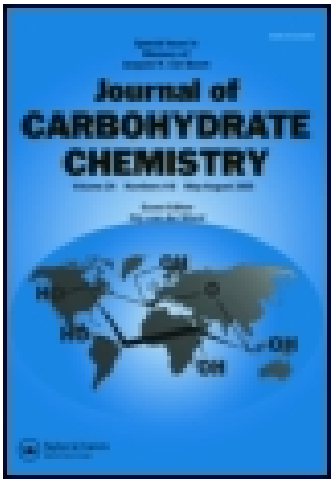


Journal of Carbohydrate Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lcar20

Syntheses and Coupling Reactions of 1,2-Anhydro-3,5-Di-O-Benzyl-α-L-Ribofuranose and 1,2-Anhydro-5-O-Benzyl-3-O-Methyl-α-L-Ribofuranose

Jun Ning [a] & Fanzuo Kong [a]
[a] Research Center for Eco-Environmental Sciences, Academia Sinica , P.O.Box 2871, Beijing, 100085, P. R. China
Published online: 19 Aug 2006.

To cite this article: Jun Ning & Fanzuo Kong (1997) Syntheses and Coupling Reactions of 1,2-Anhydro-3,5-Di-O-Benzyl-α-L-Ribofuranose and 1,2-Anhydro-5-O-Benzyl-3-O-Methyl-α-L-Ribofuranose, Journal of Carbohydrate Chemistry, 16:3, 311-325, DOI: 10.1080/07328309708006532

To link to this article: http://dx.doi.org/10.1080/07328309708006532

J. CARBOHYDRATE CHEMISTRY, 16(3), 311-325 (1997)

SYNTHESES AND COUPLING REACTIONS OF 1,2-ANHYDRO-3,5-DI-*O*-BENZYL-α-L-RIBOFURANOSE AND 1,2-ANHYDRO-5-*O*-BENZYL-3-*O*-METHYL-α-L-RIBOFURANOSE

Jun Ning and Fanzuo Kong*

Research Center for Eco-Environmental Sciences, Academia Sinica, P.O.Box 2871, Beijing 100085, P. R. China

Received August 30, 1996 - Final Form January 30, 1997

ABSTRACT

1,2-Anhydro-3,5-di-*O*-benzyl-α-L-ribofuranose (**7**) and 1,2-anhydro-5-*O*-benzyl-3-*O*-methyl-α-L-ribofuranose (**20**) were synthesized from L-arabinose via the key intermediates 3,5-di-*O*-benzyl-2-*O*-tosyl- (**5**) and 5-*O*-benzyl-3-*O*-methyl-2-*O*-tosyl-L-arabinofuranose (**18**) respectively. Condensation of the anhydro sugars with silylated uracil in the absence of catalyst gave the corresponding nucleoside derivatives with free 2'-OH in high yield. Selective glycosylation of 1,2-*O*-isopropylidene-α-D-xylofuranose with **7** afforded (1→5)-β-linked disaccharide predominantly in a good yield.

INTRODUCTION

In recent years, considerable attention has been paid to antisense oligonucleotides because such compounds are finding more and more applications in the design of chemotherapeutic agents and biochemical tools.[1] The synthesis of antisense oligonucleotides requires large quantities of L-nucleosides and L-2-deoxy-nucleosides as building blocks. In addition, L-nucleoside derivatives themselves are potential inhibitors of HIV.[2] Thus, efficient preparation of L-ribofuranose derivatives is needed.

Synthesis of L-ribofuranose derivatives, starting from D-ribono-1,4-lactone,[3] L-arabinose[4] and L-xylofuranose,[5] are extensively described in the literature. Although some of these derivatives can be obtained in a high overall yield,[6] further reactions for the preparation of L-2-deoxy-nucleosides are found to be not very satisfactory because this procedure involves nonselective and troublesome protection of the 3',5'-OH groups. These facts prompted to us to develop a new method for the synthesis of L-ribofuranose derivatives.

In our research devoted to the synthesis of 1,2-anhydrosugars and their coupling reactions, we have found that in many cases the nucleophilic opening of this class of compounds takes place via C-1 attack to give 1,2-*trans*-glycoside derivatives in high yields under mild conditions.[7] The resulting 2'-hydroxy free compounds are useful intermediates for further preparation of other derivatives. Danishefsky's group reported the synthesis of 1,2-anhydro-D-ribose derivative by oxidative conversion of the corresponding glycal with 3,3-dimethyldioxirane.[8] However a mixture of α and β 1,2-anhydrides was obtained and it could not be separated and purified until their stable nucleoside derivatives were prepared. Here we wish to report the synthesis of 1,2-anhydro-3,5-di-*O*-benzyl-α-L-ribofuranose (**7**) and 1,2-anhydro-5-*O*-benzyl-3-*O*-methyl-α-L-ribofuranose (**20**), and their coupling reaction with silylated uracil giving in high yield the corresponding nucleosides, valuable intermediates for further chemical modification at C-2.

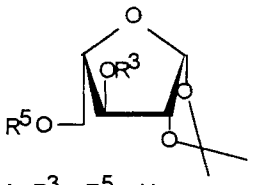
RESULTS AND DISCUSSION

The title anhydrides **7** and **20** were synthesized by "inverse ring closure"[7] of the corresponding 2-*O*-tosylates **5** and **18** respectively. Thus 1,2-*O*-isopropylidene-β-L-arabinofuranose (**1**) was prepared from L-arabinose according to the reported method.[9] Benzylation of **1** with sodium hydride and benzyl bromide in boiling oxolane yielded 3,5-di-*O*-benzyl-β-L-arabinofuranose (**2**) in 93% yield. Hydrolysis of **2** in 30% acetic acid under reflux gave 3,5-di-*O*-benzyl-L-arabinofuranose (**3**) in 90% yield as a mixture of α and β anomers. Acetylation of **3** with acetic anhydride in pyridine gave the 1,2-di-*O*-acetyl-3,5-di-*O*-benzyl-L-arabinofuranose (**4**) as an anomeric mixture in quantitative yield, which was separated by analytical LC and identified by ^{1}H NMR spectrometry.

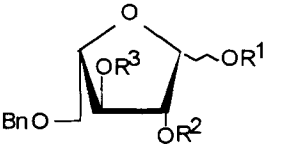
The key intermediate 3,5-di-*O*-benzyl-2-*O*-tosyl-L-arabinofuranose (**5**) was prepared from the reaction of **3** with tosyl chloride in anhydrous pyridine in the presence of potassium carbonate at 0 °C as an anomeric mixture in 60.5% yield. The pure α isomer was obtained by analytical LC, but a neat ^{1}H NMR spectrum was not obtained because of anomerization during the determination in $CDCl_3$. Acetylation of **5** with acetic anhydride in pyridine afforded 1-*O*-acetyl-3,5-di-*O*-benzyl-2-*O*-tosyl-L-arabinofuranose (**6**) quantitatively as an anomeric mixture. Ring closure of **5** with potassium *tert*-butoxide in dry oxolane quantitatively gave syrupy 1,2-anhydro-3,5-di-*O*-benzyl-α-L-ribofuranose (**7**) within 10 min. Compound **7** was very sensitive to protic solvents, and attempts to obtain an accurate elemental analysis were unsuccessful. However, **7** was characterized via ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum of compound **7** showed an upfield peak for H-2 at δ 3.58 ppm, which is the salient feature for the 1,2-epoxide ring of carbohydrate compounds.[10] Further verification of the structure was performed by alcoholysis of **7** in dry MeOH at room temperature, quantitatively giving methyl 3,5-di-*O*-benzyl-β-L-ribofuranoside (**8**). The structure of **8** was confirmed from the ^{1}H NMR spectrum of its acetylated derivative **9**. Reaction of the epoxide with silylated uracil in the absence of Lewis acid provided a mixture of **10** (60%) and **11** (26%) in a total yield of 86%. Compound **10** was unstable and easily converted to **11** under weakly acidic conditions. No evidence of the other anomer was found using analytical LC or ^{1}H NMR methods. Compound **11** with a free C-2 OH can be used for further functionalization or glycosylation as an acceptor. Acetylation of **11** gave compound **12**, further confirming the structure of **11**.

Regioselective coupling of the 1,2-anhydride **7** at 5-OH of a xylofuranose acceptor having free 3-OH and 5-OH was then carried out. Reaction of **7** with 1,2-*O*-isopropylidene-α-D-xylofuranose did not occur under the same conditions as that used for the preparation of nucleoside, but with $ZnCl_2$ as the catalyst, the starting material **7** disappeared in 3 h. The resultant mixture, after being acetylated with anhydride in pyridine, was subjected to silica gel chromatography to give *O*-(2-*O*-acetyl-3,5-di-*O*-benzyl-β- and -α-L-ribofuranosyl)-(1→5)-3-*O*-acetyl-1,2-*O*-isopropylidene-α-D-xylofuranose (**13**β and **13**α, respectively) in a ratio of 6:1 with a total yield of 68%.

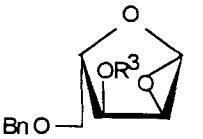
1,2-*O*-Isopropylidene-3-*O*-methyl-β-L-arabinofuranose (**14**) was prepared from L-arabinose according to the reported methods.[9] Benzylation of **14** with sodium hydride and



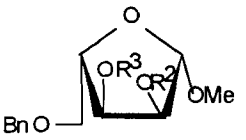
1 $R^3 = R^5 = H$
2 $R^3 = R^5 = Bn$
14 $R^3 = H$; $R^5 = Me$
15 $R^3 = Bn$; $R^5 = Me$



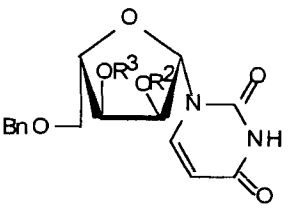
3 $R^1 = R^2 = H$; $R^3 = Bn$
4 $R^1 = R^2 = Ac$; $R^3 = Bn$
5 $R^1 = H$; $R^2 = Ts$; $R^3 = Bn$
6 $R^1 = Ac$; $R^2 = Ts$; $R^3 = Bn$
16 $R^1 = R^2 = H$; $R^3 = Me$
17 $R^1 = R^2 = Ac$; $R^3 = Me$
18 $R^1 = H$; $R^2 = Ts$; $R^3 = Me$
19 $R^1 = Ac$; $R^2 = Ts$; $R^3 = Me$



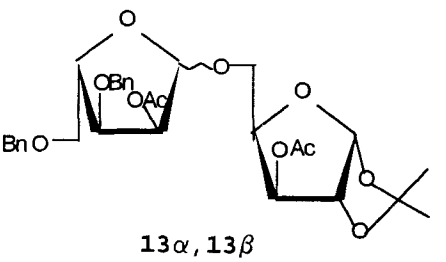
7 $R^3 = Bn$
20 $R^3 = Me$



8 $R^2 = H$; $R^3 = Bn$
9 $R^2 = Ac$; $R^3 = Bn$
21 $R^2 = H$; $R^3 = Me$
22 $R^2 = Ac$; $R^3 = Me$



10 $R^2 = TMS$; $R^3 = Bn$
11 $R^2 = H$; $R^3 = Bn$
12 $R^2 = Ac$; $R^3 = Bn$
23 $R^2 = TMS$; $R^3 = Me$
24 $R^2 = H$; $R^3 = Me$
25 $R^2 = Ac$; $R^3 = Me$



13α, **13**β

benzyl bromide in boiling oxolane afforded **15** (94%). Hydrolysis of **15** in boiling 30% acetic acid followed by tosylation with tosyl chloride in pyridine gave the 5-*O*-benzyl-3-*O*-methyl-2-*O*-tosyl-L-arabinofuranose (**18**). Ring closure of **18** under reaction conditions similar to those employed for **7** then provided the desired 1,2-anhydro compound **20** quantitatively. The structure of **20** was confirmed from its ^{1}H NMR spectrum (δ 3.70 ppm, H-2) and by methanolysis to give methyl 5-*O*-benzyl-3-*O*-methyl-β-L-ribofuranoside (**21**). Condensation of **20** with silylated uracil in the absence of Lewis acid gave a mixture of nucleosides **23** (61%) and **24** (25%), with **23** being easily converted to **24** under weakly acidic conditions. Thus we have developed a convenient method for the synthesis of L-nucleoside and 3'-*O*-methylnucleoside derivatives via the corresponding 1,2-anhydro-L-ribofuranoses which were readily prepared from L-arabinose.

EXPERIMENTAL

General methods. Melting points were determined with a "Mel-Temp" apparatus. Optical rotations were determined with a Perkin-Elmer model 241-MC automatic polarimeter for solutions in a 1dm, jacketed cell. ^{1}H NMR spectra were recorded with Varian XL-400 and XL-200 spectrometers, for solutions in $CDCl_3$ with tetramethylsilane (Me_4Si) as the internal standard. Mass spectra were recorded with a VG PLATFORM mass spectrometer using an ESI technique to introduce the sample. Analytical LC was performed with a Gilson HPLC set consisting of pump (model 306), stainless-steel columns packed with silica gel (10 x 300 mm, or 4.6 x 250 mm), a differential refractometer (132 RI detector), a UV/VI detector (model 118), and ethyl acetate-petroleum ether (bp 60-90 °C) as the eluent at a flow rate of 1-4 mL/min. Thin-layer chromatography (TLC) was performed on silica gel HF, detection being effected by charring with 30% (v/v) sulphuric acid in methanol or sometimes by UV detection. Column chromatography was conducted by elution of a column (16 x 240 mm, 18 x 300 mm, 35 x 400 mm) of silica gel (100-200 mesh). Solutions were concentrated at < 60 °C under diminished pressure.

1,2-*O*-Isopropylidene-3,5-di-*O*-benzyl-β-L-arabinofuranose (2). To a solution of 1,2-*O*-isopropylidene-β-L-arabinofuranose (**1**) (1.5 g, 7.89 mmol) in anhydrous oxolane (30 mL) was added, with vigorous stirring in an ice-cold water bath, sodium hydride

(60% in oil; 1.89 g, 47.3 mmol) and benzyl bromide (2.3 mL, 19.0 mmol). The mixture was stirred and boiled under reflux for 4 h, at the end of which time TLC (3:1 petroleum ether-EtOAc) indicated that the reaction was complete. The mixture was directly subjected to steam distillation to remove the excess benzyl bromide and by-product dibenzyl ether, and then extracted with dichloromethane. The organic layer was concentrated to a syrup that was purified by column chromatography with 4:1 petroleum ether-EtOAc to give **2** (2.72 g, 93%); $[\alpha]_D$ -10.4° (*c* 0.8, $CHCl_3$); ^1H NMR: δ 7.31 (s, 10H, 2 Ph), 5.89 (d, 1H, $J_{1,2}$ = 4.0 Hz, H-1), 4.64 (d, 1H, $J_{1,2}$ = 4.0 Hz, H-2), 4.60-4.54 (m, 4H, 2 PhC*H*$_2$), 4.26 (m, 1H, $J_{3,4}$ = 3.0 Hz, $J_{4,5}$ = 6.3 Hz, H-4), 4.02 (d, 1H, $J_{3,4}$ = 3.0 Hz, H-3), 3.63 (d, 2H, $J_{4,5}$ = 6.3 Hz, 2 H-5), 1.42, 1.33 (2s, 6H, 2 CCH_3).

Anal. Calcd for $C_{22}H_{26}O_5$: C, 71.35; H, 7.00. Found: C, 71.54; H, 7.00.

3,5-Di-*O*-benzyl-L-arabinofuranose (3). The solution of **2** (4 g, 10.8 mmol) in 30% acetic acid (100 mL) was boiled under reflux with stirring for 5 h, at the end of which time TLC (2:1 petroleum ether-EtOAc) indicated that the reaction was complete. The mixture was concentrated to a syrup that was subjected to separation by column chromatography with 2:1 petroleum ether-EtOAc as the eluent. Compound **3** was obtained as a syrupy anomeric mixture (3.21 g, 90%, α : β 1 : 1); $[\alpha]_D$ -65.1° (*c* 3.5, $CHCl_3$); ^1H NMR: δ 7.43-7.22 (m, 10H, 2 Ph), 5.29 (d, 0.5H, $J_{1,2}$ = 3.4 Hz, H-1 of β anomer), 5.22 (s, 0.5H, H-1 of α anomer), 4.75-3.40 (m, 11H, H-2,3,4,5,5', 2 PhC*H*$_2$, 2 O*H*).

Anal. Calcd for $C_{19}H_{22}O_5$: C, 69.09; H, 6.67. Found: C, 69.23; H, 6.61.

1,2-Di-*O*-acetyl-3,5-di-*O*-benzyl-L-arabinofuranose(4). Acetylation of **3** (120 mg, 0.36 mmol) with acetic anhydride (4.5 mL) in pyridine (6 mL) at room temperature for 4 h gave compound **4** in a quantitative yield as a syrupy α:β mixture (2:1). The pure samples of α and β isomer could be separated by the analytical LC with 4:1 petroleum ether-EtOAc as the eluent; for the α isomer, $[\alpha]_D$ -93.2° (*c* 2.6, $CHCl_3$); ^1H NMR: δ 7,42-7.22 (m, 10H, Ph), 6.21 (s, 1H, H-1), 5.22 (d, 1H, $J_{2,3}$ = 1.5 Hz, H-2), 4.80-4.50 (m, 4H, 2 PhC*H*$_2$), 4.40 (m, 1H, $J_{3,4}$ = 4.8 Hz, $J_{4,5}$ = 4.4 Hz, H-4), 4.00 (dd, 1H, $J_{2,3}$ = 1.5 Hz, $J_{3,4}$ = 4.8 Hz, H-3), 3.62 (d, 2H, $J_{4,5}$ = 4.4 Hz, 2 H-5'), 2.14, 2.03 (2s, 6H, 2 COC*H*$_3$).

Anal. Calcd for $C_{23}H_{26}O_7$: C, 66.67; H, 6.28. Found: C, 66,84; H, 6.30.

For the β isomer, $[\alpha]_D$ +66.1° (*c* 1.1, $CHCl_3$); ^1H NMR: δ 7.40-7.22 (m, 10H, Ph), 6.37 (d, 1H, $J_{1,2}$ = 4.6 Hz, H-1), 5.25 (dd, 1H, $J_{1,2}$ = 4.6 Hz, $J_{2,3}$ = 6.7 Hz, H-2), 4.62 (s, 2H, PhCH_2), 4.58 (s, 2H, PhCH_2), 4.38 (m, 2H, H-3,4), 3.60 (d, 2H, $J_{4,5}$ = 5.3 Hz, 2 H-5), 2.04, 1.97 (2s, 6H, 2 COCH_3).

3,5-Di-*O*-benzyl-2-*O*-tosyl-L-arabinofuranose (5). To a solution of **3** (800 mg, 2.42 mmol) in pyridine (5 mL) was added TsCl (1.5 g, 7.87 mmol) and powdered K_2CO_3 (340 mg, 2.46 mmol) at 0 °C. The mixture was stirred at 0 °C for about 20 h, then poured into ice-cold water and extracted with dichloromethane (30 mL). The organic layer was washed with cold water (50 mL), 1 N HCl (4 x 20 mL), then dried over Na_2SO_4. The solution was concentrated under diminished pressure, and the resultant residue was purified by column chromatography with 3:1 petroleum ether-EtOAc as the eluent. Compound **5** (708.6 mg, 60.5%) was obtained as an α:β mixture in a ratio of 1:3; $[\alpha]_D$ -42.9° (*c* 2.4, $CHCl_3$); ^1H NMR δ 7.85 (d, 0.5H, Ph-H of Ts for α anomer), 7.78 (d, 1.5H, Ph-*H* of Ts for β anomer), 7.47-7.14 (m, 12H, Ph*H*), 5.26 (d, 0.75H, $J_{H1,OH}$ = 6.3 Hz, H-1 of β anomer), 5.15 (dd, 0.25H, $J_{1,2}$ = 9.7 Hz, $J_{H1,OH}$ = 4.3 Hz, H-1 of α anomer), 4.79 (d, 0.75H, $J_{2,3}$ = 1.2 Hz, H-2 of β anomer), 4.82 (dd, 0.25H, H-2 of α anomer), 4.70-4.50 (m, 4H, 2 PhCH_2), 4.40-4.25 (m, 1H, H-4), 4.07-3.89 (m, 1H, H-3), 3.60-3.15 (m, 3H, 2 H-5, O*H*), 2.46 (s, 3H, PhCH_3).

Anal. Calcd for $C_{26}H_{28}O_7S_1$: C, 64.64; H, 5.79. Found: C, 64.83; H, 5.81.

1-*O*-Acetyl-3,5-di-*O*-benzyl-2-*O*-tosyl-L-arabinofuranose (6). Compound **5** (70 mg, 0.14 mmol) was treated with acetic anhydride (1.5 mL) in pyridine (2.5 mL) to afford **6** (53 mg, 98%) as a syrup (α:β = 4:1); $[\alpha]_D$ -30.9° (*c* 0.8, $CHCl_3$); ^1H NMR: δ 7.81 (d, 2 x 0.2H, Ph-*H* of Ts for β isomer), 7.80 (d, 2 x 0.8H, Ph-*H* of Ts for α anomer), 7.42-7.16 (m, 12H, Ph), 6.08 (d, 0.2H. $J_{1,2}$ = 4.2 Hz, H-1 of β anomer), 6.05 (s, 0.8H, H-1 of α anomer), 5.00 (d, 0.8H, $J_{2,3}$ = 2.0 Hz, H-2 of α anomer), 4.9 (dd, 0.2H, $J_{1,2}$ = 4.2 Hz, $J_{2,3}$ = 7.0 Hz, H-2 of β anomer), 4.62-4.40 (m, 4H, 2 PhCH_2), 4.37-4.20 (m, 1H, H-4), 4.18-4.10 (m, 1H, H-3), 3.58-3.44 (m, 2H, 2 H-5), 2.47 (s, 3H, PhCH_3), 2.02 (s, 3 x 0.8H, COCH_3 of α anomer), 1.88 (s, 3 x 0.2H, COCH_3 of β anomer).

Anal. Calcd for $C_{28}H_{30}O_8S_1$: C, 63.88; H, 5.70. Found: C, 64.11; H, 5.74.

1,2-Anhydro-3,5-di-*O*-benzyl-α-L-ribofuranose (7). To a solution of **5** (300 mg, 0.62 mmol) in dry oxolane (6 mL) was added potassium *tert*-butoxide (85 mg, 0.76

mmol). The mixture was stirred at room temperature for 10 min, at the end of which time TLC (3:1 petroleum ether-EtOAc) indicated that the starting material had disappeared. The mixture was concentrated to dryness, and the residue was repeatedly extracted with 3:1 petroleum ether-EtOAc. Concentration of the combined extracts yielded **7** as a syrup (193.7 mg, 95%); $[\alpha]_D$ -63° (*c* 1.3, $CHCl_3$); ^1H NMR: δ 7.41-7.26 (m, 10H, 2 Ph), 5.22 (d, 1H, $J_{1,2}$ = 2.0 Hz, H-1), 4.72, 4.63 (ABq, 2H, J = 12.0 Hz, PhCH_2), 4.56, 4.48 (ABq, 2H, J = 12.2 Hz, PhCH_2), 4.17 (dd, 1H, $J_{2,3}$ = 1.7 Hz, $J_{3,4}$ = 6.6 Hz, H-3), 3.92 (m, 1H, H-4), 3.63 (dd, 1H, $J_{4,5}$ = 2.8 Hz, $J_{5,5'}$ = 11.0 Hz, H-5), 3.58 (t, 1H, $J_{1,2}$ = 2.0 Hz, $J_{2,3}$ = 1.7 Hz, H-2), 3.51 (dd, 1H, $J_{4,5'}$ = 4.0 Hz, $J_{5,5'}$ = 11.0 Hz, H-5').

Methyl 3,5-di-*O*-benzyl-β-D-ribofuranoside (8). Compound **7** (50 mg, 0.15 mmol) was dissolved in anhydrous methanol (4 mL) and the solution kept for 1 h at room temperature. TLC (2:1 petroleum ether-EtOAc) indicated that the reaction was complete. The solution was concentrated to afford **8** quantitatively as a syrup; $[\alpha]_D$ -18.6° (*c* 0.8, $CHCl_3$); ^1H NMR: δ 7.40-7.20 (m, 10H, 2 Ph), 4.88 (s, 1H, H-1), 4.59 (s, 4H, 2 PhCH_2), 4.22 (t, 1H, $J_{3,4}$ = $J_{4,5}$ = 4.4 Hz, H-4), 4.12-4.03 (m, 2H, H-2,3), 3.55 (d, 2H, $J_{4,5}$ = 4.4 Hz, 2 H-5), 3.35 (s, 3H, OCH_3).

Anal. Calcd for $C_{20}H_{24}O_5$: C, 69.77; H, 6.98. Found: C, 70.22; H, 7.01.

Methyl 2-*O*-acetyl-3,5-di-*O*-benzyl-β-L-ribofuranoside (9). Compound **8** (80 mg, 0.23 mmol) was treated with acetic anhydride (1.8 mL) in pyridine (3 mL) to afford **9** (87.1 mg, 97%) as a syrup; $[\alpha]_D$ -13.6° (*c* 1.9, $CHCl_3$); ^1H NMR: δ 7.40-7.20 (m, 10H, 2 Ph), 5.20 (d, 1H, $J_{2,3}$ = 6.0 Hz, H-2), 4.88 (s, 1H, H-1), 4.60-4.40 (m, 4H, 2 PHCH_2), 4.23 (m, 1H, H-4), 4.12 (dd, 1H, $J_{2,3}$ = 6.0 Hz, $J_{3,4}$ = 9.5 Hz, H-3), 3.60 (dd, 1H, $J_{4,5}$ = 2.4 Hz, $J_{5,5'}$ = 10.0 Hz, H-5), 3.50 (dd, 1H, $J_{4,5'}$ = 6.4 Hz, $J_{5,5'}$ = 10.0 Hz, H-5'), 3.35 (s, 3H, OCH_3), 2.13 (s, 3H, COCH_3).

Anal. Calcd for $C_{22}H_{26}O_6$: C, 68.39; H, 6.74. Found: C, 68.23; H, 6.75.

1'-(3',5'-Di-*O*-benzyl-β-L-ribofuranosyl)uracil (11) and 1'-(2'-*O*-acetyl-3',5'-di-*O*-benzyl-β-L-ribofuranosyl)uracil-(12). To a stirred solution of *O,O*-bis-(trimethylsilyl)uracil (254 mg, 0.90 mmol) in dry CH_2Cl_2 (5 mL) with molecular sieves (4 A, 0.8 g) was added compound **7** (135.2 mg, 0.42 mmol) in dry CH_2Cl_2 (6 mL). The mixture was stirred for 8 h at room temperature, at the end of which time TLC (1:1

petroleum ether-EtOAc) indicated that the starting material **7** had disappeared. The mixture was diluted with CH_2Cl_2 (30 mL), filtered, and the filtrate concentrated to a syrup that was subjected to column chromatography with 1:2 petroleum ether-EtOAc as the eluent. Compounds **10** (123.3 mg, 60%) and **11** (45.5 mg, 26%) were obtained. Compound **10** was quantitatively converted to **11** within 5 min in a solution of CH_3CN (10 mL) containing HCOOH (0.4 mL). Compound **11** was isolated as white needles; mp 71-73 °C; $[\alpha]_D$ -33.1° (*c* 3.4, $CHCl_3$); ^1H NMR: δ 8.80 (s, 1H, N-*H*), 7.70 (d, 1H, $J_{5,6}$ = 8.1 Hz, H-6), 7.38 (s, 10H, 2 Ph), 5.95 (d, 1H, $J_{1',2'}$ = 4.1 Hz, H-1'), 5.27 (d, 1H, $J_{5,6}$ = 8.05 Hz, H-5), 4.70, 4.60 (ABq, 2H, J = 11.7 Hz. PhCH_2), 4.50 (s, 2H, PhCH_2), 4.30-4.18 (m, 2H, H-3,4'), 4.10 (t, 1H, $J_{1',2'} = J_{2',3'}$ = 4.1 Hz, H-2'), 3.82 (dd, 1H, $J_{4',5'}$ = 2.4 Hz, $J_{5',5''}$ = 10.5 Hz, H-5'), 3.58 (dd, 1H, $J_{4',5''}$ = 1.7 Hz, $J_{5',5''}$ = 10.5 Hz, H-5''), 2.50 (s, 1H, O*H*).

Anal. Calcd for $C_{23}H_{24}O_6N_2$. 0.5 H_2O: C, 63.74; H, 5.54. Found: C, 63.77; H, 5.59.

Compound **11** (30 mg, 0.069 mmol) was treated with acetic anhydride (0.8 mL) in pyridine (1.2 mL) to afford **12** (27.9 mg, 91%) as a syrup; $[\alpha]_D$ -18.7° (*c* 0.4, $CHCl_3$); ^1H NMR: δ 8.15 (s, 1H, N-*H*), 7.75 (d, 1H, $J_{5,6}$ = 8.2 Hz, H-6), 7.40-7.10 (m, 10H, 2 Ph), 6.03 (d, 1H, $J_{1',2'}$ = 2.5 Hz, H-1'), 5.28-5.20 (m, 2H, H-2',5), 4.60-4.30 (m, 4H, 2 PhCH_2), 4.20-4.10 (m, 2H, H-3',4'), 3.80 (dd, 1H, $J_{4',5'}$ = 1.3 Hz, $J_{5',5''}$ = 10.2 Hz, H-5'), 3.50 (dd, 1H, $J_{4',5''}$ = 1.0 Hz, $J_{5',5''}$ = 10.2 Hz, H-5''), 2.10 (s, 3H, COCH_3).

***O*-(2-*O*-Acetyl-3,5-di-*O*-benzyl-β-L-ribofuranosyl)-(1→5)-3-*O*-acetyl-1,2-*O*-isopropylidene-α-D-xylofuranose (13β) and *O*-(2-*O*-acetyl-3,5-di-*O*-benzyl-α-L-ribofuranosyl)-(1→5)-1,2-*O*-isopropylidene-3-*O*-acetyl-α-L-xylofuranose (13α).** To a solution of 1,2-*O*-isopropylidene-α-D-xylofuranose (210 mg, 1.1 mmol) in anhydrous methylene chloride (4 mL) was added 4A molecular sieves (1 g) and $ZnCl_2$ (0.5 g). The mixture was stirred for 10 min at room temperature, and then a solution of **7** (180 mg, 0.55 mmol) in methylene chloride (2 mL) was added. The mixture was stirred at room temperature for 3 h, at the end of which time TLC (2:1 petroleum ether-EtOAc) indicated that **7** had disappeared. The mixture was filtered to remove the solid material, and the filtrate was washed with water (3 x 50 mL), dried over Na_2SO_4, then

concentrated to a syrup. The syrup was dissolved in pyridine (5 mL) and to the solution was added acetic anhydride (4 mL) at room temperature. After 2 h, the mixture was poured into ice-cold water, extracted with dichloromethane (50 mL). The organic layer was washed with cold 1 N HCl (3 x 20 mL), then dried over Na_2SO_4. The solution was concentrated to a syrup that was subjected to analytical LC with 4:1 petroleum ether-EtOAc as the eluent to afford **13**β (187.9 mg, 58.3%) and **13**α (31.3 mg, 9.7%) as syrups; for the **13**β,$[\alpha]_D$ -13.0° (*c* 1.4, $CHCl_3$); ^{1}H NMR: δ 7.38-7.22 (m, 10H, 2 Ph), 5.89 (d, 1H, $J_{1,2}$ = 3.9 Hz, H-1), 5.22 (d, 1H, $J_{3,4}$ = 3.2 Hz, H-3), 5.18 (d, 1H, $J_{1',2'}$ = 4.2 Hz, H-2'), 4.97 (s, 1H, H-1'), 4.59-3.44 (12H, 2 PhCH_2, H-2,4,5a,5b,3',4,'5'a, and 5'b), 2.12, 2.08 (2s, 6H, 2COCH_3), 1.51, 1.30 (2s, 6H, 2 CCH_3).

Anal. Calcd for $C_{31}H_{38}O_{11}$: C, 63.48; H, 6.48. Found: C, 68.46; H, 6.51.

For the **13**α, $[\alpha]_D$ -115.9° (*c* 1.4, $CHCl_3$); ^{1}H NMR: δ 7.41-7.22 (m, 10H, 2 Ph), 5.91 (d, 1H, $J_{1,2}$ = 3.9 Hz, H-1), 5.28 (d, 1H, $J_{1',2'}$ = 4.6 Hz, H-1'), 5.22 (d, 1H, $J_{3,4}$ = 3.2 Hz, H-3), 4.90 (dd, 1H, $J_{1',2'}$ = 4.6 Hz, $J_{2',3'}$ = 6.9 Hz, H-2'), 4.69-4.38 (m, 6H, H-2,4, 2 PhCH_2), 4.14 (m, 1H, H-4'), 4.06 (dd, 1H, $J_{2',3'}$ = 6.9 Hz, $J_{3',4'}$ = 4.3 Hz, H-3'), 3.92 (dd, 1H, $J_{4,5a}$ = 5.9 Hz, $J_{5a,5b}$ = 10.7 Hz, H-5a), 3.78 (dd, 1H, $J_{4,5b}$ = 6.2 Hz, $J_{5a,5b}$ = 10.7 Hz, H-5b), 3.45 (dd, 1H, $J_{4',5'a}$ = 3.4 Hz, $J_{5'a,5'b}$ = 10.5 Hz, H-5'a), 3.31 (dd, 1H, $J_{4',5'b}$ = 4.0 Hz, $J_{5'a,5'b}$ = 10.5 Hz, H-5'b), 2.19, 2.04 (2s, 6H, 2 COCH_3), 1.52, 1.30 (2s, 6H, 2 CCH_3).

1,2-*O*-Isopropylidene-5-*O*-benzyl-3-*O*-methyl-β-L-arabinofuranose (15). To a solution of 1,2-*O*-isopropylidene-3-*O*-methyl-β-L-arabinofuranose[9] (**14**) (1.66 g, 5.65 mmol) in anhydrous oxolane (20 mL) was added, with vigorous stirring in an ice-cold water bath, sodium hydride (60% in oil; 1.17 g, 29.3 mmol) and benzyl bromide (0.84 mL, 6.78 mmol). Then the mixture was stirred and boiled under reflux for 4 h, at the end of which time TLC (3:1 petroleum ether-EtOAc) indicated that the reaction was complete. The mixture was directly subjected to steam distillation to remove the excess benzyl bromide and by-product dibenzyl ether, and then extracted with dichloromethane. The organic layer was concentrated to a syrup that was purified by column chromatography with 4:1 petroleum ether-EtOAc to give **15** (2.24 g, 94%); $[\alpha]_D$ -11.8° (*c* 10.0, $CHCl_3$); ^{1}H NMR: δ 7.38-7.25 (m, 5H, Ph), 5.86 (d, 1H, $J_{1,2}$ = 4.2 Hz, H-1), 4.61, 4.58 (ABq, 2H, J = 12.0 Hz, PhCH_2), 4.57 (d, 1H, $J_{1,2}$ = 4.2 Hz, H-2), 4.17 (m,

1H, $J_{3,4}$ = 2.9 Hz, $J_{4,5}$ = 6.3 Hz, H-4), 3.80 (d, 1H, $J_{3,4}$ = 2.9 Hz, H-3), 3.64 (d, 2H, $J_{4,5}$ = 6.3 Hz, 2 H-5), 3.40 (s, 3H, OCH_3), 1.45, 1.31 (2s, 6H, 2 CCH_3).

Anal. Calcd for $C_{16}H_{22}O_5$: C, 65.30; H, 7.48. Found: C, 65.43; H,7.49.

5-*O*-Benzyl-3-*O*-methyl-L-arabinofuranose (16). The solution of **15** (1.5 g, 3.91 mmol) in 30% acetic acid (80 mL) was boiled under reflux with stirring for 5 h, at the end of which time TLC (2:1 petroleum ether-EtOAc) indicated that the reaction was complete. The mixture was concentrated to a syrup that was subjected to column chromatography with 2:1 petroleum ether-EtOAc as the eluent. Compound **16** was obtained as a syrupy anomeric mixture (1.2 g, 90%, α:β 1:1); $[\alpha]_D$ -52.8° (*c* 1.5, $CHCl_3$); ^{1}H NMR: δ 7.38-7.23 (m, 5H, Ph), 5.26 (d, 0.5H, $J_{1,2}$ = 3.6 Hz, H-1 of β anomer), 5.24 (s, 0.5H, H-1 of α anomer), 4.72-3.56 (m, 9H, H-2,3,4,5,5',PhCH_2, 2 O*H*), 3.41 (s, 0.5 x 3H, OCH_3 of β anomer), 3.38 (s, 0.5 x 3H, OCH_3 of α anomer).

Anal. Calcd for $C_{13}H_{18}O_5$: C, 61.42; H, 7.09. Found: C, 61.60; H, 7.11.

1,2-Di-*O*-acetyl-5-*O*-benzyl-3-*O*-methyl-L-arabinofuranose (17). Acetylation of **16** (100 mg, 0.39 mmol) with acetic anhydride (4 mL) in pyridine (5 mL) at room temperature for 4 h gave compound **17** in a quantitative yield as a syrup consisting of α and β anomers in a ratio of 1:1; $[\alpha]_D$ +3.4° (*c* 7.5, $CHCl_3$); ^{1}H NMR: δ 7.38-7.26 (m, 5H, Ph), 6.32 (d, 0.5H, $J_{1,2}$ = 4.2 Hz, H-1 of β anomer), 6.19 (s, 0.5H, H-1 of α anomer), 5.18 (dd, 0.5H, $J_{1,2}$ = 4.2 Hz, $J_{2,3}$ = 6.5 Hz, H-2 of β anomer), 5.14 (d, 0.5H, $J_{2,3}$ = 1.7 Hz, H-2 of α anomer), 4.60 (m, 2H, PhCH_2), 4.30 (m, 0.5H, $J_{3,4}$ = 4.7 Hz, $J_{4,5}$ = 4.5 Hz, H-4 of α anomer), 4.18-4.03 (m, 2 x 0.5H, H-3,4 of β anomer), 3.78 (dd, 0.5H, $J_{2,3}$ = 1.7 Hz, $J_{3,4}$ = 4.7 Hz, H-3 of α anomer), 3.66 (d, 2 x 0.5H, $J_{4,5}$ = 5.1 Hz, 2 H-5 of β anomer), 3.63 (d, 2 x 0.5H, $J_{4,5}$ = 4.2 Hz, 2 H-5 of α anomer), 3.42 (s, 3 x 0.5H, OCH_3 of β anomer), 3.40 (s, 3 x 0.5H, OCH_3 of α anomer), 2.10, 2.04 (2s, 6 x 0.5H, 2 $COCH_3$ of β anomer), 2.08, 1.96 (2s, 6 x 0.5H, 2 $COCH_3$ of α anomer).

Anal.Calcd for $C_{17}H_{22}O_7$: C, 60.35; H, 6.51. Found: C, 60.50; H, 6.49.

5-*O*-Benzyl-3-*O*-methyl-2-*O*-tosyl-L-arabinofuranose (18). To a solution of **16** (519 mg, 2.04 mmol) in pyridine (5 mL) was added TsCl (775 mg, 4.07 mmol) and powdered K_2CO_3 (366 mg, 2.65 mmol) at 0 °C. The mixture was stirred at 0 °C for about 20 h, then poured into ice-cold water, extracted with dichloromethane (30 mL).

The organic layer was washed with cold water (50 mL), 1 N HCl (4 x 20 mL), then dried over Na_2SO_4. The solution was concentrated under diminished pressure and the resultant residue was separated by column chromatography with 3:1 petroleum ether-EtOAc as the eluent to give **18** (532.7 mg, 64%) as an α:β mixture in a ratio of 1:3; $[\alpha]_D$ -25.1° (*c* 1.5, $CHCl_3$); ^1H NMR δ 7.85 (d, 0.5H, Ph-*H* of Ts for α anomer), 7.81 (d, 1.5H, Ph-*H* of Ts for β anomer), 7.38-7.24 (m, 7H, Ph*H*), 5.26 (d, 0.75H, $J_{H1,OH}$ 5.86 Hz, H-1 of β anomer), 5.10 (dd, 0.25H, $J_{1,2}$ = 9.4 Hz, $J_{H1,OH}$ = 4.0 Hz, H-1 of α anomer), 4.73 (d, 0.75H, $J_{2,3}$ = 1.5 Hz, H-2 of β anomer), 4.71 (dd, 0.25H, H-2 of α anomer), 4.62-4.54 (m, 2H, PhCH_2), 4.36-3.76 (2H, H-3,4), 3.56 (m, 2H, 2 H-5), 3.28 (s, 3 x 0.75H OCH_3 of β anomer), 3.26 (s, 3 x 0.25H, OCH_3 of α anomer), 3.14 (1H, O*H*), 2.43 (s, 3H, PhCH_3).

Anal. Calcd for $C_{20}H_{24}O_7S_1$: C, 58.82; H, 5.88. Found: C, 58.93; H, 5.85.

1-*O*-Acetyl-5-*O*-benzyl-3-*O*-methyl-2-*O*-tosyl-L-arabinofuranose (19). Compound **18** (50 mg, 0.12 mmol) was acetylated with acetic anhydride (1 mL) in pyridine (1.5 mL) to afford **19** (52.9 mg, 98%) as a syrup (α:β 4:1); $[\alpha]_D$ -22.4° (*c* 1.1, $CHCl_3$); ^1H NMR: δ 7.81 (m, 2H, Ph-*H* of Ts), 7.42-7.25 (m, 7H, Ph), 6.03 (d, 0.2H, $J_{1,2}$ = 4.4 Hz, H-1 of β anomer), 6.01 (s, 0.8H, H-1 of α anomer), 4.92 (d, 0.8H, $J_{2,3}$ = 1.5 Hz, H-2 of α anomer), 4.82 (dd, 0.2H, $J_{1,2}$ = 4.4 Hz, $J_{2,3}$ = 6.7 Hz, H-2 of β anomer), 4.64-4.50 (m, 2H, PhCH_2), 4.19 (m, 0.8H, $J_{3,4}$ = 5.9 Hz, $J_{4,5}$ = 4.64 Hz, H-4 of α anomer), 4.12-3.95 (m, 0.4H, H-3,4 of β anomer), 3.91 (dd, 0.8H, $J_{2,3}$ 1.5 Hz, $J_{3,4}$ = 5.9 Hz, H-3 of α anomer), 3.62 (d, 2 x 0.8H, $J_{4,5}$ = 4.6 Hz, 2 H-5 of α anomer), 3.55 (d, 2 x 0.2H, $J_{4,5}$ = 4.9 Hz, 2 H-5 of β anomer), 3.35 (s, 3 x 0.8H, OCH_3 of α anomer), 3.33 (s, 3 x 0.2H, OCH_3 of β anomer), 2.47 (s, 3H, PhCH_3), 2.04 (s, 3 x 0.8H, $COCH_3$ of α anomer), 1.88 (s, 3 x 0.2H, $COCH_3$ of β anomer).

Anal. Calcd for $C_{22}H_{26}O_8S_1$: C, 58.67; H, 5.78. Found: C, 58.88; H, 5.73.

1,2-Anhydro-5-*O*-benzyl-3-*O*-methyl-5-α-L-ribofuranose (20). To a solution of **18** (170 mg, 0.42 mmol) in dry oxolane (6 mL) was added potassium *tert*-butoxide (70 mg, 0.62 mmol), and the mixture was stirred at room temperature for 10 min, at the end of which time TLC (3:1 petroleum ether-EtOAc) indicated that the starting material had disappeared. The mixture was concentrated to dryness, and the residue was repeatedly extracted with 3:1 petroleum ether-EtOAc. Concentration of the combined extracts

yielded **20** as a syrup (99.3 mg, 94%); $[\alpha]_D$ -70.8° (*c* 0.34, $CHCl_3$); ^1H NMR: δ 7.32 (s, 5H, Ph), 5.25 (d, 1H, $J_{1,2}$ = 2.2 Hz, H-1), 4.62, 4.54 (ABq, 2H, J = 12.2 Hz, PhCH_2), 4.01 (dd, 1H, $J_{2,3}$ = 2.2 Hz, $J_{3,4}$ = 6.7 Hz, H-3), 3.85 (m, 1H, H-4), 3.70 (t, 1H, $J_{1,2}$ = 2.2 Hz, $J_{2,3}$ = 2.2 Hz, H-2), 3.66 (dd, 1H, $J_{4,5}$ = 2.6 Hz, $J_{5,5'}$ = 11.4 Hz, H-5), 3.55 (dd, 1H, $J_{4,5'}$ = 4.2 Hz, $J_{5,5'}$ = 11.4 Hz, H-5'), 3.48 (s, 3H, OCH_3).

Methyl 5-*O*-benzyl-3-*O*-methyl-β-L-ribofuranoside (21). Compound **20** (50 mg, 0.196 mmol) was dissolved in anhydrous methanol (4 mL) and the solution kept for 1 h at room temperature. TLC (2:1 petroleum ether-EtOAc) indicated that the reaction was complete. The solution was concentrated to afford **21** quantitatively as a syrup; $[\alpha]_D$ -31.3° (*c* 1.5, $CHCl_3$); ^1H NMR: δ 7.28 (s, 5H, Ph), 4.80 (s, 1H, H-1), 4.55 (s, 2H, PhCH_2), 4.08 (m, 1H, H-4), 4.03 (d, 1H, $J_{2,3}$ = 4.9 Hz, H-2), 3.80 (dd, 1H, $J_{2,3}$ = 4.9 Hz, $J_{3,4}$ = 6.2 Hz, H-3), 3.51 (d, 2H, $J_{4,5}$ = 4.4 Hz, 2 H-5), 3.35, 3.26 (2s, 6H, 2 OCH_3), 2.60 (s, 1H, O*H*).

Anal. Calcd for $C_{14}H_{20}O_5$: C, 62.69; H, 7.46. Found: C, 62.90; H, 7.49.

Methyl 2-*O*-acetyl-5-*O*-benzyl-3-*O*-methyl-β-L-ribofuranoside (22). Compound **21** (60 mg, 0.22 mmol) was treated with acetic anhydride (1.5 mL) in pyridine (3 mL) to afford **22** (67.9 mg, 98%) as a syrup; $[\alpha]_D$ -28.6° (*c* 0.2, $CHCl_3$); ^1H NMR: δ 7.35 (s, 5H, Ph), 5.20 (d, 1H, $J_{2,3}$ = 4.4 Hz, H-2), 4.86 (s, 1H, H-1), 4.62 (s, 2H, PHCH_2), 4.15 (m, 1H, H-4), 3.95 (dd, 1H, $J_{2,3}$ = 4.4 Hz, $J_{3,4}$ = 7.3 Hz, H-3), 3.66 (dd, 1H, $J_{4,5}$ = 3.5 Hz, $J_{5,5'}$ = 10.2 Hz, H-5), 3.58 (dd, 1H, $J_{4,5'}$ = 5.9 Hz, $J_{5,5'}$ = 10.2 Hz, H-5'), 3.35 (s, 3H, OCH_3), 3.34 (s, 3H, OCH_3), 2.15 (s, 3H, COCH_3).

Anal. Calcd for $C_{16}H_{22}O_6$: C, 61.94; H, 7.10. Found: C, 62.01; H, 7.14.

1'-(5'-*O*-Benzyl-3'-*O*-methyl-2'-*O*-trimethylsilyl-β-L-ribofuranosyl)uracil (23), 1'-(5'-*O*-benzyl-3'-*O*-methyl-β-L-ribofuranosyl)uracil (24) and 1'-(2'-*O*-acetyl-5'-*O*-benzyl-3'-*O*-methyl-β-L-ribofuranosyl)uracil (25). To a stirred solution of *O,O*-bis-(trimethylsilyl)uracil (235 mg, 0.83 mmol) in dry CH_2Cl_2 (4 mL) with molecular sieves (4 A, 0.5 g) was added compound **20** (106 mg, 0.415 mmol) in dry CH_2Cl_2 (4 mL). The mixture was stirred for 8 h at room temperature, at the end of which time TLC (1:1 petroleum ether-EtOAc) indicated that the starting material **20** disappeared. The mixture was diluted with CH_2Cl_2 (30 mL), filtered, and filtrate concentrated to a syrup that was subjected to column chromatography with 1:2 petroleum ether-EtOAc as the eluent.

Compounds **23** (106.3 mg, 61%) and **24** (36.1 mg, 25%) were obtained. For compound **23**, ^{1}H NMR: δ 8.55 (s, 1H, N-H), 7.85 (d, 1H, $J_{5,6}$ = 8.3 Hz, H-6), 7.38-7.15 (m, 5H, Ph),5.75 (d, 1H, $J_{1',2'}$ = 3.2 Hz, H-1'), 5.23 (d, 1H, $J_{5,6}$ = 8.3 Hz, H-5), 4.55-4.42 (m, 2H, PhC*H*$_2$), 4.30-3.48 (m, 6H, H-2',3',4',5',5'', O*H*), 3.36 (s, 3H, OC*H*$_3$), 0.09 (s, 9H, Si(C*H*$_3$)$_3$).

Compound **23** was quantitatively converted to **24** within 5 min in a solution of CH_3CN (10 mL) containing HCOOH (0.4 mL). Compound **24** was obtained as white needles; mp 50-53 °C; $[\alpha]_D$ -10.4° (*c* 1.1, $CHCl_3$); ^{1}H NMR: δ 9.43 (s, 1H, N-*H*), 7.79 (d, 1H, $J_{5,6}$ = 8.1 Hz, H-6), 7.44-7.28 (m, 5H, Ph), 5.92 (d, 1H, $J_{1,'2'}$ = 4.4 Hz, H-1'), 5.40 (d, 1H, $J_{5,6}$ = 8.1 Hz, H-5), 4.58 (s, 2H, PhC*H*$_2$), 4.32-4.23 (m, 2H, H-3',4'), 3.89 (dd, 1H, H-2'), 3.87 (dd, 1H, $J_{4',5'}$ = 2.6 Hz, $J_{5',5''}$ = 10.2 Hz, H-5'), 3.69 (dd, 1H, $J_{4',5''}$ = 1.9 Hz, $J_{5',5''}$ = 10.2 Hz, H-5''), 3.48 (s, 3H, OCH_3).

Anal. Calcd for $C_{17}H_{20}O_6N_2$. 0.5 H_2O: C, 57.14; H, 5.60. Found: C, 57.20; H, 5.63.

Compound **24** (25 mg, 0.072 mmol) was treated with acetic anhydride (0.5 mL) in pyridine (1 mL) to afford **25** (26.6 mg, 95%); $[\alpha]_D$ -71.1° (*c* 0.45, $CHCl_3$); ^{1}H NMR: δ 8.59 (s, 1H, N-*H*), 7.82 (d, 1H, $J_{5,6}$ 8.3 Hz, H-6), 7.44-7.30 (m, 5H, Ph), 6.08 (d, 1H, $J_{1',2'}$ = 4.2 Hz, H-1'), 5.38 (d, 1H, $J_{5,6}$ = 8.3 Hz, H-5), 5.30 (t, 1H, $J_{1',2'}$ = 4.2 Hz, $J_{2',3'}$ = 4.2 Hz, H-2'), 4.61, 4.58 (ABq, 2H, J = 11.2 Hz, PhC*H*$_2$), 4.19 (m, 1H, H-4'), 4.02 (t, 1H, $J_{2',3'}$ = $J_{3',4'}$ = 4.2 Hz, H-3'), 3.92 (dd, 1H, $J_{4',5'}$ = 2.2 Hz, $J_{5',5''}$ = 10.2 Hz, H-5'), 3.70 (dd, 1H, $J_{4',5''}$ = 2.0 Hz, $J_{5',5''}$ = 10.2 Hz, H-5''), 3.38 (s, 3H, OCH_3), 2.15 (s, 3H, COC*H*$_3$).

REFERENCES

1. P. S. Miller and P. O. P. Ts'O, *Annu. Rep. Med. Chem.*, **23**, 295 (1988); E. Uhlmann and A. Peyman, *Chem. Rev.*, **90**, 543 (1990).
2. J. Wengel, J. Lau, E. B. Pedersen and C. M. Nielsen, *J. Org. Chem.*, **56**, 3591 (1991); C. Genu-Dellac, G. Gosselin, A. M. Aubertin, G. Obert, A. Kin and J. L. Imbach, *Antiviral Chem.*, **2**, 83 (1991).
3. T. E. Walker and H. P. C. Hogenkamp, *Carbohydr. Res.*, **32**, 413 (1974).
4. V. Bilik and J. Caplovic, *Chem. Zvesti*, **27**, 547 (1973).
5. E. M. Acton, K. J. Ryan and L. Goodman, *J. Am. Chem. Soc.*, **86**, 5352 (1964).
6. C. Evelyne, F. Olivier and C. Stanislas, *J. Carbohydr. Chem.*, **14**, 1251 (1995).

7. Y. Du and F. Kong, *Tetrahedron Lett.*, **32**, 427 (1995); Y. Du and F. Kong, *J. Carbohydr. Chem.*, **14**, 341 (1995); Y. Du and F. Kong, *J. Carbohydr. Chem.*. **15**, 797 (1996); X. Ding and F. Kong, *Carbohydr. Res.*, **286**, 161 (1996).
8. K. Chow and S. J. Danishefsky, *J. Org. Chem.*, **55**, 4211 (1990).
9. E. L. Hirst, J. K. Jones and E. Williams, *J. Am. Chem. Soc.*, **69**, 1062 (1947).
10. Q. Chen, F. Kong and L. Cao, *Carbohydr. Res.*, **240**, 107 (1993); G. Yang, F. Kong, and R. R. Fraser, *Carbohydr. Res.*, **258**, 49 (1994); H. Yamaguchi and C. Schuerch, *Carbohydr. Res.*, **81**, 192 (1980).