.G. Overend, *J. Chem. Soc. C*, (1967) 888–894.

[4] W.A. Szarek, G.W. Hay, B. Doboszewski, and M.M. Perlmutter, *Carbohydr. Res.*, 155 (1986) 107–118; J.A. Wright, *Methods Carbohydr. Chem.*, 6 (1972) 201–205; E.J. Reist and S.H. Kruse, *ibid.*, 6 (1972) 179–182.

[5] P. Szabó and L. Szabó, *J. Chem. Soc., Sect. C*, (1964) 5139–5143.

[6] E.J. Hedgley, W.G. Overend, and R.A.C. Rennie, *J. Chem. Soc., Sect. C*, (1963) 4701–4711.

[7] M. Inoue, T. Sugita, Y. Kiso, and K. Ichikawa, *Bull. Chem. Soc. Jpn.*, 49 (1976) 1063–1071; T. Takeda, S. Yasuhara, and S. Watanabe, *ibid.*, 53 (1980) 2566–2569.

[8] C.-L. Spawn, G.J. Drtina, and D.F. Wiemer, *Synthesis*, (1986) 315–317.
[9] A. Furst and F. Koller, *Helv. Chim. Acta.*, 30 (1947) 1454–1460.
[10] G. Palumbo, C. Ferreri, and R. Caputo, *Tetrahedron Lett.*, 24 (1983) 1307–1310.
[11] S. Colin-Messager, J.P. Girard, and J.C. Rossi, *Tetrahedron Lett.*, 33 (1992) 2689–2692.
[12] G. Hodosi, B. Podányi, and J. Kuszmann, *Carbohydr. Res.*, 230 (1992) 327–342; S. Hanessian, M.M. Ponpipom, and P. Lavallee, *ibid.*, 24 (1972) 45–56.
[13] Y. Leblanc, B.J. Fitzsimmons, J. Adams, F. Perez, and J. Rokach, *J. Org. Chem.*, 51 (1986) 789–793.
[14] J.P. Schaefer, J.C. Higgins, and P.K. Shenov, *Org. Synthesis*, 48 (1968) 51.
[15] P.J. Garegg and B. Samuelsson, *J. Chem. Soc., Perkin Trans. 1*, (1980) 2866–2869.
[16] G. Just and C. Luthe, *Can. J. Chem.*, 58 (1980) 1799–1805.