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Note

Synthesis of 1,2-anhydro-3,5,6-tri-*O*-benzyl-α-L-gulofuranose and 1,2-anhydro-3,5-di-*O*-benzyl-β-D-arabinofuranose

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1,2-Anhydro sugar derivatives are not only novel monomers for the synthesis of the corresponding stereoregular (1 → 2)-linked polysaccharides [1], but also serve as glycosyl donors in the stereospecific synthesis of nucleosides [2] and other useful carbohydrate derivatives [3]. Although numerous reports on 1,2-anhydro-pyranose derivatives have been published [4], only a few deal with 1,2-anhydro-furanose derivatives. Recently, the synthesis of 1,2-anhydro-ribo-, arabino-, and -galactofuranose derivatives was reported by Danishefsky's group [2,3] using direct epoxidation of the glycals with 3,3-dimethyl-oxirane. However, it would be difficult to isolate 1,2-anhydro-furanoses in pure form, and difficult to obtain 1,2-anhydro-furanoses having a *cis*-arrangement of the 3-hydroxy group and the epoxide ring by this method. Our group [5] has successfully synthesized 1,2-anhydro-gluco-, -xylo-, -manno-, and -lyxofuranose benzyl ethers via an intramolecular S_N2 reaction of the corresponding C-1 alkoxide with C-2 bearing a tosyloxy group. This may represent a general method for the synthesis of 1,2-anhydro-furanoses, and for the preparation of some rare, naturally occurring sugars through inversion of configuration at C-2. Here we wish to report the synthesis of 1,2-anhydro-3,5,6-tri-*O*-benzyl-α-L-gulofuranose (**5**) and 1,2-anhydro-3,5-di-*O*-benzyl-β-D-arabinofuranose (**10**) by this method.

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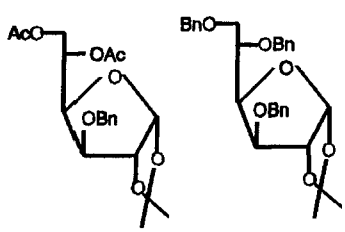
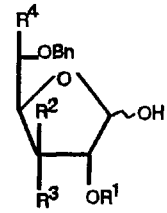
The starting material, 3,5,6-tri-*O*-benzyl-1,2-*O*-isopropylidene-β-L-idofuranose (**2**), was prepared via **1** from glucose in six steps as described previously [6]. Removal of the isopropylidene group under acidic conditions gave 3,5,6-tri-*O*-benzyl-L-idofuranose (**3**) and subsequent tosylation of **3** under phase transfer conditions afforded 3,5,6-tri-*O*-benzyl-2-*O*-toluenesulfonyl-L-idofuranose (**4**). Tosylation with pyridine–K_2CO_3–TsCl [7] was also tried, resulting in a lower yield (20%). Both **3** and **4** were obtained as anomeric mixtures. Ring closure of **4** with potassium *tert*-butoxide in THF gave the title compound (**5**) quantitatively. Compound **5** was identified from its ^{1}H NMR spectrum showing H-1 at δ 5.09 and H-2 at δ 3.41 characteristic for the epoxide ring, and from its mass spectrum showing *m/z* 432 (M^+) and *m/z* 341 ($M^+ - Bn$). Compound **5** was labile, and attempts to obtain an accurate elemental analysis were unsuccessful. Its structure was further confirmed by methanolysis, giving the corresponding methyl β-furanoside quantitatively, and by hydrolysis, giving the corresponding 1,2-diol rapidly.

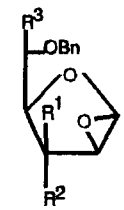


1

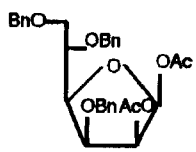
2



	R¹	R²	R³	R⁴
3	H	OBn	H	CH_2OBn
4	Ts	OBn	H	CH_2OBn
8	H	H	OBn	H
9	Ts	H	OBn	H



	R¹	R²	R³
5	OBn	H	CH_2OBn
10	H	OBn	H



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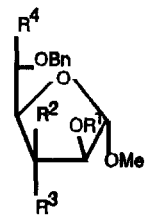

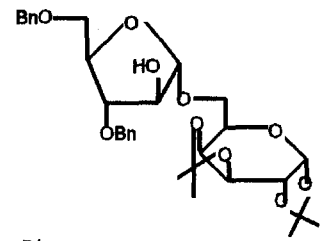

12

		R¹	R²	R³	R⁴
6		H	OBn	H	CH_2OBn
11		Ac	H	OBn	H

Tosylation of 3,5-di-*O*-benzyl-D-ribofuranose under the same phase transfer conditions as described above for **4** afforded the corresponding 2-*O*-tosylate **9** in low yield (< 20%). Increasing the tosyl chloride to 4 equiv did not improve the yield. Tosylation with 2 equiv of tosyl chloride in pyridine [7] also gave a poor yield. However, with 4 equiv of tosyl chloride in pyridine in the presence of K_2CO_3 (1.2 equiv), **9** was obtained

in satisfactory yield (78%). Treatment of **9** with potassium *tert*-butoxide in THF furnished the 1,2-anhydro arabinose ether **10** in quantitative yield. The ^{1}H NMR spectrum of **10** gave H-1 at δ 5.10 and H-2 at δ 3.41. The structure of **10** was further confirmed by methanolysis, giving the methyl α-arabinofuranoside quantitatively, and also by its coupling reaction with 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose, giving the 1,2-*trans*-linked disaccharide in high yield.

1. Experimental

General methods.—Optical rotations were determined at 20 °C with a Perkin–Elmer Model 241-MC automatic polarimeter. ^{1}H NMR spectra were recorded with a Varian XL-400 spectrometer on $CDCl_3$ solutions. Chemical shifts are given in ppm downfield from internal Me_4Si. Mass spectra were recorded with a JMS-3005 mass spectrometer, using a direct sample introduction technique. Thin-layer chromatography (TLC) was performed on silica gel HF with detection by charring with 30% (v/v) H_2SO_4 in MeOH or in some cases by a UV detector. Column chromatography was conducted by elution of a column (16 × 240 mm, 18 × 300 mm, 35 × 400 mm) of silica gel (100–200 mesh) with EtOAc–petroleum ether (60–90 °C) as the eluent. Solutions were concentrated at < 60 °C under diminished pressure.

*3,5,6-Tri-*O*-benzyl-1,2-*O*-isopropylidene-β-*L*-idofuranose* (**2**).—To a solution of 5,6-di-*O*-acetyl-3-*O*-benzyl-1,2-*O*-isopropylidene-β-L-idofuranose (**1**) [6] (4.0 g, 10.2 mmol) in toluene (30 mL) was added with vigorous stirring finely powdered KOH (22 g), and the mixture was boiled under reflux. Benzyl chloride (12 mL, 102 mmol) was added dropwise within 20 min. The reaction was carried out under reflux and vigorous agitation for 3 h, at the end of which time TLC (1:3 EtOAc–petroleum ether) indicated that the reaction was complete. After cooling to room temperature, the reaction mixture was extracted with toluene, and the organic layer was dried over Na_2SO_4 and concentrated to a syrup. Purification of the product was effected by column chromatography on silica gel with 1:3 EtOAc–petroleum ether as the eluent to give **2** (4.88 g, 98%) as a syrup; $[\alpha]_D$ −41.3° (*c* 1.6, $CHCl_3$); ^{1}H NMR: δ 7.37–7.20 (m, 15 H, Ph), 5.97 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1), 4.81, 4.68 (2 d, 2 H, *J* 11.9 Hz, CH_2Ph), 4.58 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-2), 4.53, 4.50 (2 d, 2 H, *J* 12.6 Hz, CH_2Ph), 4.41 (dd, 1 H, $J_{3,4}$ 3.7, $J_{4,5}$ 7.5 Hz, H-4), 4.35, 4.20 (2 d, 2 H, *J* 11.6 Hz, CH_2Ph), 3.92 (m, 1 H, $J_{4,5}$ 7.5, $J_{5,6}$ 3.1, $J_{5,6'}$ 5.0 Hz, H-5), 3.87 (d, 1 H, $J_{3,4}$ 3.7 Hz, H-3), 3.54 (dd, 1 H, $J_{5,6}$ 3.1, $J_{6,6'}$ 10.0 Hz, H-6), 3.47 (dd, 1 H, $J_{5,6'}$ 5.0, $J_{6,6'}$ 10.0 Hz, H-6'), 1.51, 1.33 (2 s, 6 H, CH_3). Anal. Calcd for $C_{30}H_{34}O_6$: C, 73.44; H, 6.95. Found: C, 73.37; H, 6.98.

*3,5,6-Tri-*O*-benzyl-L-idofuranose* (**3**) *and its acetate.*—To a solution of compound **2** (1.8 g, 3.7 mmol) in 1,4-dioxane (10 mL) was added M H_2SO_4 (1 mL). The mixture was boiled under reflux with stirring for 2 h, at the end of which time TLC (1:3 EtOAc–petroleum ether) showed that hydrolysis was complete. The mixture was neutralized with $NaHCO_3$, and the solvent was evaporated to give a syrup that was partitioned between water and dichloromethane. The organic layer was dried over Na_2SO_4, concentrated, and the product purified by column chromatography on silica gel with 1:1 EtOAc–petroleum ether as the eluent to give **3** (1.45 g, 87.5%) as a syrup. Since it was difficult to identify **3** from its ^{1}H NMR spectrum, **3** was acetylated with

acetic anhydride in pyridine, quantitatively giving the diacetate as an α,β mixture in a ratio of 1:3; $[\alpha]_D$ +17.1° (*c* 0.9, $CHCl_3$); ^{1}H NMR: δ 7.38–7.24 (m, 15 H, Ph), 6.41 (d, 0.75 H, $J_{1,2}$ 5.0 Hz, H-1 β), 6.17 (s, 0.25 H, H-1 α), 5.43 (t, 0.75 H, $J_{1,2}$ 5.0, $J_{2,3}$ 5.3 Hz, H-2 β), 5.26 (s, 0.25 H, H-2 α), 4.80–4.44 (m, 6 H, CH_2Ph), 4.50 (d, 0.75 H, $J_{3,4}$ 6.4 Hz, H-4 β), 4.47 (d, 0.25 H, $J_{3,4}$ 2.0 Hz, H-4 α), 4.31 (d, 0.25 H, $J_{3,4}$ 2.0 Hz, H-3 α), 4.26 (t, 0.75 H, $J_{2,3}$ 5.3, $J_{3,4}$ 6.4 Hz, H-3 β), 3.90–3.95 (m, 0.25 H, H-5 α), 3.90–3.80 (m, 0.75 H, H-5 β), 3.49–3.65 (m, 2 H, H-6,6′), 2.06 (s, 2.25 H, CH_3CO β), 2.04 (s, 0.75 H, CH_3CO α), 1.98(s, 0.75 H, CH_3CO α), 1.97 (s, 2.25 H, CH_3CO β). Anal. Calcd for $C_{31}H_{34}O_8$: C, 69.64; H, 6.42. Found: C, 69.54; H, 6.71.

3,5,6-Tri-O-*benzyl*-2-O-*toluenesulfonyl*-L-*idofuranose* (**4**).—To a solution of **3** (1.0 g, 3.5 mmol) in dichloromethane (25 mL) was added tetrabutylammonium hydrogensulfate (TBAHS) (100 mg, 0.3 mmol), 5% NaOH (7.5 mL), and tosyl chloride (700 mg, 4.6 mmol). The mixture was stirred for about 24 h at room temperature and then diluted with dichloromethane and washed with cold water. The organic phase was dried over Na_2SO_4, evaporated, and the product was purified by column chromatography on silica gel with 1:3 EtOAc–petroleum ether as the eluent. Compound **4** was obtained as an α,β mixture (960 mg, 71%) in a ratio of 1:1.3, and residual starting material (270 mg) was recovered; $[\alpha]_D$ −3.8° (*c* 1.3, $CHCl_3$); ^{1}H NMR: δ 7.70 (d, 2 H, *Ph* of Ts), 7.37–7.25 (m, 17 H, Ph), 4.86 (s, 0.57 H, H-1 β), 4.83 (s, 0.43 H, H-1 α), 4.70, 4.65 (2 d, 2 H, *J* 10.8 Hz, CH_2Ph), 4.58, 4.49 (2 d, 2 H, *J* 10.8 Hz, CH_2Ph), 4.50 (s, 0.57 H, H-2 β), 4.49 (s, 0.43 H, H-2 α), 4.48 (s, 2 H, CH_2Ph), 4.41 (dd, 1 H, $J_{3,4}$ 4.6, $J_{4,5}$ 2.1 Hz, H-4), 4.32–4.30 (m, 1 H, H-3), 3.84–3.78 (m, 1 H, H-5), 3.65–3.55 (m, 2 H, H-6,6′), 2.41 (s, 3 H, CH_3 of Ts). Anal. Calcd for $C_{34}H_{36}O_8S$: C, 67.52; H, 6.01; S, 5.30. Found: C, 67.68; H, 6.10; S, 5.21.

1,2-Anhydro-3,5,6-tri-O-*benzyl*-α-L-*gulofuranose* (**5**).—To a solution of **4** (200 mg, 0.33 mmol) in THF (10 mL) was added potassium *tert*-butoxide (50 mg, 0.45 mmol) and the mixture was stirred at room temperature for 20 min. Concentration of the mixture gave a residue that was repeatedly extracted with 1:3 EtOAc–petroleum ether. The organic extracts were concentrated to afford **5** as a colourless syrup (140 mg, 98%); ^{1}H NMR: δ 7.39–7.22 (m, 15 H, Ph), 5.09 (s, 1 H, H-1), 4.95 (s, 1 H, H-3), 4.73, 4.67 (2 d, 2 H, *J* 10.7 Hz, CH_2Ph), 4.58, 4.52 (2 d, 2 H, *J* 11.4 Hz, CH_2Ph), 4.48, 4.42 (2 d, 2 H, *J* 11.7 Hz, CH_2Ph), 4.46 (d, 1 H, $J_{4,5}$ 2.7 Hz, H-4), 4.07 (m, 1 H, $J_{4,5}$ 2.7, $J_{5,6}$ 2.4, $J_{5,6'}$ 5.7 Hz, H-5), 3.72 (dd, 1 H, $J_{5,6}$ 2.4, $J_{6,6'}$ 10.5 Hz, H-6), 3.69 (dd, 1 H, $J_{5,6'}$ 5.7, $J_{6,6'}$ 10.5 Hz, H-6′), 3.41 (s, 1 H, H-2); MS: *m/z* 432 (M^+), 341 (M^+ − Bn).

Methanolysis of **5**.—A solution of **5** (60 mg 0.14 mmol) in anhyd MeOH (5 mL) was stirred for 1 h and methyl 3,5,6-tri-*O*-benzyl-β-L-gulofuranoside (**6**) (63 mg, 96%) was obtained; $[\alpha]_D$ +2.1° (*c* 0.8, $CHCl_3$); ^{1}H NMR: δ 7.39–7.21 (m, 15 H Ph), 4.77 (s, 1 H, H-1), 4.76, 4.65 (2 d, 2 H, *J* 11.2 Hz, CH_2Ph), 4.58 (s, 2 H, CH_2Ph), 4.52, 4.45 (2 d, 2 H, *J* 10.7 Hz, CH_2Ph), 4.47 (s, 1 H, H-2), 4,45 (d, 1 H, $J_{4,5}$ 1.5 Hz, H-4), 4.40–4.04 (m, 1 H, $J_{4,5}$ 1.5, $J_{5,6}$ 2.7, $J_{5,6'}$ 4.7 Hz, H-5), 3.80 (dd, 1 H, $J_{5,6}$ 2.7, $J_{6,6'}$ 10.2 Hz, H-6), 3.75 (dd, 1 H, $J_{5,6'}$ 4.7, $J_{6,6'}$ 10.2 Hz, H-6′), 3.75 (s, 1 H, H-3), 3.31 (s, 3 H, OCH_3). Anal. Calcd for $C_{28}H_{32}O_6$: C, 72.41; H, 6.90. Found: C, 72.56; H, 6.74.

Hydrolysis of **5**.—To a solution of **5** (50 mg, 0.12 mmol) in 4 mL of anhyd acetone was added water (1 mL). The mixture was stirred at 0 °C for 1 h to give 3,5,6-tri-*O*-benzyl-L-gulofuranose as a syrup (32 mg, 62%). In order to confirm its structure, acetylation

with acetic anhydride in pyridine was carried out quantitatively giving the sole anomer, 1,2-di-*O*-acetyl-3,5,6-tri-*O*-benzyl-α-L-gulofuranose (**7**); $[\alpha]_D$ +31.4° (*c* 1.3, $CHCl_3$); ^{1}H NMR: δ 7.44–7.23 (m, 15 H, Ph), 6.33 (d, 1 H, $J_{1,2}$ 2.7 Hz, H-1), 5.28 (dd, 1 H, $J_{1,2}$ 2.7, $J_{2,3}$ 5.1 Hz, H-2), 4.78, 4.63 (2 d, 2 H, *J* 10.5 Hz, CH_2Ph), 4.54, 4.48 (2 d, 2 H, *J* 10.5 Hz, CH_2Ph), 4.44, 4.32 (2 d, 2 H, *J* 11.0 Hz, CH_2Ph), 4.24 (d, 1 H, $J_{2,3}$ 5.1 Hz, H-3), 4.29 (d, 1 H, $J_{4,5}$ 1.0 Hz, H-4), 3.96–3.87 (m, 1 H, $J_{4,5}$ 1.0, $J_{5,6}$ 3.7, $J_{5,6'}$ 4.6 Hz, H-5), 3.59 (dd, 1 H, $J_{5,6}$ 3.7, $J_{6,6'}$ 10.3 Hz, H-6), 3.48 (dd, 1 H, $J_{5,6'}$ 4.6, $J_{6,6'}$ 10.3 Hz, H-6'), 2.09 (s, 3 H, CH_3CO), 1.97 (s, 3 H, CH_3CO). Anal. Calcd for $C_{31}H_{34}O_8$: C, 69.64; H, 6.42. Found: C, 69.42; H, 6.67.

*3,5-Di-*O*-benzyl-2-*O*-toluenesulfonyl-*D*-ribofuranose* (**9**) *and its acetate.*—To a solution of 3,5-di-*O*-benzyl-D-ribofuranose (**8**) [8] (324 mg, 1 mmol) in pyridine (10 mL) was added tosyl chloride (0.8 g, 4.2 mmol) and K_2CO_3 (170 mg, 1.2 mmol). The mixture was stirred at room temperature for about 24 h, and then poured into ice-cold water and extracted with dichloromethane (40 mL). The organic layer was washed with cold N HCl (3 × 30 mL), dried over Na_2SO_4, and concentrated. The resultant residue was purified by column chromatography on silica gel with 1:3 EtOAc–petroleum ether as the eluent, and **9** (410 mg, 78%) was obtained as a syrupy α,β mixture which did not yield an interpretable ^{1}H NMR spectrum. Thus **9** was acetylated with acetic anhydride in pyridine, quantitatively giving the corresponding 1-acetate as a β anomer exclusively; $[\alpha]_D$ +46.8° (*c* 5.0, $CHCl_3$); ^{1}H NMR: δ 7.82–7.69 (d, 2 H, *Ph* of Ts), 7.40–7.20 (m, 12 H, Ph), 6.03 (s, 1 H, H-1), 5.00 (d, 1 H, $J_{2,3}$ 4.2 Hz, H-2), 4.58, 4.37 (2 d, 2 H, *J* 11.5 Hz, CH_2Ph), 4.50, 4.41 (2 d, 2 H, *J* 11.7 Hz, CH_2Ph), 4.28 (d, 1 H, $J_{2,3}$ 4.2 Hz, H-3), 4.22 (dd, 1 H, $J_{4,5}$ 2.7, $J_{4,5'}$ 3.4 Hz, H-4), 3.65 (dd, 1 H, $J_{4,5}$ 2.7, $J_{5,5'}$ 11.2 Hz, H-5), 3.48 (dd, 1 H, $J_{4,5'}$ 3.4, $J_{5,5'}$ 11.2 Hz, H-5), 2.40 (s, 3 H, CH_3 of Ts), 1.83 (s, 3 H, CH_3CO). Anal. Calcd for $C_{28}H_{30}O_8S$: C, 63.88; H, 5.70. Found: C, 63.46; H, 6.00.

*1,2-Anhydro-3,5-di-*O*-benzyl-β-*D*-arabinofuranose* (**10**).—To a solution of **9** (100 mg, 0.19 mmol) in THF (5 mL) was added potassium *tert*-butoxide (26 mg, 0.22 mmol) and the mixture was stirred at room temperature for 20 min. Concentration of the mixture gave a residue that was repeatedly extracted with 1:3 EtOAc–petroleum ether. Evaporation of the solvents from the combined supernatant and washings afforded **10** as a colourless syrup (56.9 mg, 96%); ^{1}H NMR: δ 7.48–7.12 (m, 10 H, Ph), 5.10 (s, 1 H, H-1), 4.58, 4.49 (2 d, 2 H, *J* 11.2 Hz, CH_2Ph), 4.56, 4.50 (2 d, 2 H, *J* 11.6 Hz, CH_2Ph), 4.44–4.40 (m, 1 H, H-4), 4.06 (d, 1 H, $J_{3,4}$ 2.4 Hz, H-3), 3.86 (dd, 1 H, $J_{4,5}$ 5.0, $J_{5,5'}$ 11.0 Hz, H-5), 3.67 (dd, 1 H, $J_{4,5'}$ 4.0, $J_{5,5'}$ 11.0 Hz, H-5), 3.41 (s, 1 H, H-2); MS: *m/z* 312 (M^+), 221 ($M^+ - Bn$).

Methanolysis of **10**.—Methanolysis of **10** (50 mg, 0.16 mmol) with MeOH followed by acetylation gave methyl 2-*O*-acetyl-3,5-di-*O*-benzyl-α-D-arabinofuranoside (**11**) quantitatively; $[\alpha]_D$ +5.8° (*c* 2.5, $CHCl_3$); ^{1}H NMR: δ 7.22–7.18 (m, 10 H, Ph), 5.08 (s, 1 H, H-2), 4.91 (s, 1 H, H-1), 4.72, 4.58 (2 d, 2 H, *J* 11.8 Hz, CH_2Ph), 4.52 (s, 2 H, CH_2Ph), 4.40 (d, 1 H, $J_{3,4}$ 5.0 Hz, H-3), 4.20 (m, 1 H, $J_{3,4}$ 5.0, $J_{4,5}$ 2.5, $J_{4,5'}$ 6.2 Hz, H-4), 3.80 (dd, 1 H, $J_{4,5}$ 2.5, $J_{5,5'}$ 10.5 Hz, H-5), 3.58 (dd, 1 H, $J_{4,5'}$ 6.2, $J_{5,5'}$ 10.5 Hz, H-5'), 3.40 (s, 3 H, OCH_3), 2.00 (s, 3 H, CH_3CO). Anal. Calcd for $C_{22}H_{26}O_6$: C, 68.39; H, 6.74. Found: C, 68.44; H, 6.64.

*O-(3,5-Di-*O*-benzyl-α-*D*-arabinofuranosyl)-(1 → 6)-1,2:3,4-di-*O*-isopropylidene-α-*D*-galactopyranose* (**12**).—The 1,2-anhydro sugar **10** (130 mg, 0.42 mmol) was dissolved

in anhyd dichloromethane (6 mL) containing 4 Å molecular sieves (1.0 g). To the mixture was added a solution of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (130 mg, 0.5 mmol) in dichloromethane (1.5 mL) in one portion. The mixture was stirred at room temperature for 2 h, at the end of which time (1:2 EtOAc–petroleum ether) **10** had disappeared. The solution was concentrated to a syrup which was subjected to column chromatography on silica gel with 1:2 EtOAc–petroleum ether as the eluent. Compound **12** was obtained as a syrup (202 mg, 85%); $[\alpha]_D$ −2.0° (*c* 2.0, $CHCl_3$); ^1H NMR: δ 7.40–7.20 (m, 10 H, Ph), 5.50 (d, 1 H, $J_{1,2}$ 4.6 Hz, H-1), 4.96 (s, 1 H, H-1′), 4.64, 4.53 (2 d, 2 H, *J* 12.1 Hz, CH_2Ph), 4.60, 4.48 (2 d, 2 H, *J* 11.7 Hz, CH_2Ph), 4.58 (dd, 1 H, $J_{2,3}$ 2.1, $J_{3,4}$ 7.6 Hz, H-3), 4.43 (dd, 1 H, $J_{2',3'}$ 3.5, $J_{3',4'}$ 6.7 Hz, H-3′), 4.37–4.28 (m, 3 H, H-2,2′,4′), 4.24 (dd, 1 H, $J_{3,4}$ 7.6, $J_{4,5}$ 1.5 Hz, H-4), 4.15–4.10 (m, 1 H, H-5), 4.00–3.90 (m, 2 H, H-5′,6), 3.88–3.60 (m, 2 H, H-5″,6′), 1.51, 1.40, 1.37, 1.35 (4 s, 12 H, CCH_3). Anal. Calcd for $C_{31}H_{40}O_{10}$: C, 65.03; H, 6.99. Found: C, 65.22; H,6.83.

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