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SYNTHESIS OF METHYL 2-*O*-, 3-*O*-, AND 5-*O*-β-D-RIBOFURANOSYL-β-D-RIBOFURANOSIDE *via* 1,2-*O*-CYANOETHYLIDENE DERIVATIVES OF D-RIBOFURANOSE

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ABSTRACT

Triphenylmethylium perchlorate-catalyzed glycosylation of 2-, 3- and 5-trityl ethers of methyl β-D-ribofuranoside by 1,2-*O*-cyanoethylidene derivatives of D-ribofuranose gave good yields of the corresponding 1,2-*trans*-linked disaccharide derivatives. The structural assignments of the deprotected disaccharides were confirmed by ^{1}H-n.m.r.- and ^{13}C-n.m.r. spectroscopy.

INTRODUCTION

As an approach towards the chemical synthesis of oligo- and poly-saccharides, the reaction of 1,2-*O*-(1-cyanoethylidene) derivatives of hexopyranoses and various furanoses with trityl ethers in the presence of catalytic amounts of triphenylmethylium ions, leading to the stereoselective formation of 1,2-*trans*-glycosidic bonds, has been extensively used[1–6]. In a study of the preparation of 1,3- and 1,5-β-D-ribofuranans, we have synthesized methyl 2-*O*-, 3-*O*-, and 5-*O*-β-D-ribofuranosyl-β-D-ribofuranoside, as model compounds, by use of 1,2-*O*-(1-cyanoethylidene) derivatives of D-ribofuranose.

RESULTS AND DISCUSSION

Reaction of known[7,8] 1,2,3-tri-*O*-acetyl-5-*O*-benzoyl-β-D-ribofuranose (**1**) with cyanotrimethylsilane in the presence of stannous chloride[9,10] gave a 96% yield of a 2:1 mixture of the 1,2-*O*-(*exo*- and *endo*-1-cyanoethylidene) derivatives **2** and **3**, which were separated by column chromatography on silica gel. The configuration of C-2 in the dioxolane ring was based on the different chemical shifts of the CH_3 groups in the ^{1}H-n.m.r. spectra. In agreement with reported ^{1}H-n.m.r. data of 1,2-

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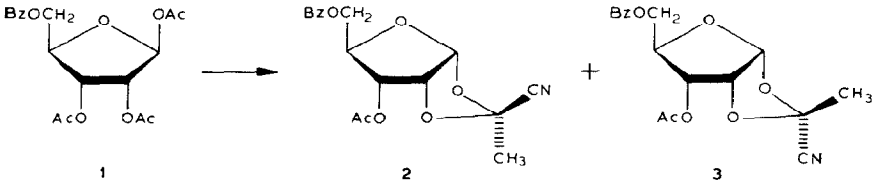
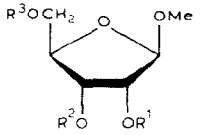
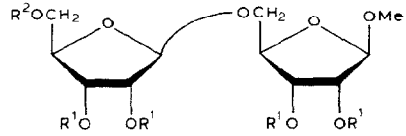


1 2 3

O-cyanoethylidene derivatives of furanoses[11], the signal attributable to the *endo*-CH_3-group of **2** was observed at δ 1.90, whereas the corresponding signal of the *exo*-group was shifted upfield to δ 1.81.

The trityl ether **5** was prepared from previously described[12] methyl 5-*O*-trityl-β-D-ribofuranoside (**4**) by reaction with acetic anhydride–pyridine in 98% yield. Tritylation of known[13] methyl 5-*O*-benzoyl-β-D-ribofuranoside (**6**) with triphenylmethylium perchlorate–2,4,6-trimethylpyridine[2] in dichloromethane afforded the 2-trityl ether **7** (36% yield) and 3-trityl ether **8** (25% yield), which were separated





4 $R^1 = R^2 = H, R^3 = Tr$
5 $R^1 = R^2 = Ac, R^3 = Tr$
6 $R^1 = R^2 = H, R^3 = Bz$
7 $R^1 = Tr, R^2 = H, R^3 = Bz$
8 $R^1 = H, R^2 = Tr, R^3 = Bz$
9 $R^1 = Tr, R^2 = Ac, R^3 = Bz$
10 $R^1 = Ac, R^2 = Tr, R^3 = Bz$

11 $R^1 = Ac, R^2 = Bz$
12 $R^1 = R^2 = H$

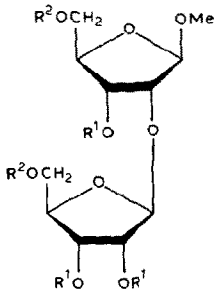
by column chromatography on silica gel. The structures of the isomers were established on the basis of their ^{1}H-n.m.r. spectra. After deuterium exchange, the signal attributable to H-3 in compound **7** was observed as a doublet of doublets at δ 3.61, whereas the signal of H-2 in compound **8** appeared as a doublet at δ 2.83. Acetylation of the isomers gave the corresponding 3-*O*-acetyl (**9**) and 2-*O*-acetyl (**10**) derivatives, respectively.

The disaccharide syntheses were performed essentially under the conditions described by Kochetkov *et al.*[3]. Thus, reaction of **5** with the *exo*-cyanoethylidene derivative **2** in the presence of a catalytic amount of triphenylmethylium perchlorate in dichloromethane gave the β-D-(1→5)-linked disaccharide derivative **11** in 64% yield.

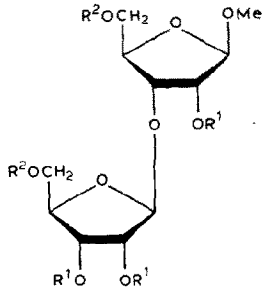
Similarly, the β-D-(1→2)- and β-D-(1→3)-linked disaccharide derivatives **13** and **15** were obtained by reaction of **10** and **9** with the *endo*-cyanoethylidene derivative **3** in 65 and 71% yield, respectively. The β-D-anomeric configuration of the

ribofuranosyl residues was assigned on the basis of the low values of the vicinal coupling constants ($J_{1,2}$ <1.5 Hz)[14]. By-products isolated from the reaction mixtures resulted from hydrolysis of **2** or **3**; no α-D-linked disaccharide derivatives, however, could be detected. Deacylation of **11, 13,** and **15** with methanolic sodium methoxide afforded methyl 5-*O*-β-D-ribofuranosyl-β-D-ribofuranoside (**12**) (95%), crystalline methyl 3-*O*-β-D-ribofuranosyl-β-D-ribofuranoside (**16**) (93%), and methyl 2-*O*-β-D-ribofuranosyl-β-D-ribofuranoside[15] (**14**) (87%).

The ^{13}C-n.m.r. spectrum of **14** was identical with that previously reported[16]. The ^{13}C-n.m.r.-spectra of **12** and **16** (Table I) are in agreement with the assigned structures. The observed glycosidation shifts are comparable to those observed for the *O*-alkylidation at O-2, -3, or -5 of methyl β-D-ribofuranoside[17]. In compound



13 R^1 = Ac, R^2 = Bz
14 R^1 = R^2 = H



15 R^1 = Ac, R^2 = Bz
16 R^1 = R^2 = H

TABLE I

^{13}C-CHEMICAL SHIFTS[a] (δ) OF DISACCHARIDES **12, 14, 16,** AND METHYL β-D-RIBOFURANOSIDE

Carbon atom	*Compound*			
	12	**14**	**16**	*β-D-RibfOMe*
1′	108.25	108.64	108.82	
2′	75.23	75.40	75.58	
3′	71.77	71.66	70.29	
4′	83.78	83.89	83.63	
5′	63.79	63.76	61.57	
1	108.99	107.67	108.73	108.72
2	74.94	81.31	74.63	74.97
3	72.01	71.10	79.78	71.57
4	82.16	84.12	81.83	83.62
5	70.28	63.44	63.52	63.55
MeO	56.08	56.30	55.80	55.92

[a]Downfield from the signal of Me_4Si (set at δ 67.40 upfield from the signal of 1,4-dioxane in D_2O at 298 K).

TABLE II

^{1}H-N.M.R. DATA[a] OF DISACCHARIDES **12, 14, 16,** AND METHYL β-D-RIBOFURANOSIDE

H atom	*Compound*			
	12	**14**	**16**	*β-D-RibfOMe*
1′ (1′,2′)	5.07 (s)	5.19 (1.0)	5.11 (0.8)	
2′ (2′,3′)	4.12 (4.5)	4.18 (4.5)	4.15 (4.5)	
3′ (3′,4′)	4.18 (7.0)	4.26 (7.0)	4.35 (7.5)	
4′ (4′,5a′)	4.03 (3.5)	4.05 (3.2)	4.07 (2.8)	
(4′,5b′)	(6.5)	(6.5)	(4.0)	
5a′ (5a′,5b′)	3.84 (−12.5)	3.86 (−12.0)	3.87 (−12.8)	
5b′	3.65	3.67	3.73	
1 (1,2)	4.93 (1.0)	5.11 (1.3)	4.92 (s)	4.89 (1.0)
2 (2,3)	4.05 (4.5)	4.09 (5.0)	4.17 (4.0)	4.03 (4.5)
3 (3,4)	4.23 (7.0)	4.27 (7.0)	4.13 (7.2)	4.15 (7.0)
4 (4,5a)	4.13 (2.5)	4.00 (3.5)	4.08 (3.0)	4.00 (3.2)
(4,5b)	(7.0)	(6.5)	(6.0)	(6.3)
5a (5a,5b)	3.98 (−11.0)	3.81 (−12.5)	3.81 (−12.2)	3.79 (−12.2)
5b	3.56	3.62	3.62	3.60
MeO	3.41	3.42	3.40	3.39

[a] ^{1}H-N.m.r. chemical shifts are downfield from the signal of sodium 4,4-dimethyl-4-silapentanoate in D_2O at 298 K; couplings are in Hz (in parentheses) and are of the first order.

16, the signals of both C-3′ and C-5′ were shifted upfield. A similar effect was observed when D-ribose is linked to a *manno*-system[16] [methyl β-D-Rib*f*-(1→7)-KDO*p*OMe]. Since the three-bond H–H couplings of the ring protons are similar to those measured in **12** or **14**, these differences did not indicate a change of the ring conformation, and were indicative only of a different CH_2OH side-chain rotamer population, also visible from the H-4′–H-5a′ and H-4′–H-5b′ proton–proton coupling constants[18] (Table II).

The assignments of the ^{1}H-n.m.r. spectra were facilitated by selective-proton decoupling. In compound **12**, the signal cluster belonging to both ribosyl residues were assigned by comparison with the spectrum of methyl β-D-ribofuranoside. In compound **16**, on saturating the H-1′ signal (δ 5.11), a total n.O.e. of 40% was observed at δ 4.15 (H-2′, the connected hydrogen atom) and at δ 4.13 (H-3, the interglycosidic neighbor hydrogen atom), thus confirming the assignment. In compound **14**, on saturation of the H-1 signal (δ 5.11), an n.O.e. of 5% was observed at δ 4.09 (H-2, the connected hydrogen atom) and one of 3% at δ 3.42 (the methyl signal), again confirming the assignment.

EXPERIMENTAL

General methods. — Melting points were determined with a Kofler hot-stage and are uncorrected. Optical rotations were measured with a Perkin–Elmer 141

polarimeter. ^{1}H-N.m.r. spectra were recorded with a Bruker WM-250 instrument at 298 K using tetramethylsilane as the internal standard for solutions in (^{2}H)chloroform. Coupling constants are of first order. ^{1}H-N.O.e. difference-spectra were measured for solutions in deuterium oxide. Proton-decoupled ^{13}C-n.m.r. spectra were recorded at 62.9 MHz for solutions in deuterium oxide at 298 K using 32 K of memory and a spectral width of 12 kHz. Chemical shifts (δ) are given from the signal of tetramethylsilane whose resonance frequency was set at δ 67.40 upfield from an external signal of 1,4-dioxane in deuterium oxide. T.l.c. was performed on Merck precoated plates (5 × 10 cm, layer-thickness 0.25 mm, Silica Gel 60 F_{254}). Spots were detected by u.v. light and by spraying with an anisaldehyde–H_2SO_4 reagent[19]. Column chromatography was performed on Merck-Lichroprep columns (size *A*, 24 × 1; *B*, 31 × 2.5; and *C*, 44 × 3.7 cm; silica gel 40–63 μm) under pressure (0.2 MPa). Acetonitrile was distilled twice from P_2O_5, dichloromethane was distilled twice from CaH_2, and nitromethane was dried over molecular sieves 3A and distilled twice from CaH_2 prior to use. Triphenylmethylium perchlorate was synthesized as described and further purified[3] when used as a catalyst for glycosylation. Solutions were concentrated *in vacuo* at 40°. Elemental analyses were performed by Dr. J. Zak, Mikroanalytisches Laboratorium am Institut für Physikalische Chemie, Universität Wien.

3-O-Acetyl-5-O-benzoyl-1,2-O-[(1-exo- and 1-exo-cyano)ethylidene]-α-D-ribofuranose (**2** *and* **3**). — Cyanotrimethylsilane (3.1 mL, 25 mmol) was added to a suspension of 1,2,3-tri-*O*-acetyl-5-*O*-benzoyl-β-D-ribofuranose (**1**) (3.17 g, 8.3 mmol) and anhydrous $SnCl_2$ (1.5 g) in dry acetonitrile (10 mL) under N_2 at room temperature. The mixture was stirred for 40 min, diluted with dichloromethane (50 mL), and extracted with saturated aqueous $NaHCO_3$. The organic layer was dried ($MgSO_4$) and evaporated. The residue was purified on a column of silica gel (*C*, 10:1 toluene–ethyl acetate). Pooling and evaporation of the fractions containing the faster-moving component gave **2** (1.76 g, 61%), colorless needles, m.p. 74–75° (ethyl acetate–hexane), $[\alpha]_D^{20}$ +88° (*c* 1.0, chloroform); ^{1}H-n.m.r.: δ 8.08–8.03 (m, 2 H) and 7.64–7.43 (m, 3 H, arom. H), 6.06 (d, 1 H, $J_{1,2}$ ~4.0 Hz, H-1), 5.06 (dd, 1 H, $J_{2,3}$ ~5.0 Hz, H-2), 4.84 (dd, 1 H, $J_{3,4}$ ~9.0 Hz, H-3), 4.67 (dd, 1 H, $J_{5a,5b}$ ~12.5, $J_{5a,4}$ ~3.0 Hz, H-5a), 4.41 (dd, 1 H, $J_{5b,4}$ ~4.5, H-5b), 3.97 (ddd, 1 H, H-4), 2.12 (s, 3 H, CH_3CO), and 1.90 (s, 3 H, *endo*-CH_3).

Anal. Calc. for $C_{17}H_{17}NO_7$: C, 58.79; H, 4.93; N, 4.03. Found: C, 59.07; H, 4.92; N, 4.02.

Further elution of the column gave **3** (yield 956 mg, 33%), colorless syrup, $[\alpha]_D^{20}$ +164° (*c* 1.4, chloroform); ^{1}H-n.m.r.: δ 8.07–8.02 (m, 2 H) and 7.63–7.43 (m, 3 H arom.), 6.03 (d, 1 H, $J_{1,2}$ ~4.0 Hz, H-1), 5.05 (dd, 1 H, $J_{2,3}$ ~5.5 Hz, H-2), 4.89 (dd, 1 H, $J_{3,4}$ ~8.5 Hz, H-3), 4.82 (ddd, 1 H, $J_{5a,4}$ ~3.0, $J_{5b,4}$ ~4.0 Hz, H-4), 4.66 (dd, 1 H, $J_{5a,5b}$ ~12.5 Hz, H-5a), 4.44 (dd, 1 H, H-5b), 2.19 (s, 3 H, CH_3CO), and 1.81 (s, 3 H, *exo*-CH_3).

Anal. Calc. for $C_{17}H_{17}NO_7$: C, 58.79; H, 4.93; N, 4.03. Found: C, 58.82; H, 4.85; N, 4.01.

*Methyl 2,3-di-*O*-acetyl-5-*O*-trityl-β-*D*-ribofuranoside* (**5**). — A solution of acetic anhydride (1 mL) in pyridine (3 mL) was added to a solution of **4** (716 mg) in pyridine (5 mL) at 0°. After being stirred for 16 h, the mixture was taken to dryness. The residue was dissolved in dichloromethane (50 mL), extracted with saturated aqueous $NaHCO_3$, dried ($MgSO_4$), and evaporated. Purification of the residue on a column of silica gel (*B*, 4:1 toluene–ethyl acetate) afforded **5**, 850 mg (98%), colorless syrup, $[\alpha]_D^{20}$ −6.5° (*c* 0.26, chloroform); ^{1}H-n.m.r.: δ 7.59–7.21 (m, 15 H, arom.), 5.42 (dd, 1 H, $J_{3,4}$ ~8.0, $J_{3,2}$ ~5.0 Hz, H-3), 5.28 (dd, 1 H, $J_{1,2}$ ~1.5 Hz, H-2), 4.95 (d, 1 H, H-1), 4.29 (ddd, 1 H, $J_{4,5a}$ ~4.5, $J_{4,5b}$ ~6.0 Hz, H-4), 3.38 (s, 3 H, OCH_3), 3.38–3.23 (m, 2 H, H-5a,5b), 2.12 and 2.02 (s, 6 H, 2 CH_3CO).

Anal. Calc. for $C_{29}H_{30}O_7$: C, 71.00; H, 6.16. Found: C, 70.67; H, 6.37.

*Methyl 5-*O*-benzoyl-2-*O*-trityl-β-*D*-ribofuranoside* (**7**) *and methyl 5-*O*-benzoyl-3-*O*-trityl-β-*D*-ribofuranoside* (**8**). — Triphenylmethylium perchlorate (2 g) was added in portions to a solution of **6** (835 mg, 3.1 mmol) and 2,4,6-trimethylpyridine (0.83 mL) in dry dichloromethane (10 mL). After being stirred for 4 h at room temperature, the mixture was diluted with dichloromethane (50 mL), washed with saturated aqueous $NaHCO_3$, dried ($MgSO_4$), and evaporated. Purification of the residue on a column of silica gel (60 × 2.5 cm; 5:1 toluene–ethyl acetate) afforded **7** as the faster moving component, yield 570 mg (36%), colorless syrup, $[\alpha]_D^{20}$ +17° (*c* 1.0, chloroform); ^{1}H-n.m.r.: δ 8.03–7.98 (m, 2 H, arom.), 7.57–7.43 (m, 3 H, arom.) 7.40–7.15 (m, 15 H, arom.), 4.42–4.22 (m, 3 H, H-4,5a,5b), 4.21 (dd, 1 H, $J_{2,3}$ ~5.0, $J_{2,1}$ ~2.0 Hz, H-2), 4.09 (d, 1 H, H-1), 3.61 (ddd, 1 H, $J_{3,OH}$ ~7.5, $J_{3,4}$ ~2.5 Hz, H-3), 3.12 (s, 3 H, CH_3O), and 2.61 (d, 1 H, OH).

Anal. Calc. for $C_{32}H_{30}O_6$: C, 75.27; H, 5.92; Found: C, 74.70; H, 6.07.

Further elution of the column afforded **8**, yield 394 mg (25%), colorless syrup, $[\alpha]_D^{20}$ −79° (*c* 1.2, chloroform); ^{1}H-n.m.r.: δ 8.05–7.98 (m, 2 H, arom.), 7.60–7.15 (m, 18 H, arom.), 4.71 (s, 1 H, H-1), 4.53 (ddd, 1 H, $J_{3,4}$ ~6.0, $J_{4,5}$ ~5.8, $J_{4,5a}$ ~2.5 Hz, H-4), 4.47 (dd, 1 H, $J_{5a,5b}$ ~12.5 Hz, H-5a), 4.39 (dd, 1 H, $J_{2,3}$ ~5.0 Hz, H-3), 3.96 (dd, 1 H, H-5b), 3.17 (s, 3 H, CH_3O), 2.83 (dd, 1 H, $J_{2,OH}$ ~2.5 Hz, H-2), and 2.47 (d, 1 H, OH).

Anal. Calc. for $C_{32}H_{30}O_6$: C, 75.27; H, 5.92. Found: C, 74.96; H, 6.01.

*Methyl 3-*O*-acetyl-5-*O*-benzoyl-2-*O*-trityl-β-*D*-ribofuranoside* (**9**). — A solution of **7** (570 mg), 4-dimethylaminopyridine (5 mg), and acetic anhydride (0.6 mL) in dry pyridine (5 mL) was stirred for 2 h at room temperature. The mixture was processed as described for **10** to give **9** (591 mg, 96%), colorless syrup, $[\alpha]_D^{20}$ +36° (*c* 2.7, chloroform); ^{1}H-n.m.r.: δ 8.07–8.02 (m, 2 H, arom.), 7.85–7.23 (m, 18 H, arom.), 4.97 (dd, 1 H, $J_{3,4}$ ~6.0, $J_{2,3}$ ~5.0 Hz, H-3), 4.57 (ddd, 1 H, $J_{4,5}$ ~4.5 Hz, H-4), 4.51 (dd, 1 H, $J_{5a,5b}$ ~11.5, $J_{5a,4}$ ~4.0 Hz, H-5a), 4.32 (dd, 1 H, H-5b), 4.23 (dd, 1 H, $J_{1,2}$ ~1.5 Hz, H-2), 3.85 (d, 1 H, H-1), 3.03 (s, 3 H, CH_3O), and 2.08 (s, 3 H, CH_3CO).

Anal. Calc. for $C_{34}H_{32}O_7$: C, 73.90; H, 5.84. Found: C, 73.47; H, 6.05.

*Methyl 2-*O*-acetyl-5-*O*-benzoyl-3-*O*-trityl-β-*D*-ribofuranoside* (**10**). — A solu-

tion of **8** (352 mg) in dry pyridine (5 mL) was treated with acetic anhydride (0.35 mL) for 2.5 h. The mixture was evaporated to dryness. The residue was dissolved in dichloromethane (40 mL), washed with saturated aqueous $NaHCO_3$, dried ($MgSO_4$), and evaporated. Purification of the residue on a column of silica gel (*B*, 2:1 toluene–ethyl acetate) afforded **10** (368 mg, 97%), colorless syrup, $[\alpha]_D^{20}$ −49° (*c* 1.0, chloroform); ^{1}H-n.m.r.: δ 7.99–7.95 (m, 2 H, arom.), 7.60–7.15 (m, 18 H, arom.), 4.67 (s, 1 H, H-1), 4.56–4.48 (m, 2 H, H-2,4), 4.39 (dd, 1 H, $J_{4,5a}$ ~1.5, $J_{5a,5b}$ ~ −12.0 Hz, H-5a), 4.02 (dd, 1 H, $J_{3,4}$ ~1.5, $J_{3,2}$ ~3.5 Hz, H-3), 3.87 (dd, 1 H, $J_{5b,4}$ ~4.5 Hz, H-5b), 3.14 (s, 3 H, CH_3O), and 2.18 (s, 3 H, CH_3CO).

Anal. Calc. for $C_{34}H_{32}O_7$: C, 73.90; H, 5.84. Found: C, 73.64; H, 6.15.

*Methyl 2,3-di-*O*-acetyl-5-*O*-(2,3-di-*O*-acetyl-5-*O*-benzoyl-β-*D*-ribofuranosyl)-β-*D*-ribofuranoside* (**11**). — In one limb of a tuning-fork-shaped tube, a solution of **5** (320 mg, 0.58 mmol) and **2** (243 mg, 0.7 mmol) in dichloromethane (2 mL) was placed, in the other limb a solution of triphenylmethylium perchlorate (20 mg, 0.06 mmol) in dichloromethane (1 mL). Nitromethane (2 mL) was twice distilled into, and lyophilized from the limb with reagents followed by drying for 3 h *in vacuo* (0.06 Pa). Dichloromethane (2 mL) was distilled into both limbs of the tube, and the solutions were mixed and kept overnight at room temperature with exclusion of light. The mixture was treated with pyridine (2 mL), diluted with dichloromethane (50 mL), and washed with saturated aqueous $NaHCO_3$. The organic layer was dried and evaporated. Purification of the residue on a column of silica gel (60 × 2.5 cm; 4:1 toluene–ethyl acetate) gave **11** (136 mg, 64%), colorless syrup, $[\alpha]_D^{20}$ −32° (*c* 1.1, chloroform); ^{1}H-n.m.r.: δ 8.10–8.05 (m, 2 H, arom.), 7.63–7.42 (m, 3 H, arom.), 5.51 (dd, 1 H, $J_{2',3'}$ ~5.0, $J_{3',4'}$ ~6.5 Hz, H-3'), 5.37 (d, 1 H, H-2'), 5.24 (dd, 1 H, $J_{2,3}$ ~5.0, $J_{3,4}$ ~7.0 Hz, H-3), 5.17 (dd, 1 H, $J_{1,2}$ ~1.0 Hz, H-2), 5.14 (s, 1 H, H-1'), 4.88 (s, 1 H, H-1), 4.60–4.41 (m, 3 H, H-4',5'a,5'b), 4.23 (ddd, 1 H, $J_{4,5a}$ ~3.5, $J_{4,5b}$ ~7.0 Hz, H-4), 3.89 (dd, 1 H, $J_{5a,5b}$ ~11.0 Hz, H-5a), 3.54 (dd, 1 H, H-5b), 3.37 (s, 1 H, CH_3O), 2.13, 2.09, 2.03, and 1.99 (s, 12 H, 4 CH_3CO).

Anal. Calc. for $C_{26}H_{32}O_{14}$: C, 54.93; H, 5.67. Found: C, 54.94; H, 5.67.

*Methyl 5-*O*-β-D-ribofuranosyl-β-D-ribofuranoside* (**12**). — A solution of **11** (70.8 mg) in dry methanol (5 mL) was stirred with 0.1M methanolic sodium methoxide (1 mL) for 12 h at room temperature. The mixture was made neutral by addition of Dowex 50 (H^+) cation-exchange resin, filtered, and evaporated. The residue was extracted with diethyl ether (3 × 5 mL) and dried to give **12**, yield 35 mg (95%), colorless syrup, $[\alpha]_D^{20}$ −23.5° (*c* 1.5, water); ^{1}H-n.m.r. and ^{13}C-n.m.r., see Tables I and II.

*Methyl 3-*O*-acetyl-5-*O*-benzoyl-2-*O*-(2,3-di-*O*-acetyl-5-*O*-benzoyl-β-*D*-ribofuranosyl)-β-*D*-ribofuranoside* (**13**). — This compound was prepared from **9** (320 mg, 0.58 mmol) and **3** (243 mg, 0.70 mmol) as described for **11**; purification of the residue on a column of silica gel (60 × 2.5 cm; 4:1 toluene–ethyl acetate) gave **13**, yield 260 mg (71%), colorless syrup, $[\alpha]_D^{20}$ +10° (*c* 0.6, chloroform); ^{1}H-n.m.r.: δ 8.13–8.05 (m, 4 H, arom), 7.61–7.41 (m, 6 H, arom.), 5.44' (dd, 1 H, $J_{3',4'}$ ~7.0, $J_{3',2'}$ ~5.0 Hz, H-3'), 5.31 (dd, 1 H, $J_{1',2'}$ ~1.0 Hz, H-2'), 5.17 (dd, $J_{2,3}$ ~5.0, $J_{3,4}$

~7.0 Hz, H-3), 5.08 (d, 1 H, H-1'), 5.00 (s, 1 H, H-1), 4.60–4.30 (m, 7 H, H-2,4,5a,5b,4',5'a,5'b), 3.22 (s, 3 H, CH_3O), 2.12, 2.11, and 2.05 (s, 9 H, 3 CH_3CO).

Anal. Calc. for $C_{31}H_{34}O_{14}$: C, 59.05; H, 5.43. Found: C, 59.77; H, 5.34.

Methyl 2-O-β-D-ribofuranosyl-β-D-ribofuranoside (**14**). — A solution of **13** (100 mg) in dry methanol (10 mL) was stirred with 0.1M methanolic sodium methoxide for 17 h at room temperature. The mixture was made neutral by addition of Dowex 50 (H^+) cation-exchange resin, filtered, and evaporated. The residue was extracted with diethyl ether (3 × 10 mL), and the extract evaporated (yield 40 mg, 87%), colorless syrup, $[\alpha]_D^{20}$ −69° (*c* 0.85, methanol), $[\alpha]_D^{20}$ −54° (*c* 1.0, water); ^{1}H-n.m.r. and ^{13}C-n.m.r., see Tables I and II.

Methyl 2-O-acetyl-5-O-benzoyl-3-O-(2,3-di-O-acetyl-5-O-benzoyl-β-D-ribofuranosyl)-β-D-ribofuranoside (**15**). — The preparation of **15** was similar to that of **11**; **10** (275 mg) and **3** (347 mg) gave 204 mg (65%) of **15** as a colorless syrup, $[\alpha]_D^{20}$ −24° (*c* 0.85, chloroform); ^{1}H-n.m.r.: δ 8.12–8.05 (m, 4 H, arom.), 7.63–7.41 (m, 6 H, arom.), 5.36 (dd, 1 H, $J_{2',3'}$ ~5.0, $J_{3',4'}$ ~6.0 Hz, H-3'), 5.29 (dd, 1 H, $J_{1',2'}$ ~1.5 Hz, H-2'), 5.20 (d, 1 H, $J_{2,3}$ ~5.0 Hz, H-2), 5.16 (d, 1 H, H-1'), 4.84 (s, 1 H, H-1), 4.63–4.31 (m, 7 H, H-3,4,5a,5b,4',5'a,5'b), 3.31 (s, 3 H, CH_3O), 2.13, 2.08, and 2.01 (s, 9 H, 3 CH_3CO).

Anal. Calc. for $C_{31}H_{34}O_{14}$: C, 59.05; H, 5.43. Found: C, 59.79; H, 5.44.

Methyl 3-O-β-D-ribofuranosyl-β-D-ribofuranoside (**16**). — A solution of **15** (80 mg) in dry methanol (5 mL) was treated with 0.1M methanolic sodium methoxide (1 mL) for 6 h at room temperature. The mixture was made neutral by addition of Dowex 50 (H^+) cation-exchange resin, filtered, and evaporated. The residue was extracted with diethyl ether (3 × 10 mL), the extract was discarded, and the residue crystallized from methanol (yield 35 mg, 93%), colorless needles, m.p. 172–173°, $[\alpha]_D^{20}$ −67° (*c* 0.5, water); ^{1}H-n.m.r. and ^{13}C-n.m.r. see Tables I and II.

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