Application of the versatile character of the tellurium atom for the synthesis of *C*-nucleoside analogues *via* sugar tellurides

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Making use of the versatile character of the tellurium atom such as its radicophilicity, nucleophilicity and electrophilicity, D-ribofuranosyl, 2-deoxy-D-ribofuranosyl and D-glucosyl *p*-methoxyphenyl tellurides have been prepared. Under suitable conditions, the corresponding anomeric radical, anomeric cation and anomeric anion, respectively, are formed from the sugar tellurides. By the following coupling reactions of the anomeric radical and anomeric cation to electron-poor and electron-rich aromatics, respectively, the corresponding *C*-nucleoside analogues have been synthesized in moderate yields. The anomeric anion has also been trapped by an electrophile such as benzaldehyde.

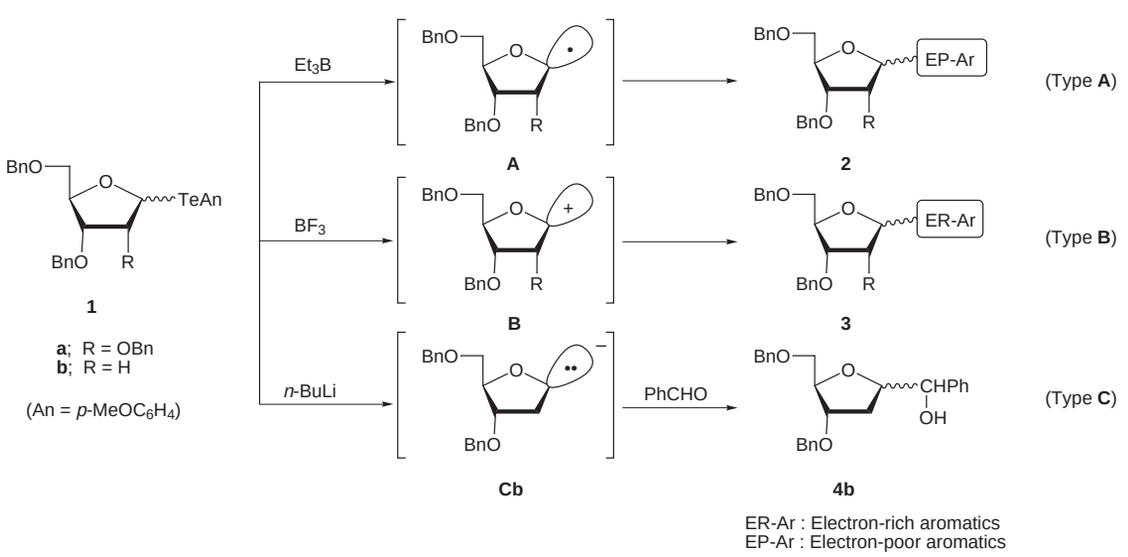
Introduction

C-Nucleosides are an important class of compounds, a number of which have been noted for their antitumour, antibacterial, or antiviral activities.[1] Therefore, synthetic studies of *C*-nucleosides have been extensive,[2] especially *via* an anomeric cation. On the other hand, relatively few examples of the coupling of an anomeric radical and a heteroaromatic base have been reported and the number of direct synthetic procedures remains limited.[3] Furthermore, the formation of *C*-nucleosides *via* an anomeric anion is also extremely rare.[4] However, for the formation of these reactive intermediates such as the anomeric cation, anomeric radical and anomeric anion, respectively, independent starting precursors have, to date, been required. We have been interested in the introduction of many types of base moiety into the *C*-nucleosides, *i.e.*, π-electron-rich aglycone unit and π-electron-poor aglycone unit, to the anomeric position in view of the chemical characteristics and biological activities of *C*-nucleosides. Recently, it has become known that tellurides have exceptional radicophilicity, electrophilicity and nucleophilicity.[5] Therefore, we have focused on sugar tellurides for the preparation of *C*-nucleosides *via* an anomeric radical, anomeric cation and anomeric anion species. The first study on sugar tellurides and their radical reactivity towards electron-deficient olefins was carried out by Barton.[6] Later, *O*-glycosidation with a glycosyl telluride *via* an anomeric cation by electrochemical oxidation was reported.[7] We have also reported on the direct introduction of an aglycone moiety to the sugar anomeric position *via* an anomeric radical, cation and anion with sugar tellurides as flexible precursors.[8] Here, we would like to report on a strategic approach to *C*-nucleosides *via* an anomeric cation, anomeric radical and anomeric anion, respectively, as shown in Scheme 1. Under suitable conditions, using the appropriate radical initiator, an anomeric radical is formed from a sugar telluride, and the reaction between the anomeric radical and electron-poor aromatic bases could be carried out; from the same telluride, by changing the reaction conditions using a Lewis acid, an anomeric cation is also formed, and the coupling reaction between the anomeric cation and electron-rich aromatics could also be carried out. Moreover, from a 2-deoxy-D-ribofuranosyl telluride, the corresponding anomeric anion is formed and an electrophile (for example, benzaldehyde) could be made to react with the sugar.

Results and discussion

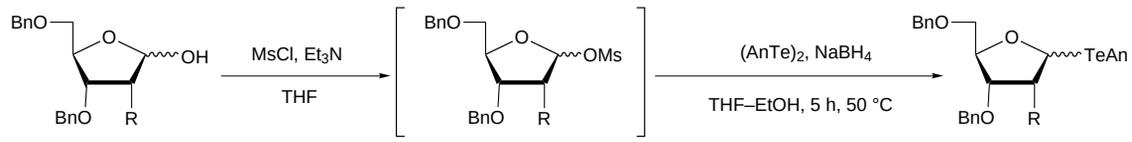
Preparation of ribofuranosyl tellurides

First, ribofuranosyl tellurides were prepared from the corresponding D-ribose and 2-deoxy-D-ribose using the method



Scheme 1 Synthetic strategy

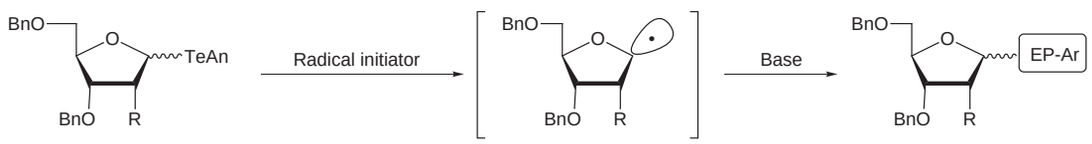
Table 1 Synthesis of ribofuranosyl tellurides and their stabilities



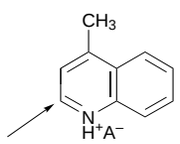
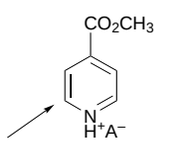
5 6 1

	Yield/% (overall)	Stability of sugar tellurides	δ_H and δ_C (ppm, $CDCl_3/SiMe_4$) (anomer position)
1a	70% ($\alpha:\beta = 1:2$)	decomposed completely after one week at rt	$\alpha:\delta_H$ 5.92 (d, $J_{1,2}$ 1.4); δ_C 80.03 $\beta:\delta_H$ 6.45 (d, $J_{1,2}$ 5.1); δ_C 80.42
1b	40 % ($\alpha:\beta = 1:1$)	decomposed completely after two days at rt	$\alpha:\delta_H$ 5.92 (dd, $J_{1,2}$ 5.8 and 8.6) $\beta:\delta_H$ 6.58 (d, $J_{1,2}$ 6.0)

Table 2 Formation of *C*-nucleoside analogues **2** *via* an anomeric radical



1 A 2

	Base (EP-Ar)	Reaction conditions	Yields (%) 2a	2b
i	 (7 equiv.)	Et_3B (10 equiv.) rt 20 h, $CHCl_3$	46 ($\alpha:\beta = 1:1$)	40 ($\alpha:\beta = 1:1$)
ii	 (7 equiv.)	Et_3B (10 equiv.) rt 20 h, $CHCl_3$	43 ($\alpha:\beta = 3:2$)	35 ($\alpha:\beta = 1:1$)

$A^- = CF_3CO_2^-$

shown in Table 1. Thus, 2,3,5-tri-*O*-benzyl-D-ribose **5a**[9] and 3,5-di-*O*-benzyl-2-deoxy-D-*erythro*-pentofuranose **5b**[10] were readily obtained in three steps from D-ribose and 2-deoxy-D-ribose. Then, the protected D-ribose and 2-deoxy-D-ribose were converted to compounds **6** which were prepared by mesylation and, subsequently, they were treated with 4-methoxyphenyl telluride anion to give the ribofuranosyl tellurides **1**. The stabilities of these sugar tellurides **1a** and **1b** were also examined.

It seemed that the ribofuranosyl tellurides **1a** and **1b** are not such stable compounds, especially in air and sunlight. The former decomposed within one week and the latter decomposed after two days at room temperature (rt). Accordingly, these tellurides have to be stored in a refrigerator before use. As compared with 2-deoxy-D-*erythro*-pentofuranosyl telluride **1b**, D-ribofuranosyl telluride **1a** shows increased stability during storage, handling, and preparative TLC purification. Probably, this is due to the OBn-stabilization effect (inductive effect) at the 2-position.

Formation of *C*-nucleoside analogues *via* an anomeric radical from D-ribofuranosyl tellurides

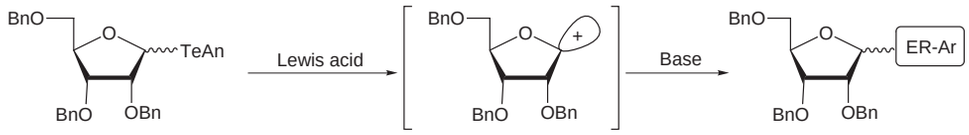
Recently, triethylborane has been used for the initiation of radical reactions[11] and the reactions are generally carried out under mild conditions (rt). Thus, the radical reaction of our ribofuranosyl tellurides with triethylborane in the presence of air was carried out at rt, to form an ethyl radical which further reacted with the sugar telluride to generate the corresponding anomeric radical, and the coupling of the anomeric radical formed with electron-poor heteroaromatics such as 4-methylquinoline and methyl isonicotinate finally gave the corresponding coupling products **2** in moderate yields (Table 2). However, none of the reactions exhibit stereoselectivity at the anomer position. The same reactions with the separated α-form and β-form of **1a** with 4-methylquinoline gave the corresponding coupling product in 40% ($\alpha:\beta = 49:51$) and 38% ($\alpha:\beta = 50:50$) yields, respectively.

Formation of *C*-nucleoside analogues *via* an anomeric cation from D-ribofuranosyl tellurides

From the same protected ribofuranosyl telluride **1a**, the corresponding anomeric cation was generated using a Lewis acid such as BF_3, and coupling between the anomeric cation and electron-rich aromatics (ER-Ar) such as benzothiophene, 1-(phenylsulfonyl)indole, and 1,3,5-trimethoxybenzene proceeded to give the corresponding products in good yields (Table 3). Here, BF_3 was chosen as the Lewis acid, because it is more suitable in terms of yields and gives cleaner reaction products than others (EtI, $ZnCl_2$), and its handling is easy. Benzothiophene gave the corresponding 3-substituted product in moderate yield, predominantly in the α-form. Trimethoxybenzene gave the corresponding β-substituted product in sufficient yield.

The same reactions with the separated α-form and β-form of compound **1a** with 1-(phenylsulfonyl)indole gave the corresponding coupling product in 80% ($\alpha:\beta = 11:89$) and 70% yield ($\alpha:\beta = 10:90$), respectively at −40 °C. The results were in

Table 3 Formation of *C*-nucleoside analogues **3a** *via* an anomeric cation



1a **Ba** **3a**

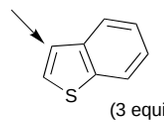
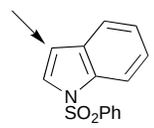
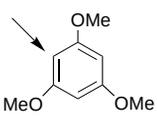
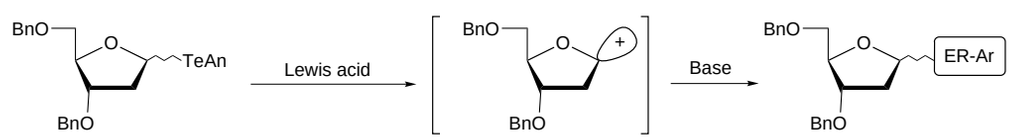
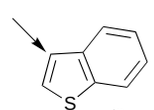
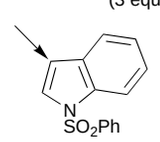
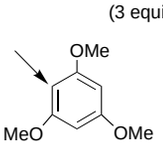
	Base (ER-Ar)	Reaction conditions	Yield (%)
iii	 (3 equiv.)	$BF_3{\cdot}Et_2O$ (7 equiv.), −78 °C, 1 h, $CHCl_3$ $BF_3{\cdot}Et_2O$ (7 equiv.), −40 °C, 1 h, $CHCl_3$	40 ($\alpha:\beta = 29:71$) 65 (α only)
iv	 (3 equiv.)	$BF_3{\cdot}Et_2O$ (7 equiv.) −78 °C, 1 h, $CHCl_3$ $BF_3{\cdot}Et_2O$ (7 equiv.) −40 °C, 1 h, $CHCl_3$ NBS (2 equiv.), rt, 1 h, $CHCl_3$	45 ($\alpha:\beta = 85:15$) 85 ($\alpha:\beta = 10:90$) 35 (β only)
v	 (3 equiv.)	$BF_3{\cdot}Et_2O$ (7 equiv.), −10 °C, 1 h, $CHCl_3$	65 (β only)

Table 4 Formation of *C*-nucleoside analogues **3b** *via* an anomeric cation



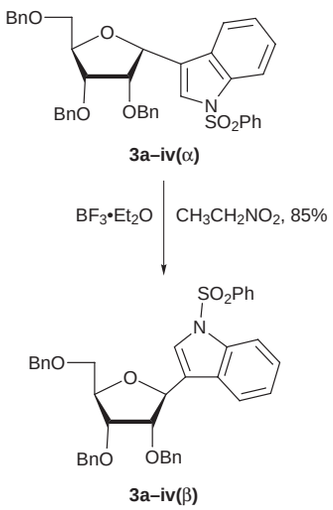
1b **Bb** **3b**

	Base (ER-Ar)	Reaction conditions	Yield (%)
iii	 (3 equiv.)	$BF_3{\cdot}Et_2O$ (4 equiv.), 0 °C, 1 h, $CHCl_3$ $BF_3{\cdot}Et_2O$ (4 equiv.), 10 °C, 1 h, $CHCl_3$	45 ($\alpha:\beta = 90:10$) 35 ($\alpha:\beta = 25:75$)
iv	 (3 equiv.)	$BF_3{\cdot}Et_2O$ (4 equiv.), −10 °C, 1 h, $CHCl_3$ $BF_3{\cdot}Et_2O$ (4 equiv.), 0 °C, 1 h, $CHCl_3$ $BF_3{\cdot}Et_2O$ (4 equiv.), 15 °C, 1 h, $CHCl_3$	50 ($\alpha:\beta = 28:72$) 50 ($\alpha:\beta = 32:68$) 65 ($\alpha:\beta = 34:66$)
v	 (3 equiv.)	$BF_3{\cdot}Et_2O$ (4 equiv.), −15 °C, 1 h, $CHCl_3$	42 (α only)

accord with those obtained with the α/β mixture. Therefore, the same intermediate, the anomeric cation, was formed regardless of whether from the α-form, β-form or a mixture of α and β forms. The same cationic reaction was also carried out with the 2-deoxy-D-*erythro*-pentofuranosyl telluride **1b** as shown in Table 4.

From Table 3, the most striking observation is that the stereoselectivity is highly dependent on the reaction temperature. Excellent selectivity with 1-(phenylsulfonyl)indole ($\alpha:\beta = 10:90$) was obtained at −40 °C, while undesired selectivity ($\alpha:\beta = 85:15$) was obtained at −78 °C. As a result, it is very interesting that at high temperature (rt) the coupling reaction gave the β-form, while the reaction at low temperature afforded the α-form predominantly for the reactions with ribofuranosyl telluride **1a**. This behaviour could be explained by the fact that the kinetically controlled product is the α-form and that the thermodynamically controlled product is the β-form. However, this behaviour did not arise in 2-deoxy-D-*erythro*-pentofuranosyl telluride **1b**, and the α/β ratios did not vary significantly according to the temperature (Table 4).

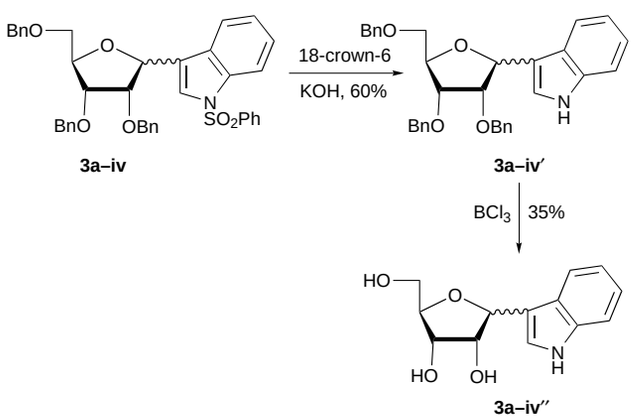
The effect of the amount of Lewis acid, BF_3, was also studied under various conditions. A minimum of 4 (mole) equivalents of BF_3 per equivalent of compound **1b** was necessary for successful completion of the reaction and 7 equivalents of BF_3 are effective for compound **1a**. Thus, the excess of BF_3 accelerated the reaction to completion.



Scheme 2 Epimerization of compound **3a–iv**

Next, epimerization of the product was performed by treatment with BF_3 in nitroethane at −15 °C (*cf.* Scheme 2). Here, the α-form **3a–iv(α)** could be converted into the β-form **3a–iv(β)** in the presence of BF_3. This fact suggests that the epimerization should take place through an ionic reaction pathway *via* ring opening at the 1,5-position in a sugar group. The result once again showed that the kinetically controlled product is the α-form and that the thermodynamically controlled product is the β-form.

The phenylsulfonyl group could be removed easily by treatment with potassium hydroxide in 1,4-dioxane solution containing 18-crown-6.[12] Next, the benzyl group was deprotected in the usual manner using boron trichloride[13] and the α- and β-form could be separated by recycling preparative HPLC (see Scheme 3).



Scheme 3 Deprotection of compound **3a–iv**

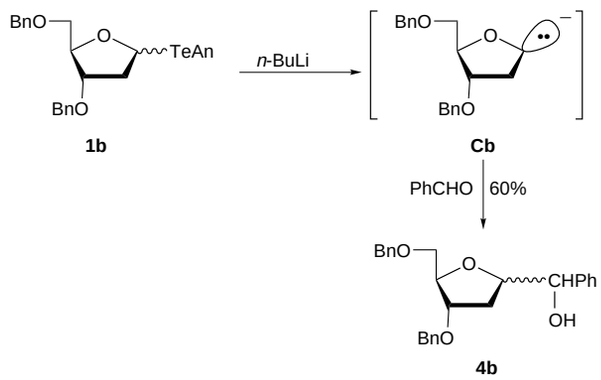
Formation of *C*-glycoside analogue *via* an anomeric anion from 2-deoxy-D-*erythro*-pentofuranosyl telluride

Complementary to the above reactions, anomeric anion C was also formed by the reaction of protected 2-deoxy-D-*erythro*-pentofuranosyl telluride **1b** and *n*-butyllithium, and subsequently was treated with an electrophile (benzaldehyde) to give the corresponding coupling product in 60% yield (Scheme 4).

As an extension of the above method, glucosyl tellurides were also prepared, and both the cationic and radical reactions were carried out.

Preparation of protected glucosyl tellurides and their reactivity

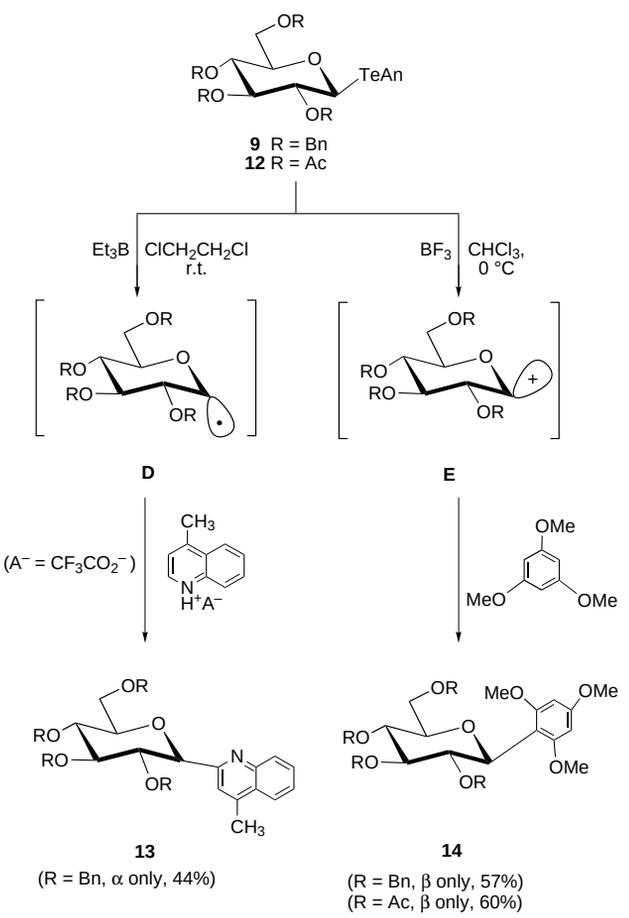
The reaction of 2,3,4,6-tetra-*O*-benzyl-D-glucose **7**,[14] easily available from D-glucose, with $^-$TeAn gave the glucosyl telluride **9** *via* the mesyl ester **8**. From acetobromoglucose **11**, prepared from pentaacetate **10**, was prepared glucosyl telluride **12**. Their



Scheme 4 Formation of *C*-glycoside analogue **4b** *via* an anomeric anion

characters are shown in Tables 5 and 6. Compared with ribofuranosyl tellurides, glycosyl tellurides were much more stable.

The radical reactions and cationic reactions of the glucosyl tellurides under the same conditions were carried out to give compounds **13** and **14**, respectively, in moderate yields (Scheme 5). Treatment of compound **9** with *n*-butyllithium in the presence of benzaldehyde gave the corresponding glycal in 68% yield *via* 1,2-elimination of the formed glucosyl anomeric anion.



Scheme 5 Formation of *C*-glucoside analogues **13** and **14**

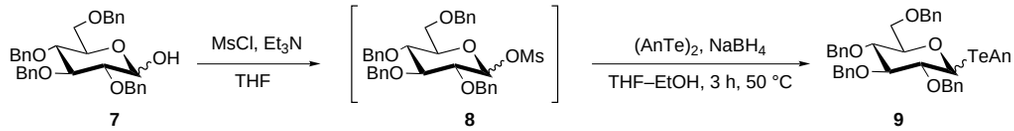
In conclusion, we have studied the chemical behaviour of sugar tellurides using the radicophilicity, nucleophilicity, and electrophilicity of the tellurium atom, and the synthetic use of *C*-nucleosides *via* the anomeric radical, anomeric cation and anomeric anion has been established.

Experimental

General

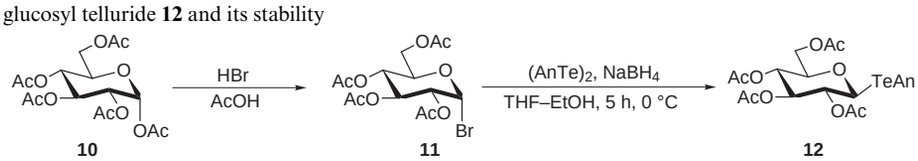
Mps were determined on a Yamato Model MP-21 and are

Table 5 Synthesis of glucosyl telluride **9** and its stability



9 Yield (%) (overall)	Mp/°C	Stability of sugar telluride (after one week at rt)	δ_H and δ_C (ppm, $CDCl_3$–$SiMe_4$ (anomer position)
85 ($\alpha:\beta = 1:3$)	72–73	decomposition 5% in $CDCl_3$ decomposition 0% in solid state	β:δ_H 5.01 (d, $J_{1,2}$ 9.9) δ_C 68.18

Table 6 Synthesis of glucosyl telluride **12** and its stability



12 Yield (%) (overall)	Mp/°C	Stability of sugar telluride (after one week at rt)	δ_H and δ_C (ppm, $CDCl_3$–$SiMe_4$) (anomer position)
58 (β only)	119	decomposition 80% in $CDCl_3$ decomposition 0% in solid state	β:δ_H 5.06 (d, $J_{1,2}$ 10.4) δ_C 66.04

uncorrected. IR spectra were recorded on a Hitachi 215 spectrometer. ^1H and ^{13}C NMR were measured [deuteriochloroform as an internal reference] with JNM-GSX-400 and JNM-GSX-500 spectrometers. Chemical shifts (δ) are expressed in ppm from $SiMe_4$ and *J*-values are in Hz. Carbon signals were assigned by DEPT† and INEPT.† 2D-NMR (COSY and NOESY‡) data were recorded on the JNM-GSX-500 spectrometer. Mass spectra were obtained on a JEOL HX-110 mass spectrometer. Optical rotations were measured on a JASCO DIP-370 polarimeter, and $[\alpha]_D$-values are given in units of 10^{-1} deg cm^2 g^{-1}. Elemental analysis was performed on a Perkin-Elmer 240 elemental analyser at the Chemical Analysis Center of Chiba University. TLC analysis was performed on thin-layer analytical plates of Kieselegel 60 F254 (E. Merck, Darmstadt) and Wakogel B-5F. Silica gel column chromatography was carried out on Wakogel C-200 or C-300. Reactions were carried out under dry argon unless otherwise stated. The following compounds were prepared according to the procedure described in the literature: 2,3,5-tri-*O*-benzyl-D-ribose **5a**,[9] 3,5-di-*O*-benzyl-2-deoxy-D-*erythro*-pentofuranose **5b**[10] and 2,3,4,6-tetra-*O*-benzyl-D-glucose **7**.[14] α-D-Glucose pentaacetate **10** is commercially available.

Preparation of sugar tellurides 1a, 1b and 9

The sugar derivative (1 mmol) (**5a**, **5b** or **7**) and triethylamine (1.5 mmol) were dissolved in dry THF (10 ml) in turn. The solution was then cooled at 0 °C and a solution of methanesulfonyl chloride (1.5 mmol) in dry THF (2.5 ml) was added dropwise to the sugar solution. The mixture was heated to 45 °C for 15 min and was then filtered through a Celite pad. The obtained filtrate was evaporated under reduced pressure to afford a light-yellow viscous oil. This compound was then treated with *p*-methoxyphenyl telluride anion prepared by the $NaBH_4$ reduction of An_2Te_2 (0.75 mmol in THF 8 ml and EtOH 4 ml). The mixture was stirred for 6 h at 50 °C. After evaporation, the organic layer was extracted with $CHCl_3$ (3 × 10 ml) and dried over Na_2SO_4. The solution was evaporated to yield the crude product, which was purified by column chromatography ($CHCl_3$) to give the sugar telluride in moderate yield.

***p*-Methoxyphenyl 2,3,5-tri-*O*-benzyl-D-ribofuranosyl telluride 1a.** Oil; ν_{max}(NaCl) 3000, 2850, 1720, 1580, 1480, 1440, 1280, 1240, 1020, 820 and 740 cm^{-1}; δ_H(400 MHz, $CDCl_3$).

α-Form.—3.45–3.48 (1 H, dd, *J* 4.1, 5′-H[a]), 3.53–3.57 (1 H, dd, *J* 3.2, 5′-H[b]), 3.79 (3 H, s, ArOCH_3), 4.15–4.16 (2 H, 2′- and 3′-H), 4.27 (1 H, m, 4′-H), 4.32–4.57 (6 H, m, benzyl H), 5.92 (1 H, d, $J_{1',2'}$ 1.4, 1′-H), 6.71 (2 H, d, *J* 8.0, ArH), 7.17–7.37 (15 H, m, Ph) and 7.65 (2 H, d, *J* 8.7, ArH); δ_C(125 MHz; $CDCl_3$) 55.11 (p, CH_3), 69.43 (s, Ar*C*H_2), 72.38 (s, Ar*C*H_2), 73.2 (s, Ar*C*H_2), 73.3 (s, Ar*C*H_2), 77.0 (t, sugar-C), 78.53 (t, sugar-C), 80.02 (t, sugar-C), 80.08 (t, sugar-C), 101.65 (q, Ar), 115.24 (t, Ar), 127.43 (t, Ph), 127.53 (t, Ph), 127.57 (t, Ph), 127.75 (t, Ph), 127.92 (t, Ph), 128.18 (q, Ar), 137.59 (q, Ar), 137.58 (q, Ar), 142.41 (t, Ar) and 160.05 (q, Ar).

β-Form.—3.57–3.68 (1 H, dd, *J* 3.8, 5′-H), 3.65–3.68 (1 H, dd, *J* 3.2, 5′-H[b]), 3.78 (3 H, ArOCH_3) 3.95 (1 H, t, *J* 5.3, 3′-H), 4.01 (1 H, t, *J* 5.5, 2′-H), 4.35 (1 H, m, *J* 5.3, 4′-H), 4.52–4.76 (6 H, m, benzyl H), 6.44 (1 H, d, $J_{1',2'}$ 5.1, 1′-H), 6.75 (2 H, d, *J* 8.7, ArH), 7.23–7.40 (15 H, m, Ph) and 7.76 (2 H, d, *J* 8.7, ArH); δ_C(125 MHz; $CDCl_3$) 55.11 (p, CH_3), 68.69 (s, Ar*C*H_2), 72.73 (s, Ar*C*H_2), 73.26 (s, Ar*C*H_2), 73.39 (s, Ar*C*H_2), 77.58 (t, sugar-C), 79.12 (t, sugar-C), 79.19 (t, sugar-C), 80.42 (t, sugar-C), 103.62 (q, Ar), 114.93 (t, Ar), 127.63 (t, Ph), 127.67 (t, Ph), 127.80 (t, Ph), 127.94 (t, Ph), 128.33 (t, Ph), 137.58 (q, Ar), 137.97 (q, Ar), 138.00 (q, Ar), 140.92 (t, Ar) and 159.56 (q, Ar) [HRMS (FAB, NBA)§ Calc. for $C_{33}H_{34}{}^{130}TeO_5$: *M*, 640.1472. Found for $C_{33}H_{34}{}^{130}TeO_5$: *M*, 640.1468; Calc. for $C_{33}H_{34}{}^{128}TeO_5$: *M*, 638.1454. Found for $C_{33}H_{34}{}^{128}TeO_5$: *M*, 638.1458; Calc. for: $C_{33}H_{34}{}^{126}TeO_5$: *M*, 636.1446. Found for $C_{33}H_{34}{}^{126}TeO_5$: *M*, 636.1462].

3′,5′-Di-*O*-benzyl-2′-deoxy-D-*erythro*-pentofuranosyl *p*-methoxyphenyl telluride 1b. Oil; ν_{max}(neat) 3100, 2920, 2860, 1580, 1500, 1460, 1360, 1280, 1250, 1100, 740 and 700 cm^{-1}; δ_H(500 MHz; $CDCl_3$) 2.25 (1 H, ddd, 2′-H[a]), 2.47 (1 H, ddd, 2′-H[b]), 3.5 (2 H, m, 5′H_2), 3.78 (3H, s, OMe) or 3.80 (3 H, s, OMe), 3.96 (1 H, m, 3′-H), 4.25 (1 H, m, 4′-H), 5.92 (dd, *J* 5.8 and 8.6, 1′-H) or 6.58 (1 H, d, *J* 6.0, 1′-H), 6.73 (d, *J* 8.5, ArH), 7.23–7.37 (10 H, m, Ph) and 7.73 (d, *J* 8.0, ArH) [HRMS (FAB,

† DEPT = distortionless enhancement by polarization transfer. INEPT = intensive nuclei enhancement by polarization transfer.

‡ COSY = chemical-shift correlation spectroscopy. NOESY = nuclear Overhauser enhancement spectroscopy.

§ HRMS = high-resolution mass spectrometery; FAB = fast-atom bombardment; NBA = *m*-nitrobenzyl alcohol matrix.

NBA, KI) Calc. for $C_{26}H_{28}KO_4{}^{130}Te$: *m/z*, 573.0671. Found for *m/z*, 573.0687; Calc. for $C_{26}H_{28}KO_4{}^{128}Te$: *m/z*, 571.0670. Found for *m/z*, 571.0741; Calc. for $C_{26}H_{28}KO_4{}^{126}Te$: *m/z*, 569.0663. Found for *m/z*, 569.0783].

4-Methoxyphenyl 2′,3′,4′,6′-tetra-*O*-benzyl-β-D-glucopyranosyl) telluride 9. Mp 72–73 °C; $[\alpha]_D^{19}$ −23.9 (*c* 1.0, $CHCl_3$); ν_{max}(neat) 2905, 2865, 1585, 1490, 1455, 1360, 1285, 1245, 1070, 910, 735 and 700 cm^{-1}; δ_H(500 MHz, $CDCl_3$) 3.42 (1 H, dd, 4′-H), 3.50 (1 H, dd, $J_{1',2'}$ 10.6, $J_{2',3'}$ 8.6, 2′-H), 3.60–3.80 (3 H, m, 5′-H and 6′-H_2), 3.64 (1 H, dd, $J_{2',3'}$ 6.0, $J_{3',4'}$ 6.0, 3′-H), 3.70 (3 H, s, OMe), 4.50 (1 H, d, J_{gem} 11.9, CH_2Ph), 4.58 (1 H, d, J_{gem} 11.9, CH_2Ph), 4.60 (1 H, d, J_{gem} 10.7, CH_2Ph), 4.78 (1 H, d, J_{gem} 10.4, CH_2Ph), 4.81 (1 H, d, J_{gem} 10.7, CH_2Ph), 4.83 (1 H, d, J_{gem} 10.4, CH_2Ph), 4.85 (1 H, d, CH_2Ph), 4.88 (1 H, d, J_{gem} 11.0, CH_2Ph), 5.01 (1 H, d, $J_{1',2'}$ 10.4, 1′-H), 6.63 (2 H, d, *J* 8.9, 3- and 5-H), 7.19–7.40 (20 H, m, CH_2*Ph*), 7.76 (2 H, d, *J* 8.9, 2- and 6-H). Couplings were observed in pairs for the following benzyl protons: 4.50, 4.58, 4.60, 4.81, 4.78, 4.83 and 4.85, 4.88; δ_C(125 MHz; $CDCl_3$) 55.01 (p, OMe), 68.18 (t, 1′-C), 68.93 (s, 6′-C), 73.38 (s, *C*H_2Ph), 74.91 (s, *C*H_2Ph), 75.01 (s, *C*H_2Ph), 75.68 (s, *C*H_2Ph), 77.87 (t, 3′-C), 81.57 (t, 4′-C), 82.11 (t, 2′-C), 86.97 (t, 5′-C), 100.77 (q, Ar), 115.02 (t, Ar), 127.47 (t, Ph), 127.62 (t, Ph), 127.67 (t, Ph), 127.71 (t, Ph), 127.78 (t, Ph), 127.83 (t, Ph), 128.16 (t, Ph), 128.25 (t, Ph), 128.29 (t, Ph), 128.35 (t, Ph), 128.42 (t, Ph), 137.92 (q, Ph), 138.08 (q, Ph), 138.28 (q, Ph), 138.36 (q, Ph), 141.55 (t, Ar), 141.70 (t, Ar), 159.99 (q, Ar) and 138.44 (q, Ph) [HRMS (FAB) Calc. for $C_{41}H_{41}O_6{}^{130}Te$: (*M* + H), 759.1965. Found for $C_{41}H_{41}O_6{}^{130}Te$: $(M + H)^+$, 759.1910].

Preparation of sugar telluride 12

The sugar derivative **11** (1.23 g, 3.00 mmol) was dissolved in dry THF (2 ml). The solution was then treated with the solution of *p*-methoxyphenyl telluride anion prepared by the $NaBH_4$ (0.15 g) reduction of An_2Te_2 (1.09 g, 2.25 mmol in THF 15 ml and EtOH 8 ml) at 0 °C. The mixture was stirred for 4 h at 0 °C. After evaporation, the organic layer was extracted with $CHCl_3$ (3 × 10 ml) and dried over Na_2SO_4. The solution was evaporated to yield the crude product, which was purified by column chromatography (hexane–AcOEt 1:1) to give the sugar telluride **12** in 84% yield.

4-Methoxyphenyl 2′,3′,4′,6′-tetra-*O*-acetyl-β-D-glucopyranosyl telluride 12. Mp 119 °C; $[a]_D^{19}$ −44.4 (*c* 1.0, $CHCl_3$); ν_{max}(neat) 2940, 1745, 1585, 1490, 1380, 1225, 1040, 920 and 820 cm^{-1}; δ_H(500 MHz; $CDCl_3$) 1.98 (3 H, s, Me), 2.00 (3 H, s, Me), 2.01 (3 H, s, Me), 2.06 (3 H, s, Me), 3.60 (1 H, ddd, $J_{4',5'}$ 9.6, $J_{5',6'a}$ 2.8, $J_{5',6'b}$ 3.8, 5′-H), 3.80 (3 H, s, OMe), 4.14 (1 H, dd, $J_{5',6'a}$ 2.6, J_{gem} 12.4, 6′-H^a), 4.18 (1 H, dd, $J_{5',6'b}$ 4.3, J_{gem} 11.4, 6′-H^b), 5.00 (1 H, dd, $J_{1',2'}$ 10.6, $J_{2',3'}$ 8.7, 2′-H), 5.00 (1 H, dd, $J_{3',4'}$ 9.8, $J_{4',5'}$ 9.8, 4′-H), 5.06 (1 H, d, $J_{1',2'}$ 10.4, 1′-H), 5.14 (1 H, dd, $J_{2',3'}$ 9.2, $J_{3',4'}$ 9.2, 3′-H), 6.79 (2 H, d, *J* 8.9, 3- and 5-H) and 7.75 (2 H, d, *J* 8.9, 2- and 6-H); δ_C(125 MHz; $CDCl_3$) 20.58 (p, *Me*), 20.63 (p, *Me*), 20.74 (p, *Me*), 20.92 (p, *Me*), 55.17 (p, OMe), 62.17 (s, 6′-C), 66.04 (t, 1′-C), 68.32, 72.31 (t, 2′-C, 4′-C), 73.65 (t, 3′-C), 78.32 (t, 5′-C), 100.28 (q, Ar), 115.17 (t, Ar), 142.48 (t, Ar), 160.55 (q, Ar), 169.42 (q, CO), 170.23 (q, CO) and 170.60 (q, CO) (Found: C, 44.9; H, 4.6. Calc. for $C_{21}H_{26}O_{10}Te$: C, 44.56; H, 4.63%).

Typical procedure for *C*-nucleoside analogues *via* anomeric radical from sugar tellurides

The sugar telluride and 7 equivalents of a heteroaromatic base, which was protonated by CF_3CO_2H (TFA), were dissolved in dry dichloromethane (4 ml). To the solution were added 4 equivalents of triethylborane as THF solution (1.0 M). After 2 h and 4 h, 2 equivalents of triethylborane were added, respectively. Then the mixture was stirred for 4 h at rt under aerobic conditions. The resulting solution was quenched with saturated aq. $NaHCO_3$. The organic layer was extracted with $CHCl_3$ and the extract was dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by PLC on silica gel (hexane–EtOAc 2:1).

4-Methyl-2-(2′,3′,5′-tri-*O*-benzyl-D-ribofuranosyl)quinoline 2a–i.[3d] Oil; ν_{max}(neat) 2840, 1590, 1445, 1350, 1205, 1120, 1085, 1045, 1025, 910, 740 and 700 cm^{-1}.

α-Form.—δ_H 2.68 (3 H, s, base Me), 3.67 (1 H, dd, J_{gem} 10.8, $J_{4',5'a}$ 4.2, 5′-H^a), 3.84 (1 H, dd, J_{gem} 10.8, $J_{4',5'b}$ 2.6, 5′-H^b), 3.97 (1 H, d, J_{gem} 11.7, CH_2O), 4.14 (1 H, d, J_{gem} 11.7, CH_2O), 4.56 (1 H, dd, $J_{3',4'}$ 8.6, $J_{2',3'}$ 4.0, 3′-H), 4.64 (1 H, d, J_{gem} 12.1, CH_2O), 5.36 (1 H, d, $J_{1',2'}$ 2.8, 1′-H), 6.80 (2 H, d, *J* 7.0, Ph), 7.10–6.99 (3 H, m, Ph), 7.35–7.25 (10 H, m, Ph), 7.55 (1 H, dd, $J_{5,6}$ 8.2, $J_{6,7}$ 7.0, 6-H), 7.68 (1 H, br s, 3-H), 7.71 (1 H, dd, $J_{7,8}$ 8.2, $J_{6,7}$ 7.0, 7-H) and 7.99–8.02 (2 H, m, 5- and 8-H). NOE (1′-H↔3′-H) was observed; δ_C(125 MHz; $CDCl_3$) 18.7 (p, base Me), 70.1 (s, C-5′), 72.6, 73.2 and 73.5 (s, CH_2O), 79.4 (t, C-3′), 80.0 (t, C-2′), 80.4 (t, C-4′), 84.5 (t, C-1′), 121.3 (t, C-3), 123.8 (t, C-6), 125.9 (t, C-5), 128.3–127.3 (t, Ph), 128.4 (t, C-4a), 129.0 (t, C-7), 129.4 (t, C-8), 137.7, 137.8 and 138.3 (q, Ph), 144.2 (q, C-4), 147.1 (q, C-8a) and 159.1 (q, C-2).

β-Form.—Mp 67–68 °C; ν_{max}(KBr) 2850, 1585, 1440, 1345, 1200, 1120, 1080, 905, 735 and 700 cm^{-1} δ_H 2.48 (3 H, s, base Me), 3.73 (1 H, dd, J_{gem} 10.8, $J_{4',5'b}$ 3.8, 5′-H^a), 3.90 (1 H, dd, J_{gem} 0.8, $J_{4',5'b}$ 2.6, 5′-H^b), 4.05 (1 H, dd, $J_{3',4'}$ 7.1, $J_{2',3'}$ 5.1, 3′-H), 4.28 (1 H, dd, $J_{2',3'}$ 5.1, $J_{1',2'}$ 3.3, 2′-H), 4.38 (1 H, d, J_{gem} 11.7, CH_2O), 4.45–4.49 (1 H, m, 4′-H), 4.57 (1 H, d, J_{gem} 10.3, CH_2O), 4.60 (1 H, d, J_{gem} 10.3, CH_2O), 4.65 (1 H, d, J_{gem} 11.9, CH_2O), 4.77 (1 H, d, J_{gem} 12.1, OCH_2), 4.84 (1 H, d, J_{gem} 12.1, CH_2O), 5.38 (1 H, d, $J_{1',2'}$ 3.3, 1′-H), 7.21–7.33 (13 H, m, Ph), 7.40 (1 H, br s, 3-H), 7.39–7.41 (2 H, m, Ph), 7.53 (1 H, ddd, $J_{5,6}$ 8.4, $J_{6,7}$ 0.9, 6-H), 7.70 (1 H, ddd, $J_{7,8}$ 8.3, $J_{6,7}$ 7.0, $J_{5,\ 7}$ 0.9, 7-H), 7.94 (1 H, ddd, $J_{5,6}$ 8.4, $J_{6,7}$ 0.9, 5-H) and 8.08 (1 H, br d, $J_{7,8}$ 8.3, 8-H). NOE (1′-H↔4′-H) was observed; δ_C(125 MHz; $CDCl_3$) 18.6 (p, base Me), 69.8 (s, C-5′), 71.4, 72.0 and 73.0 (s, CH_2O), 77.1 (t, C-3′), 81.1 (t, C-2′), 81.3 (t, C-4′), 85.5 (t, C-1′), 119.5 (t, C-3), 123.7 (t, C-6), 125.9 (t, C-5), 128.4–127.6 (t, Ph), 127.5 (t, C-4a), 129.0 (t, C-7), 129.8 (t, C-8), 138.0, 138.4 and 137.9 (q, Ph), 144.8 (q, C-4), 147.5 (q, C-8a) and 160.1 (q, C-2); (FAB) *m/z* 546 (M + H).

Methyl 2-(2′,3′,5′-tri-*O*-benzyl-D-ribofuranosyl)isonicotinate 2a–ii.[3d] Oil; ν_{max}(KBr) 3000, 2840, 1720, 1300, 1210, 1120, 1100, 740 and 700 cm^{-1}. *α-Form.*—δ_H 3.82–3.92 (2 H, m, 5′-H), 3.93 (3 H, s, CO_2Me), 4.05 (1 H, d, J_{gem} 11.8, CH_2O), 4.23 (1 H, d, J_{gem} 11.8, CH_2O), 4.29 (1 H, dd, $J_{3',4'}$ 8.5, $J_{2',3'}$ 4.1, 3′-H), 4.38 (1 H, m, 4′-H), 4.50 (1 H, dd, $J_{2',3'}$ 4.1, $J_{2',1'}$ 2.8, 2′-H), 4.55 (1 H, d, J_{gem} 11.8, CH_2O), 4.62 (1 H, d, J_{gem} 12.1, CH_2O), 5.31 (1 H, d, $J_{1',2'}$ 2.8, 1′-H), 6.89 (2 H, d, *J* 6.1, Ph), 7.17–7.12 (3 H, m, Ph), 7.35–7.26 (10 H, m, Ph), 7.75 (1 H, d, *J* 5.0, 5-H), 8.18 (1 H, s, 3-H) and 8.64 (1 H, d, $J_{5,6}$ 5.0, 6-H). NOE (1′-H↔3′-H) was observed: δ_C(125 MHz; $CDCl_3$) 52.6 (p, base CO_2*Me*), 69.8 (s, C-5′), 72.6, 73.2 and 73.5 (s, CH_2O), 79.0 (t, C-3′), 80.0 (t, C-2′), 80.3 (t, C-4′), 83.7 (t, C-1′), 121.6 (t, C-5), 121.9 (t, C-3), 127.4–128.4 (t, Ph), 137.6, 137.7 and 137.8 (q, Ph), 138.2 (q, C-4), 149.0 (t, C-6), 160.2 (q, C-2) and 165.8 (q, base CO).

β-Form.—Oil; δ_H 3.68 (1 H, dd, J_{gem} 10.7, $J_{4',5'b}$ 4.1, 5′-H^b), 3.83 (1 H, dd, J_{gem} 10.7, $J_{4',5'a}$ 3.0, 5′-H^a), 3.83 (3 H, s, CO_2Me), 4.00 (1 H, dd, $J_{3',4'}$ 7.2, $J_{2',3'}$ 5.0, 3′-H), 4.18 (1 H, dd, $J_{2',3'}$ 5.0, $J_{1',2'}$ 3.3, 2′-H), 4.41 (1 H, d, J_{gem} 11.8, CH_2O), 4.45–4.43 (1 H, m, 4′-H), 4.56 (1 H, d, J_{gem} 11.8, CH_2O), 4.68 (1 H, d, J_{gem} 12.1, CH_2O), 4.76 (1 H, d, J_{gem} 12.1, CH_2O), 5.28 (1 H, d, $J_{1',2'}$ 3.4, 1′-H), 7.23–7.36 (15 H, m, Ph), 7.73 (1 H, d, *J* 4.5, 5-H), 8.18 (1 H, s, 3-H) and 8.73 (1 H, d, $J_{5,6}$ 5.0, 6-H). NOE (1′-H↔4′-H, 1′-H↔2′-CH_2O) was observed; δ_C(125 MHz; $CDCl_3$) 52.5 (p, base CO_2*Me*), 69.5 (s, C-5′), 71.6, 73.2 and 73.3 (s, CH_2O), 77.5 (t, C-3′), 81.1 (t, C-2′), 81.5 (t, C-4′), 84.6 (t, C-1′), 120.5 (t, C-5), 121.7 (t, C-3), 128.4–127.4 (t, Ph), 137.8, 137.9 and 138.0 (q, Ph), 138.3 (q, C-4), 149.0 (t, C-6), 161.3 (q, C-2), 165.7 (q, base CO); MS (FAB) [Calc. for $C_{33}H_{34}NO_6$: (*M* + H), 540.2386. Found for $C_{33}H_{34}NO_6$: *M*, 540.2393].

2-(3′,5′-Di-*O*-benzyl-2′-deoxy-D-*erythro*-pentofuranosyl)-4-methylquinoline 2b–i. Oil; ν_{max}(neat) 2920, 2870, 2350, 1740,

1600, 1450, 1350, 1100, 740 and 700 cm^{-1}; δ_H 1.98–2.03 (1 H, m, 2′-H^a), 2.24–2.31 (1 H, m, 2′-H^b), 2.61 (3 H, s, base Me), 3.46–3.61 (2 H, m, 5′-H_2), 3.97 (1 H, m, 3′-H), 4.23 (1 H, m, 4′-H), 4.46–4.64 (2 H, m, CH_2O), 5.19 (1 H, d, $J_{1',2'}$ 5.4, 1′-H), 7.07 (1 H, s, 3-H), 7.2–7.34 (10 H, m, Ph), 7.55 (1 H, t, *J* 7.9 and 7.0, 6-H), 7.70 (1 H, t, *J* 6.8 and 8.3, 7-H), 7.95 (1 H, d, *J* 8.0, 5-H) and 8.08 (1 H, d, *J* 2.9, 8-H); HRMS (FAB, NBA) [Calc. for $C_{29}H_{30}NO_3$: (*M* + H), 440.2226. Found for $C_{29}H_{30}NO_3$: $(M + H)^+$, 440.2210].

Methyl 2-(3′,5′-di-*O*-benzyl-2′-deoxy-D-*erythro*-pentofuranosyl)isonicotinate 2b–ii. Oil; ν_{max}(neat) 2900, 2850, 1740, 1630, 1480, 1300, 740 and 700 cm^{-1}; δ_H(500 MHz, $CDCl_3$) 2.01 (1 H, m, 2′-H), 2.21 (1 H, m, 2′-H), 3.25–3.45 (2 H, m, 5-H_2), 3.98 (3 H, s, CO_2Me), 4.10 (1 H, dd, *J* 5.1 and 4.0, 4′-H), 4.20 (1 H, dd, *J* 4.9 and 6.4, 3′-H), 4.41–4.55 (4 H, m, benzyl-H), 5.46 (1 H, d, 1′-H), 7.71 (1 H, d, 6-H), 8.26 (1 H, s, 5-H) and 9.15 (1 H, d, 3-H); HRMS (FAB, NBA) [Calc. for $C_{26}H_{27}NO_5$: *M*, 433.1887. Found for $C_{26}H_{27}NO_5$: M^+, 433.1873].

4-Methyl-2-(2′,3′,4′,6′-tetra-*O*-benzyl-α-D-glucopyranosyl)quinoline 13. Oil; $[\alpha]_D^{20}$ +18.2 (*c* 1.0, $CHCl_3$); ν_{max}(neat) 3030, 2870, 1600, 1500, 1455, 1360, 1210, 1090, 1030, 720 and 700 cm^{-1}; δ_H(500 MHz; $CDCl_3$) 2.67 (3 H, s, Me), 3.69 (1 H, dd, $J_{5',6'a}$ 3.6, J_{gem} 10.7, 6′-H^a), 3.75 (1 H, dd, $J_{5',6'b}$ 4.6, J_{gem} 10.7, 6′-H^b), 3.79 (1 H, dd, $J_{3',4'}$ 6.4, $J_{4',5'}$ 8.6, 4′-H), 4.15 (1 H, d, J_{gem} 12.1, CH_2Ph), 4.16 (1 H, dd, $J_{1',2'}$ 4.7, $J_{2',3'}$ 6.3, 2′-H), 4.39 (1 H, d, J_{gem} 12.4, CH_2Ph), 4.44 (1 H, ddd, $J_{4',5'}$ 8.6, $J_{5',6'a}$ 3.3, $J_{5',6'b}$ 4.6, 5′-H), 4.45 (1 H, dd, $J_{2',3'}$ 6.4, $J_{3',4'}$ 6.4, 3′-H), 4.49 (1 H, d, J_{gem} 12.1, CH_2Ph), 4.54 (1 H, d, J_{gem} 11.4, CH_2Ph), 4.58 (1 H, d, J_{gem} 12.1, CH_2Ph), 4.68 (1 H, d, J_{gem} 11.4, CH_2Ph), 4.76 (1 H, d, J_{gem} 11.3, CH_2Ph), 4.79 (1 H, d, J_{gem} 11.6, CH_2Ph), 5.18 (1 H, d, $J_{1',2'}$ 4.6, 1′-H), 7.00–7.33 (20 H, m, CH_2*Ph*), 7.48 (1 H, s, 3-H), 7.54 (1 H, ddd, $J_{5,6}$ 8.3, $J_{6,7}$ 6.9, $J_{6,8}$ 1.2, 6-H), 7.68 (1 H, ddd, $J_{6,7}$ 6.9, $J_{7,8}$ 8.4, $J_{5,7}$ 1.4, 7-H), 7.98 (1 H, dd, $J_{5,6}$ 8.2, $J_{5,7}$ 0.9, 5-H) and 8.07 (1 H, dd, $J_{7,8}$ 8.5, $J_{6,8}$ 0.7, 8-H). Couplings were observed in pairs of the following benzyl protons: 4.15, 4.39, 4.49, 4.58, 4.54, 4.76 and 4.68, 4.79; δ_C(125 MHz; $CDCl_3$) 18.66 (p, Me), 69.34 (s, 6′-C), 73.13 (s, *C*H_2Ph), 73.36 (s, *C*H_2Ph), 73.58 (s, *C*H_2Ph), 73.63 (t, 5′-C), 75.91 (t, 1′-C), 77.10 (t, 4′-C), 79.30 (t, 2′-C), 80.02 (t, 3′-C), 122.34 (t, 3-C), 123.56 (t, 5-C), 125.95 (t, 6-C), 127.41 (t, Ph), 127.46 (t, Ph), 127.51 (t, Ph), 127.55 (t, Ph), 127.57 (t, Ph), 127.78 (t, Ph), 127.89 (t, Ph), 127.92 (t, Ph), 128.08 (t, Ph), 128.24 (t, Ph), 128.29 (t, Ph), 128.34 (t, Ph), 128.76 (t, 7-C), 130.20 (t, 8-C), 138.12 (q, Ph), 138.26 (q, Ph), 138.45 (q, Ph), 138.57 (q, Ph), 144.03 (q, Ar), 147.12 (q, Ar) and 158.98 (q, Ar); HRMS (FAB) [Calc. for $C_{44}H_{44}NO_5$: (*M* + H), 666.3219. Found: $(M + H)^+$, 666.3196].

Typical procedure for *C*-nucleoside analogues *via* anomeric cation from sugar tellurides

To a solution of ribofuranosyl telluride and 3 equivalents of aromatic heterocycle in dry $CHCl_3$ were added 5 equivalents of BF_3 dropwise. After being stirred for 1 h the reaction mixture was treated with aq. $NaHCO_3$, extracted with $CHCl_3$, and the extract was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by PLC on silica gel (hexane–EtOAc 2 : 1).

3-(2′,3′,5′-Tri-*O*-benzyl-D-ribofuranosyl)benzothiophene 3a–iii. Oil; ν_{max}(neat) 2850, 1440 and 1080 cm^{-1}; δ_H(500 MHz; $CDCl_3$) as follows.

α-Form.—δ_H 3.66 (1 H, dd, $J_{4',5'a}$ 3.3, J_{gem} 11.0, 5′-H^a), 3.82 (1 H, dd, $J_{4',5'a}$ 2.5, J_{gem} 11.0, 5′-H^b), 4.14 (1 H, dd, $J_{1',2'}$ 3.3, $J_{2',3'}$ 3.8, 2′-H), 4.28 (1 H, dd, $J_{2',3'}$ 3.8, $J_{3',4'}$ 3.3, 3′-H), 4.29 (1 H, ddd, $J_{3',4'}$ 3.3, $J_{4',5'a}$ 3.3, $J_{4',5'b}$ 8.0, 4′-H), 4.37–4.62 (6 H, m, benzyl-H), 5.46 (1 H, d, $J_{1',2'}$ 3.0, 1′-H) and 6.84–7.37 (20 H, m, benzothiophene 2-, 5-, 6-, 7-H and Ph).

β-Form.—δ_H 3.63 (2 H, dd, $J_{4',5'a}$ 3.5, J_{gem} 10.6, 5′-H^a), 3.77 (1 H, dd, $J_{4',5'a}$ 8.0, J_{gem} 10.8, 5′-H^b), 4.01 (1 H, dd, *J* 5.3, *J* 5.4, 2′-H), 4.15 (1 H, dd, $J_{2',3'}$ 5.1, $J_{3',4'}$ 5.2, 3′-H), 4.37 (1 H, dd, 4′-H), 4.44–4.67 (6 H, m, benzyl-H), 5.39 (1 H, d, $J_{1',2'}$ 5.6, 1′-H), 6.84–7.83 (20 H, m, benzothiophene 2-, 3-, 5-, 6-, 7-, 8-H and Ph); HRMS (FAB, NBA) (Calc. for $C_{34}H_{33}O_4S$: *M*, 537.2021. Found for $C_{34}H_{33}O_4S$: M^+, 537.2023).

1-Phenylsulfonyl-3-(2′,3′,5′-tri-*O*-benzyl-D-ribofuranosyl)-indole 3a–iv. Oil; ν_{max}(neat) 2820, 1440, 1360, 1170 and 730 cm^{-1}; δ_H(500 MHz; $CDCl_3$) as follows.

α-Form.—δ_H 3.51 (1 H, dd, J_{gem} 10.7, $J_{4',5'}$ 3.3, 5′-H), 3.76 (1 H, dd, J_{gem} 10.7, $J_{4',5'}$ 2.8, 5′-H), 3.92–4.02 (2 H, m, 2′- and 3′-H), 4.28–4.62 (7 H, m, 4′-H, benzyl-H), 5.27 (1 H, d, $J_{1',2'}$ 3.2, 1′-H), 6.87 (2 H, d, *J* 7.4, Ph), 7.04–8.01 (23 H, m, indole 2-, 4-, 5-, 6-, 7-H, SO_2Ph and Ph).

β-Form.—δ_H 3.60 (1 H, dd, J_{gem} 10.5, $J_{4',5'}$ 3.6, 5′-H), 3.70 (1 H, dd, J_{gem} 10.5, $J_{4',5'}$ 3.6, 5′-H), 4.03 (1 H, dd, $J_{1',2'}$ 6.6, $J_{2',3'}$ 5.4, 2′-H), 4.08 (1 H, dd, $J_{2',3'}$ 2.9, $J_{3',4'}$ 4.1, 3′-H), 4.32 (1 H, m, 4′-H), 4.39–4.68 (6 H, m, benzyl-H), 5.19 (1 H, d, $J_{1',2'}$ 5.9, 1′-H), 7.04–7.99 (25 H, m, indole 2-, 4-, 5-, 6-, 7-H, SO_2Ph and Ph).

1,3,5-Trimethoxy-2-(2′,3′,5′-tri-*O*-benzyl-β-D-ribofuranosyl)-benzene 3a–v. ν_{max}(KBr) 2900, 2360, 1610, 1500, 1460, 1410, 1350, 1220, 1200, 1150, 1120, 1080, 1040, 810, 750 and 700 cm^{-1}; δ_H(500 MHz; $CDCl_3$) 3.61 (3 H, s, OMe), 3.64 (1 H, dd, *J* 5.1, 5′-H), 3.70–3.74 (1 H, dd, *J* 3.4 and 11.2, 5′-H), 3.80 (3 H, s, OMe), 4.05–4.09 (1 H, t, *J* 6.0 and 7.5, 3′-H), 4.17–4.20 (1 H, m, 4′-H), 4.24–4.26 (1 H, t, *J* 4.6 and 6.1, 2′-H), 4.35–4.72 (6 H, m, benzyl-CH_2), 5.55 (1 H, d, $J_{1',2'}$ 4.4, 1′-H), 6.06 (2 H, s, ArH) and 7.19–7.37 (15 H, m, Ph). NOE (1′-H↔4′-H) was observed; δ_C(125 MHz; $CDCl_3$) 55.26 (p, OMe), 55.46 (p, OMe), 70.00 (s, CH_2), 71.15 (s, CH_2), 71.81 (s, CH_2), 73.19 (s, CH_2), 77.31 (t, sugar-C), 77.53 (t, sugar-C), 78.60 (t, sugar-C), 80.05 (t, sugar-C), 90.88 (t, Ar), 107.95 (q, Ph), 127.26 (t, Ar), 127.35 (t, Ar), 127.56 (t, Ar), 127.98 (t, Ar), 128.08 (t, Ar), 128.12 (t, Ar), 128.16 (t, Ar), 128.20 (t, Ar), 138.24 (q, Ph), 138.30 (q, Ph), 138.31 (q, Ph), 159.72 (q, Ph) and 161.34 (q, Ph); HRMS (FAB, NBA) [Calc. for $C_{35}H_{39}O_7$: (*M* + H), 571.2696. Found: $(M + H)^+$, 571.2695] (Calc. for $C_{35}H_{38}O_7$: C, 73.61; H, 6.71. Found: C, 73.3; H, 6.8%).

3-(3′,5′-Di-*O*-benzyl-2′-deoxy-D-*erythro*-pentofuranosyl)-benzothiophene 3b–iii. Oil; ν_{max}(neat) 3050, 2920, 2880, 2360, 1500, 1460, 1360, 1180, 1100, 840 and 720 cm^{-1}; δ_H(500 MHz; $CDCl_3$) as follows.

α-Form.—δ_H 2.28–2.32 (1 H, m, *J* 6.3 and 6.5, 2′-H^a), 2.72–2.80 (1 H, m, *J* 6.5 and 7.2, 2′-H^b), 3.60–3.70 (2 H, m, *J* 4.2, 5.2 and 6.3, 5′-H), 4.25–4.32 (1 H, dd, *J* 5.6 and 11.30, 3′-H), 4.38 (1 H, m, *J* 4.3 and 8.3, 4′-H), 4.47–4.61 (4 H, m, CH_2), 5.47 (1 H, dd, *J* 6.7 and 6.8, 1′-H) and 7.2~7.9 (15 H, m, Ph, 2-, 5-, 6-, 7- and 8-H).

β-Form.—Mp 56–58 °C; δ_H 2.15 (1 H, m, *J* 5.8 and 10.3, 2′-H^a), 2.50 (1 H, m, *J* 1.2 and 5.3, 2′-H^b), 3.54–3.59 (1 H, dd, *J* 5.8 and 10.3, 5′-H), 3.66–3.71 (1 H, dd, *J* 4.5 and 10.1, 5′-H), 4.20–4.23 (1 H, d, *J* 5.8, 3′-H), 4.35 (1 H, m, *J* 2.0 and 5.1, 4′-H), 4.58–4.61 (4 H, m, CH_2), 5.49 (1 H, dd, *J* 5.3 and 10.3, 1′-H) and 7.2–7.8 (15 H, m, Ph, 2-, 5-, 6-, 7- and 8-H); HRMS (FAB, NBA) (Calc. for $C_{27}H_{26}O_3S$: *M*, 430.1603. Found for $C_{27}H_{26}O_3S$: M^+, 430.1602).

3-(3′,5′-Di-*O*-benzyl-2′-deoxy-D-*erythro*-pentofuranosyl)-1-phenylsulfonylindole 3b–iv. Oil; ν_{max}(neat) 2860, 1450, 1370, 1180 and 750 cm^{-1}; δ_H(500 MHz; $CDCl_3$) as follows.

α-Form.—δ_H 2.22–2.29 (1 H, ddd, 2′-H^a), 2.62 (1 H, ddd, 2′-H^b), 3.62–3.69 (2 H, m, 5′-H), 4.24 (1 H, d, *J* 6.4, 3′-H), 4.30 (1 H, m, 4′-H), 4.50 (4 H, m, CH_2), 5.32 (1 H, dd, $J_{1',2'}$ 4.9 and 10.9, 1′-H), 7.1–8.0 (18 H, m, indole 2-, 4-, 5-, 6-H, SO_2Ph and Ph).

β-Form.—δ_H 2.15 (1 H, m, *J* 6.0 and 10.4, 2′-H^a), 2.28 (1 H, m, *J* 1.2, 5.2 and 13.2, 2′-H^b), 3.64–3.70 (2 H, m, *J* 4.9 and 10.9, 5′-H), 4.23 (1 H, d, *J* 6.3, 3′-H), 4.59 (4 H, m, CH_2), 5.32 (1 H, dd, $J_{1',2'}$ 4.9, $J_{1',2''}$ 10.9, 1′-H) and 7.1–8.0 (18 H, m, indole 2-, 4-, 5-, 6-H, SO_2Ph and Ph); HRMS (FAB, NBA) (Calc. for $C_{33}H_{31}NO_5S$: *M*, 553.1923. Found: M^+, 553.1934).

2-(3′,5′-Di-*O*-benzyl-2′-deoxy-D-*erythro*-pentofuranosyl)-1,3,5-trimethoxybenzene 3b–v. ν_{max}(KBr) 3450, 2900, 1500, 1460, 1320, 1220, 1200, 1140, 1100, 1060, 810, 740 and 700 cm^{-1}; δ_H(500 MHz; $CDCl_3$) as follows.

α-Form.—Mp 65–67 °C; δ_H 2.05 (1 H, m, 2′-H^a), 2.64 (1 H, m, 2′-H^b), 3.54–3.59 (1 H, dd, *J* 6.2 and 10.1, 5′-H), 3.62–3.66 (1 H, dd, *J* 4.8 and 10.7, 5′-H), 3.70 (6 H, s, OMe), 3.78 (3 H, s, OMe), 4.18 (1 H, dd, 3′-H), 4.19 (1 H, m, 4′-H), 4.54–4.66 (4 H, m, OC*H*$_2$Ph), 5.72 (1 H, dd, *J* 6.8 and 10.1, 1′-H), 6.07 (2 H, s, ArH) and 7.24–7.36 (10 H, m, Ph). NOE (1′↔2′) was observed; δ_C(125 MHz; $CDCl_3$) 55.35 (p, OMe), 55.62 (p, OMe), 71.08 (s, CH_2), 71.19 (s, CH_2), 71.66 (t, sugar-C), 73.35 (s, CH_2), 81.71 (t, sugar-C), 82.58 (t, Ar), 91.11 (t, Ar), 108.27 (q, Ph), 127.53 (t, Ar), 127.58 (t, Ar), 127.75 (t, Ar), 127.88 (t, Ar), 128.35 (t, Ar), 128.40 (t, Ar), 134.45 (q, Ph), 138.45 (q, Ph), 138.49 (q, Ph), 160.08 (q, Ph) and 160.94 (q, Ph); HRMS (FAB, NBA) [Calc. for $C_{28}H_{33}O_6$: (*M* + H), 465.2277. Found for $C_{28}H_{33}O_6$: $(M + H)^+$, 465.2258].

1,3,5-Trimethoxy-2-(2′,3′,4′,6′-tetra-*O*-benzyl-β-D-gluco-pyranosyl)benzene 14 (R = Bn). Oil; $[a]_D^{20}$ +4.05 (*c* 1.0, $CHCl_3$); ν_{max}(neat) 1940, 1740, 1610, 1590, 1500, 1455, 1230, 1205, 1155, 1120, 1060, 740 and 700 cm^{-1}; δ_H(500 MHz; $CDCl_3$) 3.55 (1 H, ddd, $J_{4',5'}$ 9.7, $J_{5',6'a}$ 1.5, $J_{5',6'b}$ 3.6, 5′-H), 3.70 (3 H, s, Me), 3.70–3.80 (2 H, m, 3′-H and 6′-H^a), 3.78 (3 H, s, Me), 3.81 (3 H, s, Me), 3.85 (1 H, dd, $J_{3',4'} = J_{4',5'} = 9.4$, 4′-H), 3.89 (1 H, dd, $J_{5',6'b}$ 3.7, J_{gem} 11.5, 6′-H^b), 4.10 (1 H, d, J_{gem} 10.4, C*H*$_2$Ph), 4.36 (1 H, dd, $J_{1',2'}$ 9.9, $J_{2',3'}$ 9.0, 2′-H), 4.51 (1 H, d, J_{gem} 10.4, C*H*$_2$Ph), 4.52 (1 H, d, J_{gem} 12.1, C*H*$_2$Ph), 4.72 (1 H, d, J_{gem} 10.9, C*H*$_2$Ph), 4.77 (1 H, d, J_{gem} 12.1, C*H*$_2$Ph), 4.89 (1 H, d, J_{gem} 10.8, C*H*$_2$Ph), 4.92 (1 H, d, $J_{1',2'}$ 9.9, 1′-H), 4.95 (1 H, d, J_{gem} 10.8, C*H*$_2$Ph), 6.10 (1 H, s, ArH), 6.16 (1 H, s, Ar) and 6.90–7.88 (20 H, m, 4 × Ph). Couplings were observed in pairs of the following benzyl protons: 4.10, 4.51, 4.52, 4.77, 4.72, 4.91 and 4.89, 4.95; δ_C(125 MHz; $CDCl_3$) 55.24 (p, Me), 55.76 (p, Me), 56.05 (p, Me), 69.12 (s, 6′-C), 72.65 (t, 1′-C), 73.14 (s, *C*H$_2$Ph), 74.39 (s, *C*H$_2$Ph), 75.03 (s, *C*H$_2$Ph), 75.77 (s, *C*H$_2$Ph), 78.44 (t, 4′-C), 79.60 (t, 5′-C), 80.00 (t, 2′-C), 87.50 (t, 3′-C), 90.89 (t, Ar), 91.81 (t, Ar), 107.83 (q, 2-C), 126.89 (t, Ph), 127.16 (t, Ph), 127.35 (t, Ph), 127.52 (t, Ph), 127.55 (t, Ph), 127.93 (t, Ph), 127.99 (t, Ph), 128.02 (t, Ph), 128.12 (t, Ph), 128.16 (t, Ph), 128.32 (t, Ph), 128.37 (t, Ph), 128.48 (t, Ph), 138.44 (q, Ph), 138.63 (q, Ph), 138.94 (q, Ph), 138.98 (q, Ph), 159.84 (q, Ar), 160.93 (q, Ar) and 161.35 (q, Ar); HRMS (FAB) [Calc. for $C_{43}H_{47}O_8$: (*M* + H), 691.3271. Found: $(M + H)^+$, 691.3236].

1,3,5-Trimethoxy-2-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-gluco-pyranosyl)benzene 14 (R = Ac). Oil; $[a]_D^{20}$ −6.77 (*c* 1.0, $CHCl_3$); ν_{max}(neat) 2940, 2840, 1750, 1610, 1590, 1460, 1370, 1230, 1040, 815 and 755 cm^{-1}; δ_H(500 MHz; $CDCl_3$) 1.74 (3 H, s, Me), 2.02 (3 H, s, Me), 2.05 (3 H, s, Me), 2.06 (3 H, s, Me), 3.78 (9 H, s, OMe), 3.71–3.83 (1 H, m, 5′-H), 4.13 (1 H, dd, $J_{5',6'a}$ 2.4, J_{gem} 12.4, 6′-H^a), 3.89 (1 H, dd, $J_{5',6'b}$ 4.6, J_{gem} 12.2, 6′-H^b), 5.05 (1 H, d, $J_{1',2'}$ 10.1, 1′-H), 3.85 (1 H, dd, $J_{3',4'} = J_{4',5'} = 9.6$, 4′-H), 5.27 (1 H, dd, $J_{2',3'} = J_{3',4'} = 9.5$, 3′-H), 4.36 (1 H, dd, $J_{1',2'} = J_{2',3'} = 9.6$, 2′-H), 6.06 (1 H, s, Ar) and 6.09 (1 H, s, Ar); δ_C(125 MHz; $CDCl_3$) 20.47 (p, *Me*), 20.70 (p, *Me*), 20.76 (p, *Me*), 20.79 (p, *Me*), 55.24 (p, OMe), 56.07 (p, OMe), 62.66 (s, 6′-C), 68.99 (t, 4′-C), 69.70 (t, 2′-C), 71.97 (t, 1′-C), 75.27 (t, 3′-C), 76.00 (t, 5′-C), 90.75 (t, Ar), 91.77 (t, Ar), 104.47 (q, 2-C), 159.79 (q, Ar), 161.18 (q, Ar) and 161.90 (q, Ar); HRMS (FAB) [Calc. for $C_{23}H_{31}O_{12}$: (*M* + H), 499.1816. Found: $(M + H)^+$, 499.1790] (Calc. for $C_{23}H_{30}O_{12}$: C, 55.42; H, 6.07. Found: C, 55.8; H, 6.0%).

Deprotection of 1-phenylsulfonyl-3-(2′,3′,5′-tri-*O*-benzyl-D-ribofuranosyl)indole 3a–iv [13]

A mixture of compound **3a–iv** (0.2 mmol), 18-crown-6 (52.8 mg, 0.2 mmol), KOH (1.0 g, 17.9 mmol), CH_3OH (2 ml) and 1,4-dioxane (2 ml) was stirred for 1 h at rt. The mixture was treated with 1 M HCl (15 ml), extracted with $CHCl_3$, and the extract was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by PLC on silica gel (developer hexane–ethyl acetate, 4:1; R_f = 0.3) (yield 85%).

3-(2′,3′,5′-Tri-*O*-benzyl-D-ribofuranosyl)indole 3a–iv′. Oil; ν_{max}(neat) 3250, 2800, 1420 and 1060 cm^{-1}; δ_H(500 MHz; $CDCl_3$) as follows.

α-Form.—δ_H 3.64–4.69 (11 H, m, 2′-, 3′-, 4′-, 5′-H and benzyl-H), 5.45 (1 H, d, $J_{1',2'}$ 3.4, 1′-H), 6.97–7.65 (20 H, m, indole 2-, 4-, 5-, 6-, 7-H and Ph) and 8.16 (1 H, br s, indole 1-H).

β-Form.—δ_H 3.55–3.60 (1 H, dd, J_{gem} 10.5, $J_{4',5'}$ 3.6, 5′-H), 3.65–3.70 (1 H, dd, J_{gem} 10.5, $J_{4',5'}$ 3.7, 5′-H), 4.05–4.14 (3 H, m, 2′- and 3′-H), 4.26–4.27 (1 H, d, *J* 4.6, 4′-H), 4.44–4.59 (6 H, m, benzyl-H), 5.24 (1 H, d, $J_{1',2'}$ 6.3, 1′-H), 6.89 (1 H, dd, $J_{4,5}$ 7.7, $J_{5,6}$ 7.2, indole 5-H), 7.02–7.47 (18 H, m, indole 2-, 6-, 7-H and Ph), 7.56 (1 H, d, $J_{4,5}$ 8.0, indole 4-H) and 8.02 (1 H, br s, indole 1-H). HRMS (FAB) (Calc. for $C_{34}H_{33}NO_4$: *M*, 519.2410. Found for $C_{34}H_{33}NO_4$: M^+, 519.2388).

To a solution of 2-(2′,3′,5′-tri-*O*-benzyl-D-ribofuranosyl)-indole **3a–iv′** (0.17 mmol) in $CHCl_3$ (20 ml) was added dropwise a solution of 1 M BCl_3 in CH_2Cl_2 (0.8 ml, 0.8 mmol) at −78 °C. After being stirred for 1 h at the same temperature, the mixture was added to dry CH_3OH–CH_2Cl_2 (1:1; 8 ml) and then neutralized with solid $NaHCO_3$ at rt. The mixture was filtered and the residue was washed with dry CH_3OH. The combined filtrate and washings were condensed, and purified by PLC on silica gel (developer $CHCl_3$–CH_3OH, 9:1; R_f = 0.2) (yield 35%).

3-(D-Ribofuranosyl)indole 3a–iv″. δ_H(500 MHz; $CDCl_3$) as follows.

α-Form.—δ_H 3.25–4.28 (8 H, m, 2′-, 3′-, 4′-, 5′-H, 2′-, 3′- and 5′-OH), 5.05 (1 H, d, $J_{1',2'}$ 6.0, 1′-H), 7.05–7.37 (4 H, m, indole 2-, 5-, 6- and 7-H), 7.68 (1 H, d, $J_{4,5}$ 7.7, indole 4-H) and 9.46 (1 H, br s, indole 1-H).

β-Form.—δ_H 3.25–4.28 (8 H, 2′-, 3′-, 4′-, 5′-H, 2′-, 3′- and 5′-OH), 4.80 (1 H, d, $J_{1',2'}$ 9.0, 1′-H), 7.05–7.37 (4 H, m, indole 2-, 5-, 6- and 7-H), 7.61 (1 H, d, $J_{4,5}$ 8.0, indole 4-H) and 9.54 (1 H, br s, indole 1-H).

Formation of *C*-glycoside analogue *via* anomeric anion from 2-deoxy-D-ribofuranosyl telluride

To a solution of 3′,5′-di-*O*-benzyl-2′-deoxy-D-*erythro*-pentafuranosyl *p*-methoxyphenyl telluride **1b** in dry THF were added 1.1 equivalents of *n*-BuLi dropwise at −78 °C and then 3 equivalents of dry benzaldehyde were added at the same temperature. The temperature was increased slowly to 0 °C and the reaction mixture was stirred for 1 h. The reaction mixture was treated with water, extracted with Et_2O, and the extract was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by PLC on silica gel (hexane–EtOAc 2:1).

α-(3′,5′-Di-*O*-benzyl-2′-deoxy-D-*erythro*-pentofuranosyl)-phenylmethanol 4b. Oil; ν_{max}(neat) 3400, 2940, 2860, 1500, 1450, 1360, 1200, 1080, 1020, 740 and 700 cm^{-1}; δ_H(500 MHz; $CDCl_3$) 1.88–1.94 (1 H, m, 2′-H^a), 2.08–2.16 (1 H, m, 2′-H^b), 2.57 (1 H, br, OH), 3.45–3.51 (2 H, m, *J* 4.8, 5′-H), 4.07 (1 H, m, *J* 2.7, 3.6 and 4.1, 3′-H), 4.37 (1 H, m, 4′-H), 4.40 (1 H, m, 1′-H), 4.45–4.60 (2 H, m, benzyl-H), 5.04 (1 H, d, methanol-H) and 7.23–7.39 (15 H, m, 3 × Ph); HRMS (FAB, NBA) [Calc. for $C_{26}H_{28}NaO_4$: (*M* + Na), 427.1885. Found for $C_{26}H_{28}NaO_4$: $(M + Na)^+$, 427.1849].

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