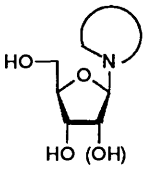
Synthesis of *C*-Nucleosides *via* Radical Coupling Reaction

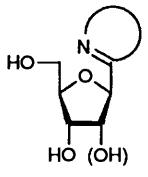
Hideo Togo,* Sachiko Ishigami, Misa Fujii, Toshihiro Ikuma and Masataka Yokoyama*
Department of Chemistry, Faculty of Science, Chiba University, Yayoi-cho 1-33, Inage-ku, Chiba 263, Japan

Photolysis of *O*-acyl derivatives of *N*-hydroxy-2-thiopyridone, prepared from tetrahydrofuran-2-carboxylic acid, D-ribofuranosylmethanoic acid, and D-ribopyranosylmethanoic acid, gave the corresponding *C*-nucleoside derivatives in the presence of heteroaromatic compounds *via* radical pathways. The essential step in this method is a radical coupling reaction of D-ribofuranosyl radical or D-ribopyranosyl radical and some heteroaromatic bases. This is a new method for the preparation of *C*-nucleosides using sugar carboxylic acids.

Study on nucleosides has attracted wide interest in view of the importance of the high biological activities of these compounds.[1] In particular, *C*-nucleosides are well known to have potent antiviral and antitumour activities. Since pseudouridine was isolated as the first *C*-nucleoside from *t*RNA in 1957,[2] many natural *C*-nucleosides such as showdomycin,[3] pyrazomycin,[4] oxazinomycin,[5] formycin,[6] pyrrolosine,[7] *etc.*, have been reported. Furthermore, many natural and unnatural *C*-nucleosides have recently been synthesized, and it has been found that most of them possess potential biochemical activities.[8] Generally, the synthetic procedures towards these *C*-nucleosides are classified as follows: (a) ionic coupling reaction of sugar and base moieties, especially for *N*-nucleosides, (b) functionalization of natural *C*-nucleosides, (c) construction of base moiety at the anomeric position of the sugar moiety, and (d) the Diels–Alder reactions with furan or cyclopentadiene derivatives. However, these methods involve many steps and are limited in the preparation of *C*-nucleosides. Thus, the development of simple introduction methods of various bases to sugars at the anomeric position is important for the study of new biochemically active *C*-nucleosides.

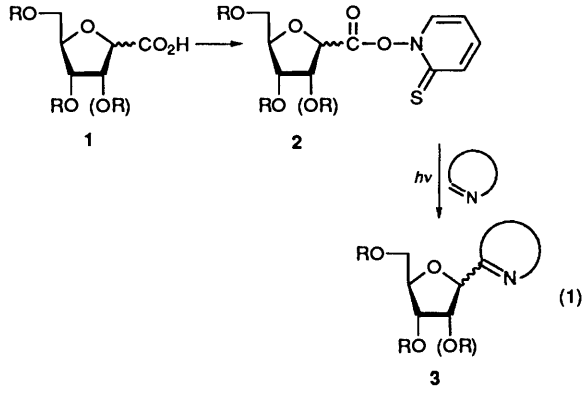


N-Nucleoside



C-Nucleoside

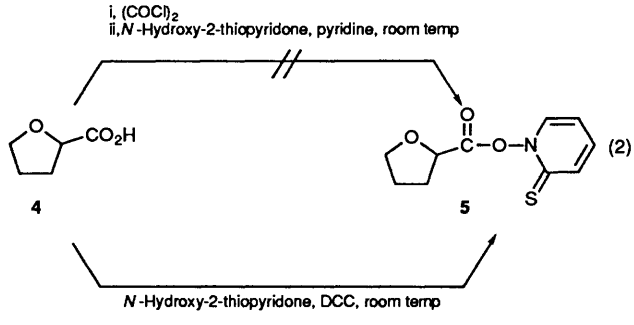
On the other hand, remarkable progress in radical chemistry has made possible the synthesis of many types of molecules,[9] in particular, Barton's decarboxylative radical reaction[10a] is superior in terms of facility, non-toxicity, and wide applicability. The general advantages of radical reactions for organic synthesis are in their mild reaction conditions, high chemoselectivity, and regioselectivity which constitute the backbone of organic compounds. For example, substitution reaction of heteroaromatic compounds by the carbon-centred radicals (alkyl radicals) produces the corresponding alkylated heteroaromatic compounds, as does the Friedel–Crafts reaction. However, the reactivity and selectivity are opposite to those of the Friedel–Crafts reaction.[10c] As is well known in nucleoside chemistry, most natural and unnatural nucleosides consist of a sugar moiety and a heteroaromatic moiety containing nitrogen atoms. The development of a new preparative method for *C*-nucleosides *via* a radical pathway, based on their biochemical interest and the reactivity of anomeric sugar carbon radicals towards heteroaromatic compounds, is very attractive and interesting. Here, as a part of our study directed towards the novel synthesis of nucleosides, we report full details on the first synthesis of *C*-nucleosides **3** starting from *O*-acyl derivative **2** of *N*-hydroxy-2-thiopyridone derived from the carboxylic acid **1** and a heteroaromatic base containing a nitrogen atom *via* the radical reaction as shown in eqn. (1).[10b,11]



(1)

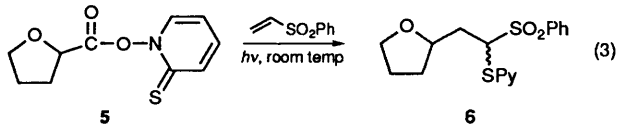
Results and Discussion

1. *Synthesis of* C-*Nucleosides containing a Furanose Ring.*—(i) *Preliminary experiments.* First we carried out model reactions with tetrahydrofuran-2-carboxylic acid **4** to establish the reaction conditions. To prepare thiohydroxamic ester **5**, the reaction conditions had to be modified, because substrate **4** was quite sensitive to the acidic conditions in the chlorination with oxalyl dichloride; furthermore, isolation of the formed ester **5** was difficult due to its rapid hydrolysis on silica gel [eqn. (2)].



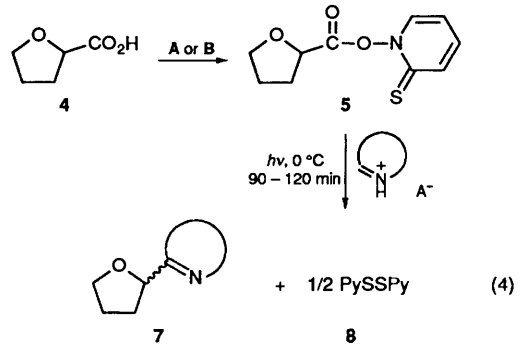
(2)

Therefore, 1,3-dicyclohexylcarbodiimide (DCC) was used as the best reagent to prepare compound **5** *in situ*. Under optimal conditions, the addition product **6** (diastereoisomeric mixture 54:46) was obtained in 95% yield by the photochemical reaction



of compound **5** with phenyl vinyl sulfone [eqn. (3)]. This result suggested that the tetrahydro-2-furyl radical was formed quantitatively under these conditions.

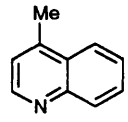
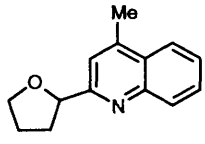
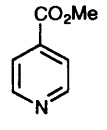
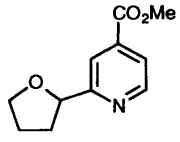
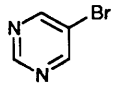
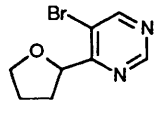
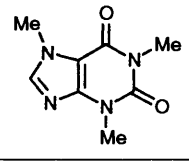
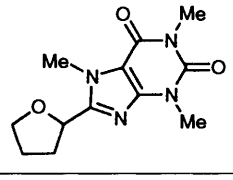
Based on these results, ester **5** was treated with some heteroaromatic compounds (**I–IV**) under the same irradiation conditions to give **7** [eqn. (4)]. The results are shown in Table 1.



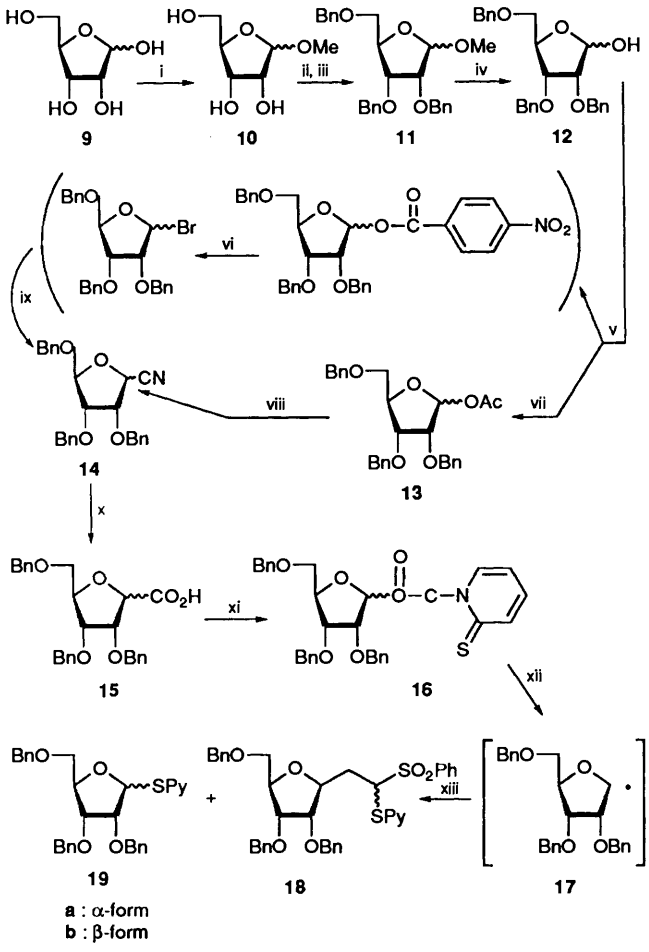
The reason why heteroaromatic compounds **I–IV** were used is that their camphorsulfonate salts are soluble in aprotic solvents such as dichloromethane, and nicotinate, pyrimidine, and caffeine are structurally similar to nicotinamide, uracil, and purine, respectively. Here, it is very important to protonate the heteroaromatic compounds by an equal amount of acid because the addition of proton increases the reactivity of heteroaromatic compounds about 10^2–10^3 times toward carbon-centred radicals.[12] In practice, the alkylation of these heteroaromatic compounds without an acid, such as camphorsulfonic acid, by the present method did not give the corresponding alkylated heteroaromatic compounds. Instead, the rearranged sulfide, pyridyl tetrahydrofuryl sulfide, was formed as a major product. In the reaction with 4-methylquinoline **I** and methyl isonicotinate **II**, the yields of *C*-nucleosides **7** were good and approximately the same as that of dipyridyl sulfide **8**, which was a direct, air-oxidized by-product of pyridine-α-thiol. These obtained products **7I–7IV** are very attractive compounds because of their structural similarity to tegafur, which is known as a carrier of a 5-fluorouracil group and is a powerful anticancer drug. Now, it was shown that the reactivity of tetrahydro-2-furyl radical as a model intermediate of furanosyl radical toward heteroaromatic compounds such as **I–IV** was moderately high and the radical reacted at the most electrophilic position of each heteroaromatic compound to give the corresponding substituted products **7**. These results suggested that the radical coupling method makes possible the direct synthesis of *C*-nucleosides with sugar carboxylic acids.

(ii) *Reaction with* D-*ribose and* 2-*deoxy*-D-*ribose derivatives.* a. *Protection with benzyl group.* 2,3,5-Tri-*O*-benzyl-D-ribofuranosylmethanoic acid **15**, which was the starting material of this radical coupling reaction, was prepared from the reaction of 2,3,5-tri-*O*-benzyl-D-ribofuranosyl bromide with mercury(II) cyanide by the literature method.[13] However, this procedure required several steps, and furthermore it uses toxic mercury(II) cyanide. Therefore, the reaction procedure was slightly modified by using trimethylsilyl cyanide (TMSCN) and the overall yield of **15** from 2,3,5-tri-*O*-benzyl-D-ribofuranose **12** could be also improved (from 36 to 61%, Scheme 1).

Table 1 Model reaction for *C*-nucleosides

Base (3 mol equiv.)	Product	Reaction conditions	Yield (%) 7	8
I			**A**	23	13
			B	54	61
II			**B**	58	60
III			**B**	31	61
IV			**B**	17	32

A: i, CH_2Cl_2 (4 cm^3), $(COCl)_2$ (1.7 mol equiv.), DMF (1 drop), 0 °C, 60 min; ii, *N*-Hydroxy-2-thiopyridone (1.5 mol equiv.), CH_2Cl_2 (10 cm^3), pyridine (2 mol equiv.). **B**: THF (4 cm^3), *N*-hydroxy-2-thiopyridone (1.05 mol equiv.), DCC (1.2 mol equiv.).



Scheme 1 *Reagents and conditions:* i, H_2SO_4, MeOH; ii, NaH, DMF; iii, BnBr; iv, HCl, AcOH, reflux; v, *p*-nitrobenzoyl chloride; vi, HBr, CH_2Cl_2; vii, Ac_2O, pyridine; viii, TMSCN, BF_3·OEt_2, CH_2Cl_2, room temp.; ix, $Hg(CN)_2$, benzene; x, KOH, MeOH, reflux; xi, *N*-hydroxy-2-thiopyridone, DCC, THF, room temp.; xii, *hv*; xiii, CH_2=$CHSO_2Ph$ (6 mol equiv.), CH_2Cl_2, 0–5 °C

In the cyanation of 2,3,5-tri-*O*-benzyl-D-ribofuranosyl bromide with mercury(II) cyanide,[13] the corresponding nitrile **14** was obtained in the α-form only. Thus 2,3,5-tri-*O*-benzyl-D-ribofuranosylmethanoic acid **15** could be obtained as the α-form. However, in the cyanation of 2,3,5-tri-*O*-benzyl-D-ribofuranosyl acetate **13** with TMSCN, the corresponding cyanide **14** was obtained as a diastereoisomeric mixture (α:β 75:25), which was separable by column chromatography. When the carboxylic acid **15a** was allowed to react with *N*-hydroxy-2-thiopyridone and DCC in tetrahydrofuran (THF) at room temperature, the expected Barton's ester **16a** was obtained as a yellow oil. However, the ester could not be purified due to its instability, though the other normal esters (adamantyl and cyclohexyl, *etc.*) were usually stable.[10a] Therefore, compound **16a** was used without purification for the next step. When a mixture of compound **16a** in THF solution and phenyl vinyl sulfone in dichloromethane solution was irradiated with a 500 W tungsten lamp for 1 h at 5 °C, the addition product **18** was obtained in 66% yield together with a small amount of by-product **19** in 9% yield *via* ribofuranosyl radical **17**.

This radical coupling reaction was then applied to the reaction with other heteroaromatic compounds such as 4-methylquinoline and methyl isonicotinate under similar conditions. When a mixture of these heteroaromatic compounds, the ester **16a** in THF solution, and boron trifluoride–diethyl ether

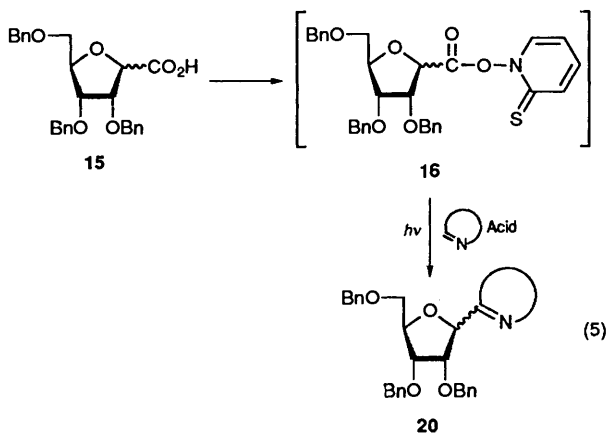


Table 2 Reaction of compound **15** with heteroaromatic compounds

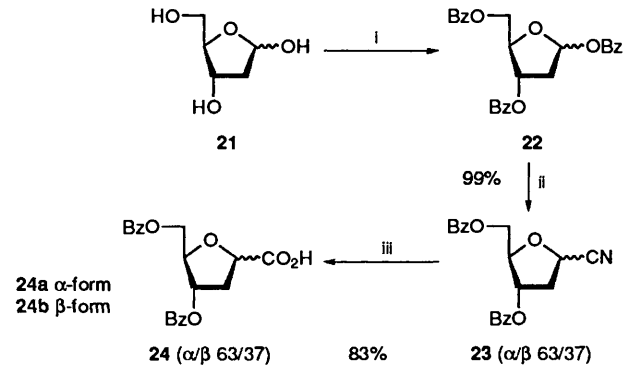
Base	Carboxylic acid	Acid	Yield (%)[a]	Ratio (α/β)
I	**15a**	CSA	40	50/50
		BF_3·OEt_2	45	33/67
	15b	TFA	55	50/50
II	**15a**	BF_3·OEt_2	44	75/25
	15b	TFA	46	73/27
III	**15b**	TFA	18	*b*

[a] Isolated yield. [b] Almost 100% β-form. ——→: C–C Bond-forming position.

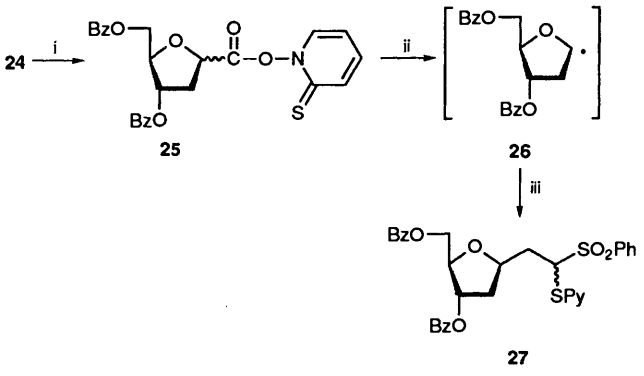
(BF_3·OEt_2) was irradiated for 3 h at 5 °C, the corresponding 4-methyl-2-(2,3,5-tri-*O*-benzyl-D-ribofuranosyl)quinoline **20I** and methyl 2-(2,3,5-tri-*O*-benzyl-D-ribofuranosyl)isonicotinate **20II** were obtained in 45% (α:β 33:67) and 44% (α:β 75:25) yield, respectively [eqn. (5)]. When this reaction was performed using camphorsulfonic acid (CSA) instead of BF_3·OEt_2, compound **20I** was obtained in 40% yield (α:β 50:50). The same stereoselectivity was also observed in the reaction with trifluoroacetic acid (TFA) instead of CSA as shown in Table 2. 2-Pyridyl 2,3,5-tri-*O*-benzyl-D-ribofuranosyl sulfide **19** was always obtained in 10–20% yield as a by-product in these reactions. The structure of the products was determined by spectroscopic and microanalytical data, and the stereochemistry of the anomeric carbon was determined by nuclear Overhauser enhancement (NOE) experiments. The stereoselectivity for the formation of α- and β-forms was not affected by using a Lewis acid in place of a protic acid, or by the reaction temperature.

Thus, the first synthesis of the target *C*-nucleosides has been achieved by using the radical coupling reaction of a ribofuranosyl radical with heteroaromatic bases. However, the deprotection of compounds **20** was somewhat disappointing because the yield of free *C*-nucleoside was extremely low and many undesired products were formed by palladium on carbon or palladium hydroxide on carbon in the presence or absence of cyclohexene under hydrogen.

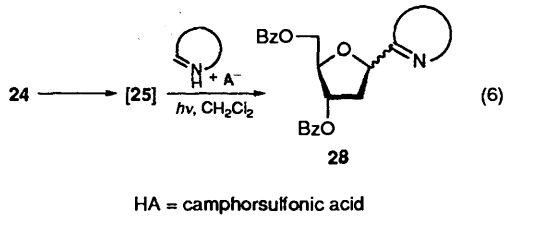
b. *Protection with benzoyl group.* Here, the starting material 3,5-di-*O*-benzoyl-2-deoxy-D-*erythro*-pentofuranosylmethanoic acids **24a** and **24b** were obtained from 2-deoxy-D-ribose **21** in



Scheme 2 *Reagents and conditions:* i, pyridine, PhCOCl, 15 °C, 1 h; ii, TMSCN, BF_3-OEt_2, CH_2Cl_2, room temp., 5 h; iii, HCl, 1,4-dioxane, reflux, 7 h

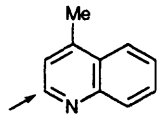
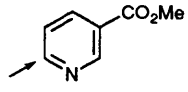
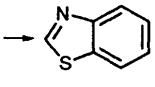
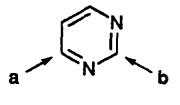


Scheme 3 *Reagents and conditions:* i, *N*-hydroxy-2-thiopyridone, DCC, THF, room temp.; ii, *hv*; iii, CH_2=$CHSO_2Ph$ (6 mol equiv.), CH_2Cl_2, room temp.



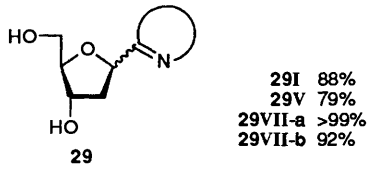
HA = camphorsulfonic acid

Table 3 Reaction of compound **24** with heteroaromatic compounds

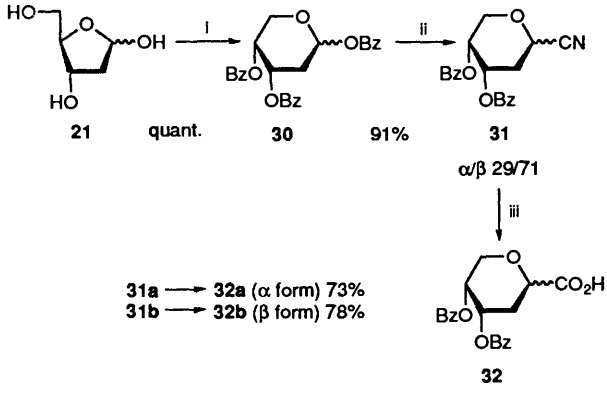
Base (7 mol equiv.)	Temp. (T/°C)	Yield (%)[a]	Ratio (α/β)
I 	30–33	70 (**28I**)	13/87
V 	35–39	45 (**28V**)	84/16
VI 	0–3	26 (**28VI**)	*b*
VII 	32–37	56 (**28VII**) (**a**:**b** 81:19)	78/22

[a] Isolated yield. [b] Almost 100% α-form. ——→: C–C Bond-forming position.

moderate yields as shown in Scheme 2. In the key step the use of TMSCN gave cyanide derivatives **23** in 99% yield. In order to examine the nucleophilicity of anomeric radical **26** towards electron-deficient olefinic compounds (Scheme 3), thiohydroxamic acid ester **25**, which was prepared from acid **24**, was treated with phenyl vinyl sulfone under irradiation with a tungsten lamp to give the product **27** (β form) in 62% yield. This result suggested that the anomeric radical **26** was formed from hydroxamate **25** in good yield under these conditions. Using the same procedure, the thiohydroxamic acid ester **25** was irradiated in the presence of heteroaromatic compounds to afford the corresponding *C*-nucleosides **28** as shown in eqn. (6) and the results are summarized in Table 3. The stereoselectivity depended on the heteroaromatic compounds used. Thus, the major product **28I** from 4-methylquinoline was the β-form, while the major products **28V**, **28VI**, **28VII** carrying methyl nicotinate, benzothiazole, and pyrimidine moieties adopted the α-form. Probably, the stereoselectivity of α- or β-form depends on their thermodynamic stabilities. Compound **28** could be easily deprotected by ammonia in methanol to give free alcohols **29** in high yields.



2. *Synthesis of C-Nucleosides containing a Pyranose Ring.*— Glycopyranosyl *N*-nucleosides have also been studied.[14] Some of them showed biological activity. The preparation of pyranosyl *C*-nucleosides *via* the same radical coupling manner is interesting and important in view of the reactivity of pyranosyl radicals to heteroaromatic compounds. Here, 2-deoxy-D-ribopyranose was used as a pyranose skeleton. The starting material, 3,4-di-*O*-benzoyl-2-deoxy-D-ribopyranosylmethanoic acids **32a** and **32b**, was obtained from 2-deoxy-D-ribose **21** in high yields as shown in Scheme 4. Compound **30** was cyanized



Scheme 4 *Reagents and conditions:* i, PhCOCl, pyridine, 15 °C, 4 h; ii, TMSCN, BF_3-OEt_2, CH_2Cl_2, room temp., 5 h; iii, HCl, 1,4-dioxane, reflux, 7 h

by TMSCN to afford cyanide derivatives **31a** and **31b**, which could be easily separated by column chromatography on silica gel. These cyanides could be hydrolysed by the same procedure as described in Scheme 3 to give the corresponding acids **32a** and **32b** in good yield, respectively.

The thiohydroxamic acid ester **33** was irradiated in the presence of heteroaromatic compounds to give the corresponding *C*-nucleosides **35** containing a six-membered ring as a sugar moiety in moderate yields as shown in eqn. (7) and Table 4. The

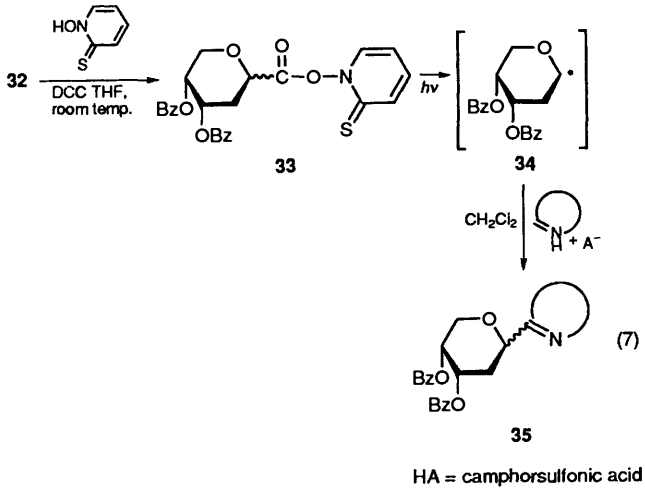
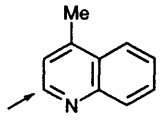
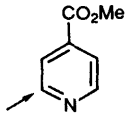
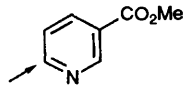
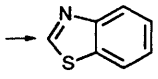
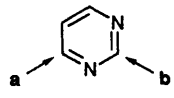
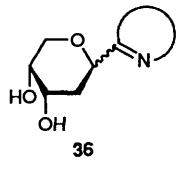


Table 4 Reaction of compound **32b** with heteroaromatic compounds

Base	Temp. (T/°C)	Yield (%)[a]	Ratio (α/β)
I 	30–33	70 (**35I**)	14/86
	30–33	66[b]	7/93
II 	10–15	45 (**35II**)	c
V 	ice-bath	45 (**35V**)	c
VI 	ice-bath	26 (**35VI**)	c
VII 	32–37	56 (**35VII**) (**a**:**b** 71:29)	c
	33–37	40[b] (**a**:**b** 71:29)	c

[a] Isolated yield. [b] Compound **32a** was used. [c] Almost 100% β-form. ——›: C–C Bond-forming position.

major product **35I** possessing a 4-methylquinoline system was the β-form. Further, the reaction products **35** carrying methyl isonicotinate, methyl nicotinate, benzothiazole, and pyrimidine moieties adopted the β-form only. The stereoselectivities with some heteroaromatic compounds did not change in the range of 0 to 50 °C. Compounds **35** could be easily deprotected by ammonia in methanol to give free alcohols **36** in good yield.



36I 93%
36VI 82%
36VII-a 88%

In conclusion, the key step in this procedure for the synthesis of *C*-nucleosides is the radical coupling reaction of a ribofuranosyl radical **17**, **26**, or a ribopyranosyl radical **34** with some heteroaromatic compounds. This procedure has outstanding advantages such as the short synthetic route for *C*-nucleosides containing furanose and pyranose rings as sugar moieties from 2-deoxy-D-ribose and D-ribose, easy deprotection, and its application in principle to various heteroaromatic bases. Most of the new type *C*-nucleosides may be synthesized by the coupling reaction of an anomeric radical with heteroaromatic compounds.

Experimental

General.—M.p.s were determined with a Yamato Model MP-21. IR spectra were recorded on a Hitachi 215 spectrometer. Optical rotations were determined on a JASCO DIP-370 digital polarimeter, and are given in units of 10^{-1} deg cm^2 g^{-1} for $[\alpha]_D$. ^{1}H and ^{13}C NMR were measured [deuteriochloroform as solvent (unless specified otherwise) with tetramethylsilane as internal reference] with JEOL MH-100, JNM-FX-270, 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. Abbreviations: p, primary; s, secondary; t, tertiary; q, quaternary. 2D-NMR (COSY and NOESY) data were recorded on JEOL JNM-GSX-400 and JNM-GSX-500 spectrometers. Mass spectra were obtained on Hitachi M-60 and JEOL HX-110 mass spectrometers. 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 Kieselgel 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, oxygen-free argon unless otherwise stated.

Preparation of Tetrahydrofuran-2-carboxylic Acid **4**.—Compound **4** was obtained in 95% yield by the reduction of 2-furoic acid with 5% palladium on carbon in ethyl acetate. B.p. 110 °C/2 mmHg (lit.,[15] 117 °C/9 mmHg).

Typical Procedure for C–C *Bond Formation* 1.—To a solution of acid **4** (0.23 g, 2.0 mmol) in THF (3 cm^3) were added *N*-hydroxy-2-thiopyridone (0.27 g, 2.1 mmol) and DCC (0.50 g, 2.4 mmol). The mixture was stirred for 1 h at room temperature in the dark, then was filtered quickly, and phenyl vinyl sulfone (1.68 g, 10 mmol) and dichloromethane (5 cm^3) were added to the filtrate. The obtained solution was irradiated by a tungsten lamp (500 W) at room temperature. Work-up afforded *phenyl 1-pyridylsulfanyl-2-(tetrahydro-2″-furyl)ethyl sulfone* **6** as an oil (diastereoisomeric mixture, 54:46); ν_{max}(neat)/cm^{-1} 2900, 2850, 1565, 1440, 1410, 1300, 1140, 1060 and 760; δ_H 8.25–8.16 (1 H, m, 6′-H), 7.94–7.84 (2 H, m, *o*-Ph), 7.48–7.26 (4 H, m, *m*- and *p*-Ph, 4′- and 5′-H), 6.99–6.84 (2 H, m, *m*-Ph and 3′-H), 5.89 (1 H, dd, J_{vic} 12.0, J_{vic} 2.9, 1-H^a), 5.79 (1 H, dd, J_{vic} 11.6, J_{vic} 4.8, 1-H^b), 4.28–4.13 (1 H, m, 2″-H), 3.91–3.67 (2 H, m, 5″-H_2) and 2.60–1.50 (6 H, m, 3″-, 4″- and 2-H_2); HRMS (FAB) (M + H), 350.0884. $C_{17}H_{20}NO_3S_2$ requires (M + H), 350.0883.

Typical Procedure for C–C *Bond Formation* 2.—Compound **4** (0.232 g, 2 mmol) was dissolved in THF (3 cm^3). To the solution were added *N*-hydroxy-2-thiopyridone (0.267 g, 2.1 mmol) and DCC (0.495 g, 2.4 mmol). After being stirred for 1 h at room temperature in the dark, the mixture was filtered. To the filtrate were added dichloromethane (10 cm^3) and 4-methylquinolinium camphorsulfonate (2.25 g, 6 mmol), and the obtained solution was irradiated by a tungsten lamp till the yellow colour of the ester faded away. After concentration, saturated aq. $NaHCO_3$ was added to the residue, and the mixture was extracted with dichloromethane. Excess of base was removed by column chromatography [eluent ethyl acetate–hexane (1:3)], and finally the coupling product **7** was obtained (0.23 g, 54%) after preparative TLC (PLC). Other coupling products were also obtained by the same procedure.

4-Methyl-2-(tetrahydro-2′-furyl)quinoline **7I**, oil; ν_{max}(neat)/cm^{-1} 3040, 2900, 2850, 1590, 1060 and 760; δ_H 8.05 (1 H, dd, $J_{7,8}$ 8.1, $J_{6,8}$ 0.8, 8-H), 7.97 (1 H, dd, $J_{5,6}$ 8.6, $J_{5,7}$ 1.2, 5-H), 7.68 (1 H, ddd, $J_{7,8}$ 8.1, $J_{6,7}$ 6.8, $J_{5,7}$ 1.2, 7-H), 7.52 (1 H, ddd, $J_{5,6}$ 8.6, $J_{6,7}$ 6.8, $J_{6,8}$ 0.8, 6-H), 7.45 (1 H, br s, 3-H), 5.14 (1 H, t, $J_{2',3'}$ 7.6, 2′-H), 4.18 (1 H, dd, J_{gem} 14.0, $J_{4',5'}$ 7.1, 5′-H), 4.05 (1 H, dd, J_{gem} 14.0, $J_{4',5'}$ 7.0, 5′-H), 2.70 (3 H, br s, Me), 2.60–2.40 (1 H, m, 3′-H) and 2.18–1.96 (3 H, m, 3′-H and 4′-H_2): HRMS (EI) *m/z* 213.1156 (M^+). $C_{14}H_{15}NO$ requires M, 213.1153 (Found: C, 78.5; H, 6.95; N, 6.5. $C_{14}H_{15}NO$ requires C, 78.84; H, 7.09; N, 6.57%).

Methyl 2-(tetrahydro-2′-furyl)isonicotinate **7II**, oil; ν_{max}(neat)/cm^{-1} 2940, 2850, 1725, 1600, 1560, 1435, 1295, 1215, 1110, 1068 and 770; δ_H 8.70 (1 H, dd, $J_{5,6}$ 4.9, $J_{3,6}$ 0.7, 6-H), 8.00 (1 H, dd, $J_{3,5}$ 1.7, $J_{3,6}$ 0.7, 3-H), 7.72 (1 H, dd, $J_{5,6}$ 4.9, $J_{3,5}$ 1.7, 5-H), 5.08 (1 H, dd, $J_{2',3'}$ 6.9, $J_{2',3'}$ 5.9, 2′-H), 4.17–4.11 (1 H, m, 5′-H), 4.05–3.94 (1 H, m, 5′-H), 3.96 (3 H, s, CO_2Me), 2.52–2.40 (1 H, m, 3′-H) and 2.06–1.96 (3 H, m, 3′-H and 4′-H_2); MS (EI) *m/z* 207 (M^+).

5-Bromo-4-(tetrahydro-2′-furyl)pyrimidine **7III**, oil; ν_{max}(Nujol)/cm^{-1} 2900, 2840, 1650, 1540, 1450, 1380, 1225 and 1080; δ_H 9.10 (1 H, s, 2-H), 8.76 (1 H, s, 6-H), 5.31 (1 H, dd, $J_{2',3'}$ 6.6, $J_{2',3'}$ 1.7, 2′-H), 4.25–4.20 (1 H, m, 5′-H), 4.07–3.99 (1 H, m, 5′-H), 2.49–2.43 (1 H, m, 3′-H) and 2.15–1.96 (3 H, m, 3′-H and 4′-H_2); MS (EI) *m/z* 228 (^{79}Br) and 230 (^{81}Br).

8-(Tetrahydro-2′-furyl)caffeine **7IV**, oil; ν_{max}(KBr)/cm^{-1} 3300, 2920, 2870, 1700, 1660, 1540, 1435, 1340, 1220, 1060, 1050, 985, 770 and 750; δ_H 5.03 (1 H, t, $J_{2',3'}$ 7.1, 2′-H), 4.04 (3 H, s, Me), 4.00–3.88 (2 H, m, 5′-H_2), 3.57 (3 H, s, Me), 3.40 (3 H, s, Me), 2.65–2.52 (1 H, m, 3′-H_2) and 2.35–1.99 (3 H, m, 3′- and 4′-H_2); HRMS (FAB) *m/z* 265.1303 (M + H). $C_{12}H_{17}N_4O_3$ requires *m/z* 265.1300 (Found: C, 54.4; H, 5.9; N, 21.4. $C_{12}H_{16}N_4O_3$ requires C, 54.53; H, 6.10; N, 21.20%).

Preparation of 2,3,5-*Tri*-O-*benzyl*-D-*ribofuranosylmethanoic Acid* **15**.—The reported procedure[13] was modified as follows: an ice-cold solution of HBr (1.42 g, 17.6 mmol) in dry dichloromethane (30 cm^3) (3.5% w/w) was added to an ice-cold solution of 2,3,5-tri-*O*-benzyl-1-*O*-(*p*-nitrobenzoyl)-β-D-ribofuranose (10 g, 17.6 mmol) in dry dichloromethane (30 cm^3). The mixture was stirred for 5 min at 0 °C, then the *p*-nitrobenzoic acid precipitate was filtered off, and washed with dry dichloromethane (20 cm^3). The combined filtrate was concentrated and the dark syrup was dissolved in dry benzene (120 cm^3). To this solution was added $Hg(CN)_2$ (12 g, 47 mmol), and the mixture was stirred at room temperature. After 4 h, the reaction mixture was concentrated, and the residue was dissolved in dichloromethane (120 cm^3) and filtered. The filtrate was washed successively with 40% aq. KI (60 cm^3 × 3) and water, dried over Na_2SO_4, and concentrated to a syrup. Column chromatography of the residue on silica gel with dichloromethane afforded α-nitrile **14a** (3.4 g, 45%).

As an alternative method, compound **13** (6.14 g, 13.3 mmol) was dissolved in dry dichloromethane (50 cm^3), and then TMSCN (2.2 cm^3, 16.1 mmol) and a catalytic amount of BF_3·OEt_2 were added at 0 °C. After the mixture had been stirred for 6 h at 0 °C, the solvent was removed. The residue was dissolved in dichloromethane, and washed with saturated aq. $NaHCO_3$. After column chromatography [ethyl acetate–hexane (1:5)], 2,3,5-tri-*O*-benzyl-D-ribofuranosyl cyanide **14** was obtained (5.0 g, 88%). The two anomeric isomers were separated in this step and the α:β ratio was 75:25.

2,3,5-Tri-*O*-benzyl-α-D-ribofuranosyl cyanide **14a**, oil; ν_{max}(neat)/cm^{-1} 3020, 2900, 2850, 2320, 1495, 1450, 1360, 1215, 1100, 915, 745 and 705; δ_H 7.40–7.18 (15 H, m, Ph), 4.75–4.68 (4 H, m, 1.5 × CH_2O and 1-H), 4.53 (1 H, d, J_{gem} 12.2, CH_2O), 4.48 (1 H, d, J_{gem} 12.2, CH_2O), 4.42 (1 H, d, J_{gem} 12.2, CH_2O), 4.33 (1 H, m, 4-H), 4.15 (1 H, dd, $J_{3,4}$ 5.8, $J_{2,3}$ 4.9, 3-H), 3.99 (1 H, dd, $J_{2,3}$ 4.9, $J_{1,2}$ 4.2, 2-H), 3.53 (1 H, dd, J_{gem} 10.8, $J_{4,5}$ 3.3, 5-H) and 3.45 (1 H, dd, J_{gem} 10.8, $J_{4,5}$ 3.3, 5-H).

2,3,5-Tri-*O*-benzyl-β-D-ribofuranosyl cyanide **14b**, oil; ν_{max}(neat)/cm^{-1} 3020, 2900, 2850, 2320, 1500, 1450, 1360, 1210, 1100, 1030, 915, 745 and 705; δ_H 7.38–7.23 (15 H, m, Ph), 4.66–4.45 (7 H, m, CH_2O and 1-H), 4.30 (1 H, br t, $J_{2,3}$ 5.0, 3-H), 4.23 (1 H, m, 4-H), 4.05 (1 H, br t, $J_{2,3}$ 5.0, 2-H), 3.57 (1 H, dd, J_{gem} 10.7, $J_{4,5}$ 3.6, 5-H) and 3.51 (1 H, dd, J_{gem} 10.7, $J_{4,5}$ 4.0, 5-H).

A solution of 20% KOH in methanol (50 cm^3) was added to compound **14** (6 g, 14 mmol) in a mixture of methanol (20 cm^3), THF (2 cm^3), and water (2 cm^3). The mixture was heated to reflux for 4 h, concentrated, and acidified with 6 mol dm^{-3} HCl. The product was extracted with ethyl acetate, dried over Na_2SO_4 and concentrated to give crude acid **15** as a syrup. Column chromatography of the residue on silica gel [ethyl acetate–hexane–acetic acid (10:20:3)] afforded acid **15** (2.9 g, 72%).

2,3,5-Tri-*O*-benzyl-α-D-ribofuranosylmethanoic acid **15a**, oil; ν_{max}(neat)/cm^{-1} 3500–2700, 1740, 1350, 1205, 1110, 1070, 1020, 740 and 700; δ_H 7.50–7.10 (16 H, m, Ph and CO_2H), 4.76 (1 H, d, J_{gem} 11.7, CH_2O), 4.64 (1 H, d, J_{gem} 11.7, CH_2O), 4.55 (1 H, d, J_{vic} 4.7, CH_2O), 4.53 (1 H, d, J_{vic} 4.7, CH_2O), 4.46 (1 H, s, 1-H), 4.44 (1 H, d, J_{gem} 11.7, CH_2O), 4.31 (1 H, dd, $J_{3,4}$ 8.8, $J_{4,5}$ 2.9, 4-H), 4.20 (1 H, d, J_{gem} 11.7, CH_2O), 4.14 (1 H, d, $J_{2,3}$ 4.7, 2-H), 3.96 (1 H, dd, $J_{3,4}$ 8.8, $J_{2,3}$ 4.7, 3-H), 3.82 (1 H, dd, J_{gem} 10.0, $J_{4,5}$ 2.9, 5-H) and 3.52 (1 H, d, J_{gem} 10.0, 5-H); NOE (1-H ↔ 5-H) was observed.

2,3,5-Tri-*O*-benzyl-β-D-ribofuranosylmethanoic acid **15b**, oil; ν_{max}(neat)/cm^{-1} 3400–2600, 1730, 1340, 1140–980, 910, 730 and 700; δ_H 10.80 (1 H, br s, CO_2H), 7.41–7.19 (15 H, m, Ph), 4.79 (1 H, d, J_{gem} 11.8, CH_2O), 4.67 (1 H, br s, 1-H), 4.59 (1 H, d, J_{gem} 11.8, CH_2O), 4.58 (1 H, d, J_{gem} 11.8, CH_2O), 4.48 (1 H, d, J_{gem} 11.8, CH_2O), 4.45 (1 H, d, J_{gem} 11.6, CH_2O), 4.32 (1 H, dd, $J_{3,4}$ 9.4, $J_{4,5}$ 2.8, 4-H), 4.21 (1 H, d, J_{gem} 11.6, CH_2O), 4.14 (1 H, d, $J_{2,3}$ 4.4, 2-H), 3.97 (1 H, dd, $J_{3,4}$ 9.4, $J_{2,3}$ 4.4, 3-H), 3.87 (1 H, dd, J_{gem} 10.5, $J_{4,5}$ 2.8, 5-H) and 3.54 (1 H, d, J_{gem} 10.5, 5-H); NOE (1-H ↔ 4-H) was observed.

Preparation of Phenyl 1′-*Pyridylsulfanyl*-2-(2″,3″,5″-*tri*-O-*benzyl*-β-D-*ribofuranosyl*)*ethyl Sulfone* **18**.—A mixture of acid **15a** (0.225 g, 0.50 mmol) and *N*-hydroxy-2-thiopyridone (0.070 g, 0.55 mmol) in THF (2 cm^3) was cooled to 0 °C, and a solution of DCC (0.125 g, 0.60 mmol) in THF (2 cm^3) was added to the solution. After being stirred for 3 h at room temperature, precipitated 1,3-dicyclohexylurea was filtered off and washed with THF (5 cm^3). To the filtrate was added a solution of phenyl vinyl sulfone (0.420 g, 2.50 mmol) in dichloromethane (1 cm^3). The mixture was irradiated for 3 h at 5 °C. Hydrazine hydrate (0.50 g) was added to the reaction mixture, the obtained solution was stirred for 15 min at room temperature, then was extracted with diethyl ether, and the organic layer was concentrated. Column chromatography of the residue on silica gel [ethyl acetate–hexane (1:2)] afforded sulfone **18** as a diastereoisomeric mixture (2:1) (0.225 g, 66%). *Phenyl* 1′-*pyridylsulfanyl*-2-(2″,3″,5″-*tri*-O-*benzyl*-β-D-*ribofuranosyl*)*ethyl sulfone* **18** had $[\alpha]_D^{24}$ −29.3 (*c* 0.30, $CHCl_3$); ν_{max}(neat)/cm^{-1} 3020, 2870, 1570, 1440, 1415, 1305, 1240, 1150, 1125, 1085, 745 and 700; δ_H 8.11 (1 H, ddd, $J_{5',6'}$ 4.8, $J_{4',6'}$ 1.8, $J_{3',6'}$ 0.9, major Py-6′-H), 8.05 (1 H, ddd, $J_{5',6'}$ 4.9, $J_{4',6'}$ 1.8, $J_{3',6'}$ 0.9, minor Py-6′-H), 7.92–7.84 (2 H, m, SO_2Ph), 7.42–7.25 (19 H, m, m, SO_2Ph, Ph-, and Py-4′-H), 6.97–6.94 (1 H, m, Py-5′-H), 6.87–6.82 (1 H, m, Py-3′-H), 5.91 (1 H, dd, $J_{1,2}$ 12.3, $J_{1,2}$ 2.6, major 1-H), 5.86 (1 H, dd, $J_{1,2}$ 10.6, $J_{1,2}$ 3.1, minor 1-H), 4.57–4.45 (6 H, m, CH_2O), 4.36–4.29 (1 H, m, 1″-H), 4.19–4.13 (1 H, m, 4″-H), 3.92–3.87 (1 H, m, 3″-H), 3.82 (1 H, t, J_{vic} 5.5, minor 2″-H), 3.70 (1 H, t, J_{vic} 5.6, major 2″-H), 3.50–3.45 (2 H, m, 5″-H), 2.63 (1 H, ddd, J_{gem} 14.7, J_{vic} 7.7, J_{vic} 3.2, minor CH_2), 2.48 (1 H, ddd, J_{gem} 14.1, J_{vic} 9.9, J_{vic} 2.7, major CH_2) and

2.18–2.07 (1 H, m, 2-H); NOE [$PhO_2S(SPy)CHCH_2$ ↔ 3′-H] was observed; MS (FAB) *m/z* 682 (M + H) (Found: C, 68.3; H, 5.9; N, 1.9. $C_{39}H_{39}NO_6S_2$ requires C, 68.70; H, 5.76; N, 2.05%).

Typical Procedure for the Preparation of C-*Nucleosides* **20**.—A mixture of β-acid **15b** (0.225 g, 0.50 mmol) and *N*-hydroxy-2-thiopyridone (0.070 g, 0.55 mmol) in dry THF (2 cm^3) was cooled to 0 °C, and a solution of DCC (0.125 g, 0.60 mmol) in dry THF (2 cm^3) was added to the solution. After the mixture had been stirred for 3 h at room temperature, precipitated 1,3-dicyclohexylurea was filtered off, and washed with dry THF (5 cm^3). To this solution, 4-methylquinoline (0.34 cm^3, 2.50 mmol), boron trifluoride–diethyl ether (0.31 cm^3, 2.50 mmol) in THF (1 cm^3), and *N*,*N*-dimethylformamide (5 cm^3) were added, and the mixture was stirred for 5 min at 0 °C before being irradiated for 3 h at 5 °C. Then the reaction mixture was neutralized with saturated aq. $NaHCO_3$ and extracted with dichloromethane. After removal of the solvent, column chromatography of the residue on silica gel [ethyl acetate–hexane (1:2)] afforded compound **20I** (0.147 g, 45% yield) (α:β 1:2).

4-Methyl-2-(2′,3′,5′-tri-*O*-benzyl-α-D-ribofuranosyl)-quinoline **20I**, oil; $[\alpha]_D^{23}$ −29.3 (*c* 0.58, $CHCl_3$); ν_{max}(neat)/cm^{-1} 2840, 1590, 1445, 1350, 1205, 1120, 1085, 1045, 1025, 910, 740 and 700; δ_H 8.02–7.99 (2 H, m, 5- and 8-H), 7.71 (1 H, ddd, $J_{7,8}$ 8.2, $J_{6,7}$ 7.0, $J_{5,7}$ 1.3, 7-H), 7.68 (1 H, br s, 3-H), 7.55 (1 H, ddd, $J_{5,6}$ 8.2, $J_{6,7}$ 7.0, $J_{6,8}$ 1.3, 6-H), 7.35–7.25 (10 H, m, Ph), 7.10–6.99 (3 H, m, Ph), 6.80 (2 H, d, J_o 7.0, Ph), 5.36 (1 H, d, $J_{1',2'}$ 2.8, 1′-H), 4.64 (1 H, d, J_{gem} 12.1, CH_2O), 4.56 (1 H, d, J_{gem} 12.1, CH_2O), 4.56 (1 H, d, J_{gem} 11.9, CH_2O), 4.57–4.54 (1 H, m, 4′-H), 4.44 (1 H, m, 2′-H), 4.42 (1 H, d, J_{gem} 11.9, CH_2O), 4.28 (1 H, dd, $J_{3',4'}$ 8.6, $J_{2',3'}$ 4.0, 3′-H), 4.14 (1 H, d, J_{gem} 11.7, CH_2O), 3.97 (1 H, d, J_{gem} 11.7, CH_2O), 3.84 (1 H, dd, J_{gem} 10.8, $J_{4',5'b}$ 2.6, 5′-H^b), 3.67 (1 H, dd, J_{gem} 10.8, $J_{4',5'a}$ 4.2, 5′-H^a) and 2.68 (3 H, d, *J* 0.6, base Me); NOE (1′-H ↔ 3′-H) was observed; δ_C 159.1 (q, C-2), 147.1 (q, C-8a), 144.2 (q, C-4), 138.3, 137.8 and 137.7 (q, Ph), 129.4 (t, C-8), 129.0 (t, C-7), 128.4 (t, C-4a), 128.3–127.3 (t, Ph), 125.9 (t, C-5), 123.8 (t, C-6), 121.3 (t, C-3), 84.5 (t, C-1′), 80.4 (t, C-4′), 80.0 (t, C-2′), 79.4 (t, C-3′), 73.5, 73.2 and 72.6 (s, CH_2O), 70.1 (s, C-5) and 18.7 (p, base Me); MS (FAB) *m/z* 546 (M + H).

(β-*form*) m.p. 67–68 °C; $[\alpha]_D^{23}$ +127.1 (*c* 0.43, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 2850, 1585, 1440, 1345, 1200, 1080, 1120, 905, 735 and 700; δ_H 8.08 (1 H, br d, $J_{7,8}$ 8.3, 8-H), 7.94 (1 H, dd, $J_{5,6}$ 8.4, $J_{5,7}$ 0.9, 5-H), 7.70 (1 H, ddd, $J_{7,8}$ 8.3, $J_{6,7}$ 7.0, $J_{5,7}$ 0.9, 7-H), 7.53 (1 H, ddd, $J_{5,6}$ 8.4, $J_{6,7}$ 7.0, $J_{6,8}$ 0.9, 6-H), 7.41–7.39 (2 H, m, Ph), 7.40 (1 H, br s, 3-H), 7.33–7.21 (13 H, m, Ph), 5.38 (1 H, d, $J_{1',2'}$ 3.3, 1′-H), 4.84 (1 H, d, J_{gem} 12.1, CH_2O), 4.77 (1 H, d, J_{gem} 12.1, CH_2O), 4.65 (1 H, d, J_{gem} 11.9, CH_2O), 4.60 (1 H, d, J_{gem} 10.3, CH_2O), 4.57 (1 H, d, J_{gem} 10.3, CH_2O), 4.49–4.45 (1 H, m, 4′-H), 4.38 (1 H, d, J_{gem} 11.9, CH_2O), 4.28 (1 H, dd, $J_{2',3'}$ 5.1, $J_{1',2'}$ 3.3, 2′-H), 4.05 (1 H, dd, $J_{3',4'}$ 7.1, $J_{2',3'}$ 5.1, 3′-H), 3.90 (1 H, dd, J_{gem} 10.8, $J_{4',5'a}$ 2.9, 5′-H^a), 3.73 (1 H, dd, J_{gem} 10.8, $J_{4',5'b}$ 3.8, 5′-H^b) and 2.48 (3 H, d, *J* 0.7, base Me); NOE (1′-H ↔ 4′-H) was observed; δ_C 160.1 (q, C-2), 147.5 (q, C-8a), 144.8 (q, C-4), 138.4, 138.0 and 137.9 (q, Ph), 129.8 (t, C-8), 129.0 (t, C-7), 128.4–127.6 (t, Ph), 127.5 (t, C-4a), 125.9 (t, C-5), 123.7 (t, C-6), 119.5 (t, C-3), 85.5 (t, C-1′), 81.3 (t, C-4′), 81.1 (t, C-2′), 77.1 (t, C-3′), 73.4, 72.0 and 71.4 (s, CH_2O), 69.8 (s, C-5) and 18.6 (p, base Me); MS (FAB) *m/z* 546 (M + H) (Found: C, 78.95; H, 6.6; N, 2.5. $C_{36}H_{35}NO_4$ requires C, 79.24; H, 6.47; N, 2.57%).

Methyl 2-(2′,3′,5′-*tri*-O-*benzyl*-α-D-*ribofuranosyl*)*isonicotinate* **20II** oil; $[\alpha]_D^{23}$ +54.3 (*c* 0.54, $CHCl_3$); ν_{max}(neat)/cm^{-1} 3000, 2840, 1720, 1300, 1210, 1120, 1100, 740 and 700; δ_H 8.64 (1 H, d, $J_{5,6}$ 5.0, 6-H), 8.18 (1 H, d, $J_{3,5}$ 1.4, 3-H), 7.75 (1 H, dd, $J_{5,6}$ 5.0, $J_{3,5}$ 1.4, 5-H), 7.35–7.26 (10 H, m, Ph), 7.17–7.12 (3 H, m, Ph), 6.89 (2 H, d, J_o 6.1, Ph), 5.31 (1 H, d, $J_{1',2'}$ 2.8, 1′-H), 4.62 (1 H, d, J_{gem} 12.1, CH_2O), 4.55 (1 H, d, J_{gem} 11.8, CH_2O), 4.54 (1 H, d, J_{gem} 12.1, CH_2O), 4.50 (1 H, dd, $J_{2',3'}$ 4.1, $J_{1',2'}$ 2.8, 2′-H), 4.43 (1 H, d, J_{gem} 11.8, CH_2O), 4.38 (1 H, m, 4′-H), 4.29 (1 H, dd, $J_{3',4'}$ 8.5, $J_{2',3'}$ 4.1, 3′-H), 4.23 (1 H, d, J_{gem} 11.8, CH_2O), 4.05 (1 H, d, J_{gem} 11.8, CH_2O), 3.93 (3 H, s, CO_2Me), 3.82 (1 H, dd, J_{gem} 10.7, $J_{4',5'a}$ 2.5, 5′-H^a) and 3.65 (1 H, dd, J_{gem} 10.7, $J_{4',5'b}$ 3.9, 5′-H^b); NOE (1′-H ↔ 3′-H) was observed; δ_C 165.8 (q, base CO), 160.2 (q, C-2), 149.0 (t, C-6), 138.2 (q, C-4), 137.8, 137.7 and 137.6 (q, Ph), 128.4–127.4 (t, Ph), 121.9 (t, C-3), 121.6 (t, C-5), 83.7 (t, C-1′), 80.3 (t, C-4′), 80.0 (t, C-2′), 79.0 (t, C-3′), 73.5, 73.2 and 72.6 (s, CH_2O), 69.8 (s, C-5) and 52.6 (p, base CO_2Me); MS (FAB) *m/z* 540 (M + H) (Found: C, 73.15; H, 6.2; N, 2.6. $C_{33}H_{33}NO_6$ requires C, 73.45; H, 6.16; N, 2.60%).

(β-*form*) oil; $[\alpha]_D^{23}$ +15.6 (*c* 0.15, $CHCl_3$); δ_H 8.73 (1 H, d, $J_{5,6}$ 5.0, 6-H), 8.18 (1 H, d, $J_{3,5}$ 1.4, 3-H), 7.73 (1 H, dd, $J_{5,6}$ 5.0, $J_{3,5}$ 1.4, 5-H), 7.36–7.23 (15 H, m, Ph), 5.28 (1 H, d, $J_{1',2'}$ 3.3, 1′-H), 4.76 (1 H, d, J_{gem} 12.1, CH_2O), 4.68 (1 H, d, J_{gem} 12.1, CH_2O), 4.67 (1 H, d, J_{gem} 12.1, CH_2O), 4.59 (1 H, d, J_{gem} 12.1, CH_2O), 4.56 (1 H, d, J_{gem} 11.8, CH_2O), 4.45–4.43 (1 H, m, 4′-H), 4.41 (1 H, d, J_{gem} 11.8, CH_2O), 4.18 (1 H, dd, $J_{2',3'}$ 5.0, $J_{1',2'}$ 3.3, 2′-H), 4.00 (1 H, dd, $J_{3',4'}$ 7.2, $J_{2',3'}$ 5.0, 3′-H), 3.83 (3 H, s, Me), 3.83 (1 H, dd, J_{gem} 10.7, $J_{4',5'a}$ 3.0, 5′-H^a) and 3.68 (1 H, dd, J_{gem} 10.7, $J_{4',5'b}$ 4.1, 5′-H^b); NOE (1′-H ↔ 4′-H, 1′-H ↔ 2′-CH_2O) was observed; δ_C 165.7 (q, base CO), 161.3 (q, C-2), 149.9 (t, C-6), 138.3 (q, C-4), 138.0, 137.9 and 137.8 (q, Ph), 128.4–127.4 (t, Ph), 121.7 (t, C-3), 120.5 (t, C-5), 84.6 (t, C-1′), 81.5 (t, C-4′), 81.1 (t, C-2′), 77.5 (t, C-3′), 73.3, 72.1 and 71.6 (s, CH_2O), 69.5 (s, C-5) and 52.5 (p, base CO_2Me); MS (FAB) *m/z* 540 (M + H).

5-*Bromo*-4-(2′,3′,5′-*tri*-O-*benzyl*-β-D-*ribofuranosyl*)*pyrimidine* **20III** oil; $[\alpha]_D^{23}$ −7.0 (*c* 0.15, $CHCl_3$); ν_{max}(neat)/cm^{-1} 3000, 2850, 1550, 1450, 1385, 1360, 1270, 1205, 1100, 1010, 740 and 700; δ_H 8.99 (1 H, s, 2-H), 8.76 (1 H, s, 6-H), 7.34–7.22 (15 H, m, Ph), 5.48 (1 H, m, $J_{1',2'}$ 5.0, 1′-H), 4.64 (1 H, d, J_{gem} 11.8, CH_2O), 4.60 (1 H, d, J_{gem} 12.1, CH_2O), 4.58 (1 H, d, J_{gem} 12.1, CH_2O), 4.56 (1 H, d, J_{gem} 11.8, CH_2O), 4.54 (1 H, d, J_{gem} 12.1, CH_2O), 4.52 (1 H, d, J_{gem} 12.1, CH_2O), 4.43 (1 H, br q, $J_{3',4'}$ = $J_{4',5'}$ = 5.0, 4′-H), 4.37 (1 H, br t, $J_{1',2'}$ = $J_{2',3'}$ = 5.0, 2′-H), 4.18 (1 H, br t, $J_{2',3'}$ = $J_{3',4'}$ = 5.0, 3′-H), 3.67 (1 H, dd, J_{gem} 10.5, $J_{4',5'a}$ 5.0, 5′-H^a) and 3.64 (1 H, dd, J_{gem} 10.5, $J_{4',5'b}$ 5.0, 5′-H^b); NOE (1′-H ↔ 4′-H) was observed; MS (FAB) *m/z* 561 (^{79}Br) and 563 (^{81}Br) (Found: C, 63.6; H, 5.1; N, 4.8. $C_{30}H_{29}BrN_2O_4$ requires C, 64.17; H, 5.21; N, 4.99%).

Preparation of 3,5-*Di*-O-*benzoyl*-2-*deoxy*-D-*ribofuranosylmethanoic Acid* **24**.—1,3,5-Tri-*O*-benzoyl-2-deoxy-D-ribofuranose **22**[16] was obtained by the following procedure. A mixture of free saccharide **21** (0.50 g, 3.73 mmol) and benzoyl chloride (2.1 g, 14.92 mmol) in dry dichloromethane (10 cm^3) was stirred for 0.5 h at ~15 °C. Then, pyridine (4 cm^3) in dry dichloromethane (8 cm^3) was added dropwise over a period of 1 h at 14–18 °C. After the addition, the mixture was stirred for 1 h over the same temperature range, washed twice with water, dried over $MgSO_4$, and filtered. After concentration of the filtrate, the residue was chromatographed on silica gel [ethyl acetate–hexane (1:1)]. The obtained mixture was then purified by PLC (dichloromethane) to give compound **22** (0.87 g, 52%).

Compound **22** (0.45 g, 1.00 mmol) was dissolved in dry dichloromethane (5 cm^3) under Ar, and TMSCN (0.17 cm^3, 1.20 mmol) was added to the solution at 0 °C. Then, BF_3·OEt_2 (0.37 cm^3, 3.00 mmol) was added to the mixture, which was then stirred for 1.5 h at 0 °C before being quenched with saturated aq. $NaHCO_3$, extracted with dichloromethane, dried over Na_2SO_4, and filtered. After removal of the solvent, the residue was chromatographed [chloroform–ethyl acetate (40:1)] to give nitrile **23** (0.349 g, 99%), as a mixture of α and β forms (α:β 63:27).

3,5-*Di*-O-*benzoyl*-2-*deoxy*-D-*ribofuranosyl cyanide* **23** oil; ν_{max}(neat)/cm^{-1} 1700, 1250, 1070–1065 and 710; δ_H 8.14–8.00 (4 H, m, Ph), 7.63–7.45 (6 H, m, Ph), 5.65–5.61 (1 H, m,

3'-H), 5.07 (0.3 H, dd, $J_{1,2}$ 8.2, $J_{1,2}$ 1.6, minor 1-H), 4.93 (0.7 H, dd, $J_{1,2}$ 9.1, $J_{1,2}$ 6.7, major 1-H), 4.71–4.52 (3 H, m, 4-H and 5-H_2) and 2.81–2.60 (2 H, m, 2-H_2); HRMS (FAB) [Found: (M + H), 352.1186. $C_{20}H_{18}NO_5$ requires *m/z*, 352.1185].

To a solution of nitrile **23** (0.43 g, 1.23 mmol) in 1,4-dioxane (10 cm^3) was added conc. HCl (1.0 cm^3). The mixture was heated for 3.5 h at 80–82 °C in a sealed tube. After removal of the solvent, the residue was chromatographed on silica gel [ethyl acetate–hexane–acetic acid (50:50:1)] to give acid **24** (0.378 g, 83%). *3,5-Di-O-benzoyl-2-deoxy-D-ribofuranosylmethanoic acid* **24** oil; ν_{max}(neat)/cm^{-1} 3600–2800, 1795–1640, 1595, 1580, 1490, 1445, 1310, 1180, 1030, 810, 720 and 695; δ_H 8.08–8.03 (3 H, m, Ph), 7.96–7.92 (1 H, m, Ph), 7.62–7.37 (6 H, m, Ph), 6.68–6.16 (1 H, br s, CO_2H), 5.58–5.54 (1 H, m, 3-H), 4.88–4.82 (1 H, m, 1-H), 4.76–4.51 (3 H, m, 4-H and 5-H_2) and 2.82–2.43 (2 H, m, 2-H_2); HRMS (FAB) [Found: (M + H), 371.1130. $C_{20}H_{19}O_7$ requires *m/z*, 371.1131].

Typical Procedure for the Preparation of C-*Nucleosides* **28**.—Compound **24** (0.185 g, 0.50 mmol) was dissolved in dry THF (3 cm^3), and then *N*-hydroxy-2-thiopyridone (0.067 g, 0.525 mmol) and DCC (95%; 0.124 g, 0.60 mmol) were added to the solution at 0 °C. After being stirred for 1.5 h at room temperature in the dark, the reaction mixture was filtered under Ar, and the filtrate was added to a solution of 4-methylquinolinium camphorsulfonate (1.31 g, 3.5 mmol) in dry dichloromethane (4 cm^3). The yellow solution was stirred, and irradiated by a 500 W tungsten lamp for 2.5 h at 30–33 °C. The reaction mixture was quenched with saturated aq. $NaHCO_3$ and extracted with dichloromethane. The organic extracts were dried over Na_2SO_4, filtered, and the filtrate was concentrated. The residue was chromatographed [ethyl acetate–hexane (1:3–1:1)] and further purified by PLC on silica gel [ethyl acetate–hexane (1:1)] to give compound **28I** (0.187 g, 70%; α:β 13:87) as an oil. The reaction product mixtures **28V** and **28VI** were extracted with ethyl acetate, and purified by PLC [chloroform–ethyl acetate (20:1–10:1)] after removal of the excess of base by column chromatography [chloroform–ethyl acetate (40:1–20:1)]. The reaction product mixture of compound **28VII** was purified by PLC [dichloromethane–diethyl ether (2:1)] after removal of the excess of base by column chromatography [chloroform–ethyl acetate (40:1–20:1)].

2-(3',5'-Di-O-benzoyl-2'-deoxy-α-D-ribofuranosyl)-4-methylquinoline **28I** had m.p. 115–117 °C; $[\alpha]_D^{24}$ −53.0 (*c* 0.92, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 1710, 1590, 1450, 1370, 1315, 1270, 1180, 1100, 1070, 925, 890, 770 and 720; δ_H 8.12 (2 H, dd, J_o 8.3, J_m 1.4, Ph), 8.07–8.05 (3 H, m, 8-H and Ph), 7.96 (1 H, d, $J_{5,6}$ 7.4, 5-H), 7.71 (1 H, t, J_o 7.4, Ph), 7.62 (1 H, t, $J_{7,8}$ 7.4, 7-H), 7.58–7.50 (3 H, m, 3- and 6-H and Ph), 7.49 (2 H, t, J_o 7.4, Ph), 7.39 (2 H, t, J_o 7.4, Ph), 5.70 (1 H, d, $J_{2'a,3'}$ 5.8, 3'-H), 5.60–5.55 (1 H, br s, 1'-H), 4.83 (1 H, dd, J_{gem} 11.7, $J_{4',5'a}$ 3.6, 5'-H^a), 4.70 (1 H, dd, J_{gem} 11.7, $J_{4',5'b}$ 3.6, 5'-H^b), 4.67 (1 H, td, $J_{4',5'}$ 3.6, $J_{3',4'}$ 1.7, 4'-H), 2.88–2.76 (1 H, br s, 2'-H^a), 2.56 (3 H, s, Me) and 2.44 (1 H, ddd, J_{gem} 14.0, $J_{1',2'b}$ 10.7, $J_{2'b,3'}$ 6.1, 2'-H^b); NOE (4'-H ↔ base Me) was observed; δ_C 166.3 and 166.2 (q, benzoyl CO), 160.5 (q, base C-2), 147.2 (q, base C-8a), 145.5 (q, base C-4), 133.4–128.4 (Ph), 129.8 (t, base C-8), 128.5 (t, base C-7), 127.5 (q, base C-4a), 126.2 (t, base C-5), 123.8 (t, base C-6), 118.5 (t, base C-3), 83.6 (t, C-1'), 82.6 (t, C-4'), 77.4 (t, C-3'), 64.9 (s, C-5'), 26.3 (s, C-2') and 18.7 (p, base Me); HRMS (FAB) [Found: (M + H) 468.1810. $C_{29}H_{26}NO_5$ requires *m/z*, 468.1811. Found: C, 73.8; H, 5.3; N, 3.2. $C_{29}H_{25}NO_5$ requires C, 74.50; H, 5.39; N, 3.00%].

(β-*form*) oil; $[\alpha]_D^{24}$ −47.0 (*c* 0.80, $CHCl_3$); ν_{max}(neat)/cm^{-1} 1710, 1590, 1440, 1315, 1265, 1100, 1065, 760 and 710; δ_H 8.12 (2 H, dd, J_o 7.4, J_m 1.2, Ph), 8.08–8.00 (1 H, m, Ph), 8.01 (1 H, d, $J_{7,8}$ 7.4, 8-H), 7.71 (1 H, t, J_o 7.4, Ph), 7.64 (1 H, s, 3-H), 7.63–7.54 (2 H, m, 5- and 7-H), 7.54 (2 H, dd, J_o 7.4, J_m 1.2, Ph), 7.48 (2 H, t, J_o 7.4, Ph), 7.44 (1 H, tt, $J_{5,6}$ 7.4, $J_{6,8}$ 1.4, 6-H), 7.17 (2 H, t, J_o 7.4, Ph), 5.67–5.65 (2 H, m, 3'- and 1'-H), 4.81 (1 H, td, $J_{4',5'}$ 4.4, $J_{3',4'}$ 1.9, 4'-H), 4.65 (1 H, dd, J_{gem} 11.8, $J_{4',5'a}$ 4.4, 5'-H^a), 4.62 (1 H, dd, J_{gem} 11.8, $J_{4',5'b}$ 4.4, 5'-H^b), 3.07 (1 H, dt, J_{gem} 14.0, $J_{1',2'a}$ = $J_{2'a,3'}$ = 7.0, 2'-H^a), 2.82 (1 H, ddd, J_{gem} 14.0, $J_{2'b,3'}$ 3.6, $J_{1',2'b}$ 2.5, 2'-H^b) and 2.70 (3 H, d, *J* 0.6, Me); NOE (5'-H^a ↔ Me, 5'-H^b ↔ Me) was observed; δ_C 166.4 and 165.8 (q, benzoyl CO), 162.3 (q, base C-2), 147.4 (q, base C-8a), 145.0 (q, base C-4), 133.2–128.1 (Ph), 129.8 (t, base C-8), 128.5 (t, base C-7), 127.3 (q, base C-4a), 126.1 (t, base C-5), 123.7 (t, base C-6), 118.7 (t, base C-3), 83.1 (t, C-1'), 82.0 (t, C-4'), 76.7 (t, C-3'), 64.9 (s, C-5'), 38.7 (s, C-2') and 18.9 (p, base Me); HRMS (FAB) [Found: (M + H), 468.1810. $C_{29}H_{26}NO_5$ requires *m/z*, 468.1811. Found: C, 74.0; H, 5.4; N, 2.9. $C_{29}H_{25}NO_5$ requires C, 74.50; H, 5.39; N, 3.00%].

Methyl 6-(3',5'-di-O-benzoyl-2'-deoxy-α-D-ribofuranosyl)-nicotinate **28V** had m.p. 110–111 °C; $[\alpha]_D^{24}$ +0.9 (*c* 1.03, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 1710, 1590, 1445, 1430, 1355, 1270, 1115, 1025, 880 and 715; δ_H 9.15 (1 H, d, $J_{2,4}$ 2.0, 2-H), 8.32 (1 H, dd, $J_{4,5}$ 8.2, $J_{2,4}$ 2.0, 4-H), 8.09 (2 H, d, J_o 7.1, Ph), 7.73 (1 H, d, $J_{4,5}$ 8.2, 5-H), 7.61–7.57 (3 H, m, Ph), 7.52–7.45 (3 H, m, Ph), 7.32–7.28 (2 H, m, Ph), 5.61 (1 H, dt, $J_{2'a,3'}$ 6.2, $J_{2'b,3'}$ = $J_{3',4'}$ = 2.0, 3'-H), 5.53 (1 H, dd, $J_{1',2'a}$ 8.4, $J_{1',2'b}$ 3.7, 1'-H), 4.74 (1 H, td, $J_{4',5'}$ 4.6, $J_{3',4'}$ 2.0, 4'-H), 4.61 (2 H, d, $J_{4',5'}$ 4.6, 5'-H), 3.97 (3 H, s, CO_2Me), 3.01 (1 H, ddd, J_{gem} 13.9, $J_{1',2'a}$ 8.4, $J_{2'a,3'}$ 6.2, 2'-H^a) and 2.70 (1 H, ddd, J_{gem} 13.9, $J_{1',2'b}$ 3.7, $J_{2'b,3'}$ 2.0, 2'-H^b); NOE (1'-H ↔ 5'-H, 4'-H ↔ base-CO_2Me) was observed; δ_C 166.9 (q, base CO), 166.3 and 165.7 (q, benzoyl CO), 165.7 (q, base C-6), 150.3 (t, base C-2), 137.8 (t, base C-4), 133.3–128.3 (q and t, Ph), 124.5 (q, base C-3), 119.4 (t, base C-5), 83.1 (t, C-1'), 81.2 (t, C-4'), 76.4 (t, C-3'), 64.7 (s, C-5'), 52.4 (p, base CO_2Me) and 38.6 (s, C-2'); HRMS (FAB) [Found: 462.1550 (M + H). $C_{26}H_{24}NO_7$ requires *m/z*, 462.1553].

(β-*form*) oil; $[\alpha]_D^{24}$ −30.7 (*c* 0.18, $CHCl_3$); ν_{max}(neat)/cm^{-1} 1720, 1590, 1445, 1430, 1375, 1260, 1180, 1080, 1025, 860, 780 and 715; δ_H 9.12 (1 H, d, $J_{2,4}$ 2.2, 2-H), 8.25 (1 H, dd, $J_{4,5}$ 8.2, $J_{2,4}$ 2.2, 4-H), 8.10 (2 H, dd, J_o 7.9, J_m 1.3, Ph), 8.00 (2 H, dd, J_o 7.9, J_m 1.3, Ph), 7.63 (1 H, d, $J_{4,5}$ 8.2, 5-H), 7.61 (1 H, tt, J_o 7.9, J_m 1.3, Ph), 7.55 (1 H, tt, J_o 7.9, J_m 1.3, Ph), 7.48 (2 H, t, J_o 7.9, Ph), 7.41 (2 H, t, J_o 7.9, Ph), 5.64 (1 H, br d, $J_{2'b,3'}$ 6.1, 3'-H), 5.45 (1 H, dd, $J_{1',2'b}$ 10.6, $J_{1',2'a}$ 5.7, 1'-H), 4.74 (1 H, dd, J_{gem} 12.6, $J_{4',5'a}$ 4.5, 5'-H^a), 4.66–4.62 (2 H, m, 4'-H and 5'-H^b), 3.95 (3 H, s, CO_2Me), 2.79 (1 H, dd, J_{gem} 13.9, $J_{1',2'a}$ 5.7, 2'-H^a) and 2.32 (1 H, ddd, J_{gem} 13.9, $J_{1',2'b}$ 10.6, $J_{2'b,3'}$ 6.1, 2'-H^b); NOE (1'-H ↔ 4'-H, 5'-H ↔ base-CO_2Me) was observed; δ_C 166.3 and 166.1 (q, benzoyl CO), 165.6 (q, base CO), 165.0 (q, base C-6), 150.3 (t, base C-2), 138.1 (t, base C-4), 133.5–128.5 (q and t, Ph), 125.0 (q, base C-3), 119.4 (t, base C-5), 83.6 (t, C-1'), 81.4 (t, C-4'), 76.8 (t, C-3'), 64.7 (s, C-5'), 52.4 (p, base CO_2Me) and 39.9 (s, C-2'); HRMS (FAB) [Found: (M + H), 462.1553. $C_{26}H_{24}NO_7$ requires *m/z*, 462.1553].

2-(3',5'-Di-O-benzoyl-2'-deoxy-α-D-ribofuranosyl)benzothiazole **28VI** oil; $[\alpha]_D^{24}$ −59.9 (*c* 0.16, $CHCl_3$); ν_{max}(neat)/cm^{-1} 1720, 1590, 1445, 1310, 1265, 1180, 1070, 1030, 770 and 710; δ_H 8.09 (2 H, dd, J_o 8.2, J_m 1.5, Ph), 8.01 (2 H, dd, J_o 8.2, J_m 1.5, Ph), 7.98 (1 H, d, $J_{4,5}$ 8.2, 4-H), 7.85 (2 H, dd, $J_{6,7}$ 8.1, $J_{5,7}$ 0.6, 7-H), 7.62 (1 H, tt, J_o 7.5, J_m 1.5, Ph), 7.52 (1 H, tt, J_o 7.5, J_m 1.5, Ph), 7.50–7.46 (3 H, m, 5-H and Ph), 7.39–7.34 (3 H, m, 6-H and Ph), 5.72 (1 H, dd, $J_{1',2'b}$ 10.1, $J_{1',2'a}$ 5.9, 1'-H), 5.70 (1 H, d, $J_{2'b,3'}$ 5.9, 3'-H), 4.73–4.64 (3 H, m, 4'-H and 5'-H_2), 2.88 (1 H, ddd, J_{gem} 13.9, $J_{1',2'a}$ 5.9, $J_{2'a,3'}$ 1.3, 2'-H^a) and 2.59 (1 H, ddd, J_{gem} 13.9, $J_{1',2'b}$ 10.1, $J_{2'b,3'}$ 5.9, 2'-H^b); NOE (1'-H ↔ 5'-H^a) was observed; HRMS (FAB) [Found: (M + H), 460.1217. $C_{26}H_{22}NO_5S$ requires *m/z*, 460.1219].

4-(3',5'-Di-O-benzoyl-2'-deoxy-α-D-ribofuranosyl)pyrimidine **28VII-a** had $[\alpha]_D^{24}$ +20.6 (*c* 0.74, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 1695, 1570, 1540, 1440, 1250, 1170, 1070, 870 and 710; δ_H 9.16 (1 H, d, $J_{2,5}$ 1.3, 2-H), 8.74 (1 H, d, $J_{5,6}$ 5.3, 6-H), 8.10 (2 H, dd, J_o

8.4, J_m 1.3, Ph), 7.67 (1 H, ddd, $J_{5,6}$ 5.3, $J_{2,5}$ 1.3, $J_{\text{long range}}$ 0.9, 5-H), 7.62–7.46 (6 H, m, Ph), 7.35–7.32 (2 H, m, Ph), 5.60 (1 H, ddd, $J_{2'a,3'}$ 6.0, $J_{2'b,3'}$ 2.0, $J_{3',4'}$ 1.8, 3'-H), 5.42 (1 H, dd, $J_{1',2'a}$ 8.8, $J_{1',2'b}$ 3.1, 1'-H), 4.71 (1 H, td, $J_{4',5'}$ 4.9, $J_{3',4'}$ 1.8, 4'-H), 4.60 (2 H, d, $J_{4',5'}$ 4.9, 5'-H), 2.98 (1 H, ddd, J_{gem} 14.1, $J_{1',2'a}$ 8.8, $J_{2'a,3'}$ 6.0, 2'-H_a) and 2.72 (1 H, ddd, J_{gem} 14.1, $J_{1',2'b}$ 3.1, $J_{2'b,3'}$ 2.0, 2'-H^b); NOE (1'-H ↔ 3'-H, 1'-H ↔ 5'-H, 3'-H ↔ 5'-H, 4'-H ↔ 5-H) was observed; δ_C 171.2 (q, base C-4), 166.3 and 165.6 (q, benzoyl CO), 158.4 (t, base C-2), 157.4 (t, base C-6), 133.4–128.4 (q and t, Ph), 117.3 (t, base C-5), 83.4 (t, C-1'), 80.3 (t, C-4'), 76.3 (t, C-3'), 64.6 (s, C-5') and 38.1 (s, C-2'); HRMS (FAB) [Found: (M + H), 405.1450. $C_{23}H_{21}N_2O_5$ requires m/z, 405.1450. Found: C, 68.0; H, 4.9; N, 6.9. $C_{23}H_{20}N_2O_5$ requires C, 68.30; H, 4.90; N, 6.93%].

(β-*form*) $[\alpha]_D^{24}$ −3.9 (*c* 0.76, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 1710, 1570, 1250, 1065 and 710; δ_H 9.12 (1 H, d, $J_{2,5}$ 1.3, 2-H), 8.67 (1 H, d, $J_{5,6}$ 4.7, 6-H), 8.09 (2 H, dd, J_o 8.3, J_m 1.3, Ph), 7.98 (2 H, dd, J_o 8.3, J_m 1.3, Ph), 7.61 (1 H, tt, J_o 7.4, J_m 1.3, Ph), 7.58–7.54 (2 H, m, Ph and 5-H), 7.50–7.46 (2 H, m, Ph), 7.43–7.39 (2 H, m, Ph), 5.63 (1 H, br d, $J_{2'b,3'}$ 5.9, 3'-H), 5.33 (1 H, dd, $J_{1',2'b}$ 10.6, $J_{1',2'a}$ 5.9, 1'-H), 4.74 (1 H, dd, J_{gem} 13.6, $J_{4',5'a}$ 5.7, 5'-H^a), 4.65–4.60 (2 H, m, 4'-H and 5'-H^b), 2.80 (1 H, ddd, J_{gem} 13.9, $J_{1',2'a}$ 5.9, $J_{2'a,3'}$ 1.3, 2'-H^a) and 2.31 (1 H, ddd, J_{gem} 13.9, $J_{1',2'b}$ 10.6, $J_{2'b,3'}$ 5.9, 2'-H^b); NOE (1'-H ↔ 4'-H) was observed; HRMS (FAB) [Found: (M + H), 405.1449. $C_{23}H_{21}N_2O_5$ requires m/z, 405.1450].

2-(3',5'-*Di*-O-*benzoyl*-2'-*deoxy*-α-D-*ribofuranosyl*)*pyrimidine* **28VII-b** had $[\alpha]_D^{24}$ +30.0 (*c* 0.16, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 1720, 1710, 1565, 1450, 1420, 1320, 1280, 1105, 1090, 1080, 1030, 875, 725, 720 and 695; δ_H 8.76 (2 H, d, $J_{4,5} = J_{5,6}$ = 5.0, 4- and 6-H), 8.09–8.07 (2 H, m, Ph), 7.72–7.70 (2 H, m, Ph), 7.57 (1 H, dt, J_o 7.3, J_m 1.3, Ph), 7.52 (1 H, dt, J_o 7.5, J_m 1.3, Ph), 7.44 (2 H, br t. J_o 7.8, Ph), 7.34 (2 H, br t, J_o 7.8, Ph), 7.21 (1 H, t, $J_{4,5} = J_{5,6}$ = 5.0, 5-H), 5.63 (1 H, br dt, $J_{2'a,3'}$ 6.4, $J_{2'b,3'}$ 3.3, 3'-H), 5.56 (1 H, dd, $J_{1',2'a}$ 8.1, $J_{1',2'b}$ 4.4, 1'-H), 4.89 (1 H, td, $J_{4',5'}$ 4.2, $J_{3',4'}$ 3.1, 4'-H), 4.05 (2 H, d, $J_{4',5'}$ 4.2, 5'-H), 3.02 (1 H, ddd, J_{gem} 13.7, $J_{1',2'a}$ 8.1, $J_{2',3'}$ 6.4, 2'-H^a) and 2.75 (1 H, ddd, J_{gem} 13.7, $J_{1',2'b}$ 4.4, $J_{2'b,3'}$ 3.3, 2'-H^b); NOE (1'-H ↔ 5'-H, 3'-H ↔ 5'-H) was observed; δ_C 170.1 (q, base C-2), 166.3 and 165.8 (q, benzoyl CO), 157.2 (t, base C-4 and -6), 133.2–128.3 (q and t, Ph), 119.5 (t, base C-5), 82.8 (t, C-1'), 81.3 (t, C-4'), 76.2 (t, C-3'), 64.8 (s, C-5') and 38.5 (s, C-2'); HRMS (FAB) [Found: (M + H), 405.1451. $C_{23}H_{21}N_2O_5$ requires m/z, 405.1450. Found: C, 67.9; H, 5.0; N, 6.65. $C_{23}H_{20}N_2O_5$ requires C, 68.30; H, 4.99; N. 6.93%].

Preparation of 3,4-*Di*-O-*benzoyl*-2-*deoxy*-D-*ribopyranosylmethanoic Acid* **32**.—To a solution of deoxyribose **21** (22.0 g, 0.164 mol) in dry pyridine (340 cm^3) was added benzoyl chloride (73.0 cm^3, 0.629 mol) dropwise at 0 °C under nitrogen. The mixture was stirred for 4 days at 15 °C, quenched with saturated aq. $NaHCO_3$, and extracted with chloroform (200 cm^3 × 3). The organic layer was washed with water, dried over Na_2SO_4, and filtered, and the filtrate was concentrated. The resultant syrup was dissolved in dichloromethane, and then diethyl ether was added to the solution to give crystals of 1,3,4-tri-*O*-benzoyl-2-deoxy-D-ribopyranose **30**[16] quantitatively (73 g).

To a solution of compound **30** (4.46 g, 10.0 mmol) in dry dichloromethane (40 cm^3) were added TMSCN (1.60 cm^3, 12.0 mmol) and BF_3·OEt_2 (3.68 cm^3, 30.0 mmol) at 0 °C. After being stirred for 1 h at room temperature, the mixture was quenched with saturated aq. $NaHCO_3$ and extracted with dichloromethane. The organic layer was dried over Na_2SO_4, and filtered, and the filtrate was concentrated. After column chromatography on silica gel [chloroform–ethyl acetate (40:1)], 3,4-di-*O*-benzoyl-2-deoxy-D-ribopyranosyl cyanide **31** was obtained (3.41 g, 97%). The two anomeric isomers **31a** and **31b** were easily separated at this stage (α:β 29:71).

3,4-*Di*-O-*benzoyl*-2-*deoxy*-α-D-*ribopyranosyl cyanide* **31** had m.p. 117–118 °C; $[\alpha]_D^{24}$ −13.4 (*c* 1.06, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 1705, 1450, 1260, 1100 and 710; δ_H 8.09 (2 H, d, J_o 7.4, Ph), 7.97 (2 H, d, J_o 7.4, Ph), 7.57 (2 H, dd, J_o 12.9, J_m 6.9, Ph), 7.46–7.40 (4 H, m, Ph), 5.67 (1 H, dd, $J_{3',4'}$ 6.9, $J_{2',3'}$ 3.6, 3'-H), 5.40 (1 H, td, $J_{3',4'}$ 6.9, $J_{4',5'b}$ 3.6, 4'-H), 4.72 (1 H, t, $J_{1',2'}$ 5.3, 1'-H), 4.32 (1 H, dd, J_{gem} 12.1, $J_{4',5'a}$ 7.3, 5'-H^a), 3.96 (1 H, dd, J_{gem} 12.1, $J_{4',5'b}$ 3.6, 5'-H^b) and 2.55–2.43 (2 H, m, 2'-H_2); NOE (1'-H ↔ 3'-H, 1'-H ↔ 5'-H^a, 1'-H ↔ 5'-H^b) was observed; MS (FAB) m/z, 352 (M + H).

(β-*form*) had m.p. 267–269 °C; $[\alpha]_D^{24}$ −134.7 (*c* 1.07, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 1700, 1450, 1260, 1070 and 710; δ_H 8.02 (2 H, dd, J_o 8.4, J_m 1.3, Ph), 7.95 (2 H, dd, J_o 8.4, J_m 1.3, Ph), 7.61–7.54 (2 H, m, Ph), 7.46–7.26 (4 H, m, Ph), 5.69 (1 H, dt, $J_{2'a,3'}$ 9.9, $J_{3',4'}$ 3.7, 3'-H), 5.53 (1 H, dt, $J_{3',4'}$ 3.7, $J_{4',5'}$ 3.0, 4'-H), 4.98 (1 H, t, $J_{1',2'a}$ 4.7, 1'-H), 4.24–4.15 (2 H, m, 5'-H_2), 2.61 (1 H, ddd, J_{gem} 14.6, $J_{2'a,3'}$ 9.9, $J_{1',2'a}$ 4.7, 2'-H^a) and 2.35 (1 H, dd, J_{gem} 14.6, $J_{2'b,3'}$ 5.0, 2'-H^b); NOE (1'-H ↔ Ph, 2'-H^b ↔ 4'-H, 4'-H ↔ Ph) was observed; MS (FAB) m/z, 352 (M + H).

To a solution of nitrile **31b** (1.76 g, 5.00 mmol) in 1,4-dioxane (10 cm^3) was added conc. HCl (1 cm^3). After being stirred for 7 h at 80 °C in a sealed tube, the reaction mixture was diluted with diethyl ether, filtered to remove ammonium chloride, dried over Na_2SO_4, and filtered, and the filtrate was concentrated. The residue was chromatographed on silica gel [ethyl acetate–hexane–acetic acid (50:50:1)] to give crystals of the acid **32b** (β-form) (0.144 g, 78%). Acid **32a** (α-form) was prepared from nitrile **31a** by the same procedure (0.135 g, 73%).

3,4-*Di*-O-*benzoyl*-2-*deoxy*-α-D-*ribopyranosylmethanoic acid* **32** had m.p. 153–155 °C; $[\alpha]_D^{24}$ −94.9 (*c* 0.48, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 3500–2800, 1695, 1440, 1265, 1195, 1100 and 720; δ_H 8.06 (2 H, dd, J_o 8.3, J_m 1.1, Ph), 7.92 (2 H, dd, J_o 8.3, J_m 1.4, Ph), 7.59 (1 H, tt, J_o 7.4, J_m 1.1, Ph), 7.50 (1 H, tt, J_o 7.4, J_m 1.4, Ph), 7.46 (2 H, t, J_o 7.8, Ph), 7.37 (2 H, t, J_o 7.8, Ph), 5.49 (2 H, m, 3'- and 4'-H), 4.44 (1 H, dd, J_{gem} 12.9, $J_{4',5'a}$ 3.6, 5'-H^a), 4.31 (1 H, dd, $J_{1',2'b}$ 10.2, $J_{1',2'a}$ 3.3, 1'-H), 3.93 (1 H, dd, J_{gem} 12.9, $J_{4',5'b}$ 1.9, 5'-H^b), 2.51 (1 H, ddd, J_{gem} 13.1, $J_{2'a,3'}$ 3.6, $J_{1',2'a}$ 3.3, 2'-H^a) and 2.42 (1 H, ddd, J_{gem} 13.1, $J_{1',2'b}$ 10.2, $J_{2'b,3'}$ 2.8, 2'-H^b); NOE (1'-H ↔ 3'-H, 1'-H ↔ 5'-H^b, 3'-H ↔ 5'-H) was observed; HRMS (FAB) [Found: (M + H), 371.1128. $C_{20}H_{19}O_7$ requires m/z, 371.1130. Found: C, 64.5; H, 4.9. $C_{20}H_{18}O_7$ requires C, 64.86; H, 4.90%].

(β-*form*) had m.p. 106–108 °C; $[\alpha]_D^{24}$ +29.3 (*c* 0.80, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 3500–2400, 1690, 1430, 1260, 1090 and 710; δ_H 8.06 (2 H, d, J_o 7.4, Ph), 7.90 (2 H, dd, J_o 8.5, J_m 1.3, Ph), 7.62 (1 H, dt, J_o 7.4, J_m 0.8, Ph), 7.53 (1 H, t, J_o 7.4, Ph), 7.48 (2 H, t, J_o 7.7, Ph), 7.36 (2 H, t, J_o 7.7, Ph), 5.82 (1 H, br s, 3'-H), 5.36 (1 H, ddd, $J_{4',5'b}$ 9.5, $J_{4',5'a}$ 4.9, $J_{3',4'}$ 3.2, 4'-H), 4.59 (1 H, dd, $J_{1',2'b}$ 10.7, $J_{1',2'a}$ 3.0, 1'-H), 4.28 (1 H, dd, J_{gem} 11.3, $J_{4',5'a}$ 4.9, 5'-H^a), 4.07 (1 H, dd, J_{gem} 11.3, $J_{4',5'b}$ 9.5, 5'-H^b), 2.60 (1 H, ddd, J_{gem} 14.5, $J_{2'a,3'}$ 4.5, $J_{1',2'a}$ 3.0, 2'-H^a) and 2.26 (1 H, ddd, J_{gem} 14.5, $J_{1',2'b}$ 10.7, $J_{2'b,3'}$ 2.8, 2'-H^b); NOE (1'-H ↔ 5'-H^b) was observed; MS (FAB) m/z, 371 (M + H) (Found: C, 65.0; H; 4.6%).

Typical Procedure for the Preparation of C-*Nucleosides* **35**.—Compound **32b** (0.185 g, 0.50 mmol) was dissolved in dry THF (3 cm^3), and then *N*-hydroxy-2-thiopyridone (0.067 g, 0.525 mmol) and DCC (95%; 0.124 g, 0.60 mmol) were added to the solution at 0 °C. After being stirred for 1.5 h at room temperature in the dark, the reaction mixture was filtered under Ar into a solution of 4-methylquinolinium camphorsulfonate (1.31 g, 3.50 mmol) in dichloromethane (4 cm^3). The yellow solution of the ester was stirred and irradiated with a tungsten lamp for 2.5 h at 30–33 °C, quenched with saturated aq. $NaHCO_3$, and extracted with dichloromethane, the extract was dried over Na_2SO_4 and filtered, and the filtrate was concentrated. The residue was chromatographed [ethyl acetate–

hexane (1:3–1:1)] and further purified by PLC on silica gel [ethyl acetate–hexane (1:1)] to give the α-form of product **35I** as a foam (0.023 g, 10%) and the β-form of product **35I** as a foam (0.142 g, 60%) respectively. The α:β ratio was 14:86.

2-(3′,4′-*Di*-O-*benzoyl*-2′-*deoxy*-α-D-*ribopyranosyl*)-4-*methylquinoline* **35I** had m.p. 147–149 °C; $[\alpha]_D^{24}$ −147.8 (*c* 0.68, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 1705, 1445, 1260, 1100, 765 and 715; δ_H 8.15 (2 H, dd, J_o 8.3, J_m 1.1, Ph), 8.06 (1 H, d, $J_{7,8}$ 8.5, 8-H), 8.00 (1 H, d, $J_{5,6}$ 8.3, 5-H), 7.90 (2 H, dd, J_o 8.3, J_m 1.1, Ph), 7.71 (1 H, tt, $J_{7,8}$ 8.3, $J_{5,7}$ 1.1, 7-H), 7.63–7.54 (3 H, m, 6-H and Ph), 7.50–7.46 (3 H, m, 3-H and Ph), 7.34–7.31 (2 H, m, Ph), 5.64–5.60 (2 H, m, 3′- and 4′-H), 4.90 (1 H, dd, $J_{1',2'b}$ 11.3, $J_{1',2'a}$ 2.2, 1′-H), 4.52 (1 H, dd, J_{gem} 13.2, $J_{4',5'a}$ 1.4, 5′-H^a), 4.06 (1 H, m, 5′-H^b), 2.74 (3 H, s, base Me), 2.71–2.68 (1 H, m, 2′-H^a) and 2.49 (1 H, dt, J_{gem} 12.4, $J_{1',2'b}$ 11.3, 2′-H^b); NOE (1′-H ↔ 5′-H^b) was observed; δ_C 166.0 and 165.0 (q, benzoyl CO), 159.7 (q, base C-2), 147.2 (q, base C-8a), 145.3 (q, base C-4), 133.2–129.8 (q and t, Ph), 129.7 (t, base C-8), 129.3 (t, Ph), 128.5 (t, base C-7), 128.3 (t, Ph), 128.3 (q, base C-4a), 126.2 (t, base C-5), 123.7 (t, base C-6), 118.7 (t, base C-3), 79.4 (t, C-1′), 70.4 (t, C-3′), 68.7 (s, C-5′), 68.3 (t, C-4′), 32.8 (s, C-2′) and 19.0 (p, base Me); MS (FAB) *m*/*z* 468 (M + H) (Found: C, 74.75; H, 5.3; N, 2.9. $C_{29}H_{25}NO_5$ requires C, 74.50; H, 5.39; N, 3.00%).

(β-*form*) m.p. 149–151 °C; $[\alpha]_D^{24}$ −15.6 (*c* 1.08, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 1720, 1590, 1450, 1265, 1105, 770 and 725; δ_H 8.17 (2 H, d, J_o 7.7, Ph), 8.06 (1 H, d, $J_{7,8}$ 8.5, 8-H), 8.00 (1 H, d, $J_{5,6}$ 8.3, 5-H), 7.92 (2 H, d, J_o 7.7, Ph), 7.70 (1 H, dd, $J_{7,8}$ 8.5, $J_{6,7}$ 7.2, 7-H), 7.63 (1 H, t, J_o 7.7, Ph), 7.56 (1 H, dd, $J_{5,6}$ 8.3, $J_{6,7}$ 7.2, 6-H), 7.59–7.49 (4 H, m, 3-H and Ph), 7.35 (2 H, t, J_o 7.7, Ph), 5.96 (1 H, m, 3′-H), 5.48 (1 H, ddd, $J_{4',5'b}$ 10.2, $J_{4',5'a}$ 5.2, $J_{3',4'}$ 3.0, 4′-H), 5.18 (1 H, dd, $J_{1',2'b}$ 11.3, $J_{1',2'a}$ 2.5, 1′-H), 4.30 (1 H, dd, J_{gem} 10.2, $J_{4',5'a}$ 5.2, 5′-H^a), 4.23 (1 H, t, J_{gem} = $J_{4',5'b}$ = 10.2, 5′-H^b), 2.75 (3 H, s, base Me), 2.68 (1 H, ddd, J_{gem} 14.7, $J_{2'a,3'}$ 4.1, $J_{1',2'a}$ 2.5, 2′-H^a) and 2.34 (1 H, ddd, J_{gem} 14.7, $J_{1',2'b}$ 11.3, $J_{2'b,3'}$ 2.5, 2′-H^b); NOE (3′-H, 5′-H^a, 5′-H^b ↔ base Me) was observed; δ_C 165.7 and 165.5 (q, benzoyl CO), 159.8 (q, base C-2), 147.2 (q, base C-8a), 145.4 (q, base C-4), 133.3–129.8 (q and t, Ph), 129.8 (t, base C-8), 129.3 (t, Ph), 128.5 (t, base C-7), 127.6 (q, base C-4a), 126.2 (t, base C-5), 123.7 (t, base C-6), 119.0 (t, base C-3), 76.0 (t, C-1′), 68.4 (t, C-3′), 67.9 (t, C-4′), 64.5 (s, C-5′), 35.8 (s, C-2′) and 18.9 (p, base Me); MS (FAB) *m*/*z* 468 (M + H) (Found: C, 74.0; H, 5.4; N, 2.9%).

Methyl 2-(3′,4′-*di*-O-*benzoyl*-2-*deoxy*-β-D-*ribopyranosyl*)-*isonicotinate* **35II** had m.p. 48–50 °C; $[\alpha]_D^{24}$ +44.2 (*c* 0.49, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 1710, 1590, 1430, 1265, 1095, 770 and 710; δ_H 8.71 (1 H, d, $J_{5,6}$ 5.1, 6-H), 8.14 (2 H, dd, J_o 8.2, J_m 1.3, Ph), 8.10 (1 H, s, 3-H), 7.91 (2 H, dd, J_o 8.2, J_m 1.3, Ph), 7.78 (1 H, dd, $J_{5,6}$ 5.1, $J_{3,5}$ 1.5, 5-H), 7.62 (1 H, tt, J_o 7.4, J_m 1.3, Ph), 7.50 (3 H, m, Ph), 7.35 (2 H, t, J_o 7.7, Ph), 5.92 (1 H, d, $J_{3',4'}$ 3.1, 3′-H), 5.43, (1 H, ddd, $J_{4',5'b}$ 10.4, $J_{4',5'a}$ 5.3, $J_{3',4'}$ 3.1, 4′-H), 5.10 (1 H, dd, $J_{1',2'b}$ 11.4, $J_{1',2'a}$ 2.5, 1′-H), 4.30 (1 H, dd, J_{gem} 11.0, $J_{4',5'a}$ 5.3, 5′-H^a), 4.20 (1 H, dd, J_{gem} 11.0, $J_{4',5'b}$ 10.4, 5′-H^b), 3.98 (3 H, s, CO_2Me), 2.64 (1 H, ddd, J_{gem} 14.7, $J_{2'a,3'}$ 4.0, $J_{1',2'a}$ 2.5, 2′-H^a) and 2.20 (1 H, ddd, J_{gem} 14.7, $J_{1',2'b}$ 11.4, $J_{2'b,3'}$ 2.6, 2′-H^b); NOE was not observed; HRMS (FAB) [Found: (M + H), 462.1544. $C_{26}H_{24}NO_7$ requires *m*/*z*, 462.1553. Found: C, 67.6; H, 4.9; N, 2.85. $C_{26}H_{23}NO_7$ requires C, 67.67; H, 5.02; N, 3.04%].

Methyl 6-(3′,4′-*di*-O-*benzoyl*-2′-*deoxy*-α-D-*ribopyranosyl*)-*nicotinate* **35V** had ν_{max}(KBr)/cm^{-1} 1700, 1590, 1430, 1250, 1095, 1020, 770 and 710; δ_H 9.16 (1 H, dd, $J_{2,4}$ 2.2, $J_{2,5}$ 0.7, 2-H), 8.35 (1 H, dd, $J_{4,5}$ 8.3, $J_{2,4}$ 2.2, 4-H), 8.10 (2 H, dd, J_o 8.4, J_m 1.3, Ph), 7.89 (2 H, dd, J_o 8.4, J_m 1.3, Ph), 7.69 (1 H, d, $J_{4,5}$ 8.3, 5-H), 7.59 (1 H, tt, J_o 7.5, J_m 1.3, Ph), 7.52–7.45 (3 H, m, Ph), 7.33 (2 H, t, J_o 7.5, Ph), 5.61–5.55 (2 H, br s and ddd, $J_{2'b,3'}$ 11.7, $J_{3',4'}$ 4.8, $J_{2'a,3'}$ 3.3, 3′- and 4′-H), 4.82 (1 H, dd, $J_{1',2'b}$ 11.5, $J_{1',2'a}$ 2.2, 1′-H), 4.48 (1 H, dd, J_{gem} 13.2, $J_{4',5'a}$ 2.0, 5′-H^a), 4.02 (1 H, dd, J_{gem} 13.2, $J_{4',5'b}$ 12.3, 5′-H^b), 3.96 (3 H, s, CO_2Me), 2.68–2.64 (1 H, m, 2′-H^a) and 2.31 (1 H, q, J_{gem} = $J_{1',2'b}$ = 11.5, 2′-H^b); NOE (1′-H ↔ 5′-H^b) was observed; HRMS (FAB) [Found: (M + H), 462.1557. $C_{26}H_{24}NO_7$ requires *m*/*z*, 462.1553].

(β-*form*) had m.p. 135–137 °C; $[\alpha]_D^{24}$ +87.4 (*c* 0.29, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 1710, 1590, 1450, 1270, 1105, 1015, 770 and 715; δ_H 9.14 (1 H, dd, $J_{2,4}$ 2.1, $J_{2,5}$ 0.8, 2-H), 8.35 (1 H, dd, $J_{4,5}$ 8.1, $J_{2,4}$ 2.1, 4-H), 8.14 (2 H, dd, J_o 8.4, J_m 1.4, Ph), 7.90 (2 H, dd, J_o 8.4, J_m 1.3, Ph), 7.62 (2 H, tt, J_o 7.4, J_m 1.5, Ph), 7.51 (3 H, m, 5-H and Ph), 7.37 (2 H, dd, J_m 3.1, J_m 1.5, Ph), 5.92 (1 H, br d, $J_{3',4'}$ 3.1, 3′-H), 5.42 (1 H, ddd, $J_{4',5'b}$ 10.6, $J_{4',5a}$ 5.4, $J_{3',4'}$ 3.1, 4′-H), 5.09 (1 H, dd, $J_{1',2'b}$ 11.3, $J_{1',2'a}$ 2.6, 1′-H), 4.29 (1 H, dd, J_{gem} 10.9, $J_{4',5'a}$ 5.4, 5′-H^a), 4.18 (1 H, t, $J_{4',5'b}$ 10.6, 5′-H^b), 3.96 (3 H, s, CO_2Me), 2.67 (1 H, ddd, J_{gem} 14.7, $J_{2'a,3'}$ 4.2, $J_{1',2'a}$ 2.6, 2′-H^a) and 2.14 (1 H, ddd, J_{gem} 14.7, $J_{1',2'b}$ 11.3, $J_{2'b,3'}$ 2.5, 2′-H^b); NOE (1′-H ↔ 3′-H, 1′-H ↔ 5′-H^a, 1′-H ↔ 5′-H^b) was observed; δ_C 165.6 (q, base CO), 165.53, 165.46 (q, benzoyl CO), 164.4 (q, base C-6), 150.1 (t, base C-2), 138.1 (t, base C-4), 133.3–128.4 (q and t, Ph), 125.0 (t, base C-3), 119.0 (q, base C-5), 74.9 (t, C-1′), 68.2 (t, C-3′), 67.6 (t, C-4′), 64.0 (s, C-5′), 52.4 (p, base Me) and 36.0 (s, C-2′); HRMS (FAB) [Found: (M + H), 462.1547. $C_{26}H_{24}NO_7$ requires *m*/*z*, 462.1553. Found: C, 67.55; H, 4.95; N, 3.2. $C_{26}H_{23}NO_7$ requires C, 67.67; H, 5.02; N, 3.04%].

2-(3′,4′-*Di*-O-*benzoyl*-2′-*deoxy*-α-D-*ribopyranosyl*)*benzothiazole* **35VI** had ν_{max}(KBr)/cm^{-1} 1695, 1430, 1270, 1240, 1095, 765 and 710; δ_H 8.10 (2 H, dd, J_o 8.4, J_m 1.3, Ph), 8.01 (1 H, ddd, $J_{4,5}$ 8.2, $J_{4,6}$ 1.1, $J_{4,7}$ 0.7, 4-H), 7.93 (1 H, ddd, $J_{6,7}$ 8.1, $J_{5,7}$ 1.1, $J_{4,7}$ 0.7, 7-H), 7.89 (2 H, dd, J_o 8.4, J_m 1.3, Ph), 7.59 (1 H, ddt, J_o 7.5, J_m 1.5, J_m 1.3, Ph), 7.52–7.39 (5 H, m, 5- and 6-H and Ph), 7.32 (2 H, dd, J_o 8.1, J_o 7.5, Ph), 5.63 (1 H, m, 4′-H), 5.58 (1 H, ddd, $J_{2'b,3'}$ 11.5, $J_{2'a,3'}$ 4.8, $J_{3',4'}$ 3.1, 3′-H), 5.09 (1 H, dd, $J_{1',2'b}$ 11.5, $J_{1',2'a}$ 2.6, 1′-H), 4.50 (1 H, dd, J_{gem} 13.2, $J_{4',5'a}$ 2.5, 5′-H^a), 4.07 (1 H, dd, J_{gem} 13.2, $J_{4',5'b}$ 11.3, 5′-H^b), 2.81 (1 H, dddd, J_{gem} 12.6, $J_{2'a,3'}$ 4.8, $J_{1',2'a}$ 2.6, $J_{long\ range}$ 1.1, 2′-H^a) and 2.58 (1 H, dq, J_{gem} 12.6, $J_{1',2'b}$ = $J_{2'b3'}$ = 11.5, 2′-H^b); NOE (1′-H ↔ 3′-H, 1′-H ↔ 5′-H^b) was observed; δ_C 171.0 (q, base C-2), 165.9 and 165.5 (q, benzoyl CO), 152.9 (q, base C-3a), 134.8 (q, base C-7a), 133.3–128.4 (q and t, Ph), 126.1 (t, base C-6), 125.2 (t, base C-5), 123.2 (t, base C-7), 121.8 (t, base C-4), 76.0 (t, C-1′), 69.5 (t, C-3′), 68.7 (s, C-5′), 68.0 (t, C-4′) and 32.7 (s, C-2′); HRMS (FAB) [Found: (M + H), 460.1221. $C_{26}H_{22}NO_5S$ requires *m*/*z*, 460.1217].

(β-*form*) had m.p. 201–203 °C; $[\alpha]_D^{24}$ −8.7 (*c* 0.29, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 1720, 1450, 1275, 1260, 1105, 770 and 720; δ_H 8.04 (2 H, dd, J_o 8.3, J_m 1.4, Ph), 7.93 (1 H, d, $J_{4,5}$ 8.3, 4-H), 7.85 (3 H, m, 7-H and Ph), 7.54 (1 H, t, $J_{5,6}$ 7.4, 5-H), 7.45 (1 H, t, $J_{5,6}$ 7.4, 6-H), 7.42 (3 H, t, J_o 7.7, Ph), 7.35–7.28 (3 H, m, Ph), 5.86 (1 H, m, 3′-H), 5.38 (1 H, ddd, $J_{4',5'b}$ 10.2, $J_{4',5'a}$ 5.1, $J_{3',4'}$ 3.0, 4′-H), 5.30 (1 H, dd, $J_{1',2'b}$ 10.7, $J_{1',2'a}$ 2.8, 1′-H), 4.24 (1 H, dd, J_{gem} 11.0, $J_{4',5'a}$ 5.1, 5′-H^a), 4.14 (1 H, dd, J_{gem} 11.0, $J_{4',5'b}$ 10.2, 5′-H^b), 2.74 (1 H, ddd, J_{gem} 14.6, $J_{2'a,3'}$ 4.5, $J_{1',2'a}$ 2.8, 2′-H^a) and 2.32 (1 H, ddd, J_{gem} 14.6, $J_{1',2'b}$ 10.7, $J_{2'b,3'}$ 2.8, 2′-H^b); NOE (1′-H ↔ 5′-H^b) was observed; δ_C 171.2 (q, base C-2), 165.4 (q, benzoyl CO), 152.9 (q, base C-3a), 134.8 (q, base C-7a), 133.4–128.4 (q and t, Ph), 126.2 (t, base C-6), 125.2 (t, base C-5), 123.1 (t, base C-7), 121.9 (t, base C-4), 73.0 (t, C-1′), 68.0 (t, C-3′), 67.3 (t, C-4′), 64.7 (s, C-5′) and 35.6 (s, C-2′); HRMS (FAB) [Found: (M + H), 460.1224. $C_{26}H_{22}NO_5S$ requires *m*/*z*, 460.1217. Found: C, 65.45; H, 4.5; N, 2.85. $C_{26}H_{21}NO_5S$ requires C, 67.96; H, 4.61; N, 3.05%].

4-(3′,4′-*Di*-O-*benzoyl*-2′-*deoxy*-α-D-*ribopyranosyl*)*pyrimidine* **35VII-a** had m.p. 91–92 °C; $[\alpha]_D^{24}$ +58.3 (*c* 0.57, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 1710, 1565, 1420, 1260, 1110, 990, 850, 755 and 710; δ_H 9.16 (1 H s, 2-H), 8.79 (1 H, br s, 6-H), 8.13 (2 H, dd, J_o 8.4, J_m 1.3, Ph), 7.91 (2 H, dd, J_o 8.4, J_m 1.3, Ph), 7.65–7.60 (2 H, m, 5-H and Ph), 7.54–7.48 (3 H, m, Ph), 7.38–7.26 (2 H, m, Ph), 5.92 (1 H, dd, $J_{2'a,3'}$ 4.0, $J_{3',4'}$ 3.1, 3′-H), 5.39 (1 H, ddd, $J_{4',5'b}$ 10.7, $J_{4',5'a}$ 5.3, $J_{3',4'}$ 3.1, 4′-H), 4.97 (1 H, dd, $J_{1',2'b}$ 11.4, $J_{1',2'a}$ 2.6, 1′-H), 4.29 (1 H, dd, J_{gem} 10.7, $J_{4',5'a}$ 5.3, 5′-H^a), 4.16 (1 H, t, J_{gem} = $J_{4',5'b}$ = 10.7, 5′-H^b), 2.70 (1 H, ddd, J_{gem} 14.7, $J_{2'a,3'}$ 4.0,

$J_{1',2'a}$ 2.6, 2'-H^a) and 2.08 (1 H, ddd, J_{gem} 14.7, $J_{1',2'b}$ 11.4, $J_{2'b,3'}$ 2.2, 2'-H^b); NOE (1'-H ↔ 5'-H^b) was observed; δ_C 168.7 (q, base C-4), 165.5 and 165.4 (q, benzoyl CO), 158.2 (t, base C-2), 157.7 (t, base C-6), 133.4–128.4 (q and t, Ph), 117.6 (t, base C-5), 73.9 (t, C-1'), 68.1 (t, C-3'), 67.4 (t, C-4'), 64.3 (s, C-5') and 35.6 (s, C-2'); HRMS (FAB) [Found: (M + H), 405.1433. $C_{23}H_{21}N_2O_5$ requires *m/z*, 405.1450. Found: C, 68.4; H, 4.9; N, 6.7. $C_{23}H_{20}N_2O_5$ requires C, 68.31; H, 4.98; N, 6.93%].

2-(3',4'-*Di*-O-*benzoyl*-2'-*deoxy*-β-D-*ribopyranosyl*)*pyrimidine* **35VII-b** had $[\alpha]_D^{24}$ +28.6 (*c* 0.90, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 1705, 1560, 1430, 1260, 1100, 995, 910, 810 and 710; δ_H 8.80 (2 H, d, $J_{4,5} = J_{5,6}$ = 5.0, 4- and 6-H), 8.13 (2 H, dd, J_o 8.3, J_m 1.4, Ph), 7.91 (1 H, dd, J_o 8.3, J_m 1.4, Ph), 7.62 (1 H, tt, J_o 7.4, J_m 1.4, Ph), 7.53–7.48 (3 H, m, Ph), 7.37–7.34 (2 H, m, Ph), 7.28 (1 H, t, $J_{4,5} = J_{5,6}$ = 5.0, 5-H), 5.95 (1 H, br s, 3'-H), 5.49 (1 H, ddd, $J_{4',5'b}$ 10.4, $J_{4',5'a}$ 5.2, $J_{3',4'}$ 3.0, 4'-H), 5.19 (1 H, dd, $J_{1',2'b}$ 11.1, $J_{1',2'a}$ 2.6, 1'-H), 4.35 (1 H, dd, J_{gem} 10.4, $J_{4',5'a}$ 5.2, 5'-H^a), 4.23 (1 H, t, $J_{gem} = J_{4',5'b}$ = 10.4, 5'-H^b), 2.61 (1 H, ddd, J_{gem} 14.3, $J_{2'a,3'}$ 4.4, $J_{1',2'a}$ 2.6, 2'-H^a) and 2.46 (1 H, ddd, J_{gem} 14.3, $J_{1',2'b}$ 11.1, $J_{2'b,3'}$ 2.8, 2'-H^b); NOE (1'-H ↔ 5'-H^b) was observed; δ_C 167.9 (q, base C-2), 165.6 and 165.4 (q, benzoyl CO), 157.5 (t, base C-4 and -6), 133.3–128.4 (q and t, Ph), 120.2 (t, base C-5), 75.6 (t, C-1'), 68.1 (t, C-3'), 67.7 (t, C-4'), 64.8 (s, C-5') and 34.8 (s, C-2'); HRMS (FAB) [Found: (M + H), 405.1454. $C_{23}H_{21}N_2O_5$ requires *m/z*, 405.1450. Found: C, 68.1; H, 4.9; N, 6.9. $C_{23}H_{20}N_2O_5$ requires C, 68.31; H, 4.98; N, 6.93%].

Typical Procedure for the Deprotection.—Compound **28I** (β-form; 0.787 g, 0.17 mmol) was dissolved in dry methanol (15 cm^3) which was saturated with ammonia at 0 °C. After being stirred for one day at room temperature in a sealed tube, the reaction mixture was concentrated, and chromatographed on silica gel (ethyl acetate) to give compound **29I** (0.039 g, 88%). Deprotection of other compounds was carried out by the same procedure [dichloromethane–methanol (10:1) or ethyl acetate alone].

2-(2'-*Deoxy*-β-D-*ribofuranosyl*)-4-*methylquinoline* **29I** had $[\alpha]_D^{24}$ +2.0 (*c* 0.43, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 3320, 3200–2500, 1590, 1560, 1440, 1350, 1260, 1130, 1090, 1050, 1010, 890 and 765; δ_H 8.03 (1 H, dd, $J_{7,8}$ 8.4, $J_{6,8}$ 1.3, 8-H), 8.00 (1 H, dd, $J_{5,6}$ 8.4, $J_{5,7}$ 1.5, 5-H), 7.72 (1 H, ddd, $J_{7,8}$ 8.4, $J_{6,7}$ 7.0, $J_{5,7}$ 1.5, 7-H), 7.58 (1 H, ddd, $J_{5,6}$ 8.4, $J_{6,7}$ 7.0, $J_{6,8}$ 1.3, 6-H), 7.36 (1 H, d, $J_{long\ range}$ 0.7, 3-H), 5.40 (1 H, dd, $J_{2'a,3'}$ 8.8, $J_{3',4'}$ 1.7, 3'-H), 4.40 (1 H, d, $J_{1',2'a}$ 6.4, 1'-H), 4.31 (1 H, ddd, $J_{4',5'b}$ 5.7, $J_{4',5'a}$ 3.8, $J_{3',4'}$ 1.7, 4'-H), 3.74 (1 H, dd, J_{gem} 11.5, $J_{4',5'a}$ 3.8, 5'-H^a), 3.64 (1 H, dd, J_{gem} 11.5, $J_{4',5'b}$ 5.7, 5'-H^b), 2.74 (3 H, d, $J_{long\ range}$ 0.7, Me), 2.63 (1 H, ddd, J_{gem} 13.9, $J_{2'a,3'}$ 8.8, $J_{1',2'a}$ 6.4, 2'-H^a), 2.44 (1 H, d, J_{gem} 13.9, 2'-H^b), 2.02 (1 H, br s, OH) and 1.71 (1 H, br s, OH); NOE (3'-H ↔ base Me, 5'-H^a ↔ base Me) was observed; HRMS (FAB) [Found: (M + H), 260.1285. $C_{15}H_{18}NO_3$ requires *m/z*, 260.1287].

6-(2-*Deoxy*-α-D-*ribofuranosyl*)*nicotinamide* **29V** was an oil; ν_{max}(neat)/cm^{-1} 3500–3000, 1680–1580, 1555, 1520, 1410, 1030, 950, 870, 790 and 750; δ_H(CD_3OD) 8.95 (1 H, d, $J_{2,4}$ 2.2, 2-H), 8.26 (1 H, dd, $J_{4,5}$ 8.2, $J_{2,4}$ 2.2, 4-H), 7.71 (1 H, d, $J_{4,5}$ 8.2, 5-H), 5.22 (1 H, dd, $J_{1',2'a}$ 7.9, $J_{1',2'b}$ 6.2, 1'-H), 4.36 (1 H, dd, $J_{2'a,3'}$ 6.4, $J_{2'b,3'}$ 4.9, 3'-H), 4.10 (1 H, dd, $J_{4',5'b}$ 5.1, $J_{4',5'a}$ 4.0, 4'-H), 3.70 (1 H, dd, J_{gem} 11.7, $J_{4',5'a}$ 4.0, 5'-H^a), 3.63 (1 H, dd, J_{gem} 11.7, $J_{4',5'b}$ 5.1, 5'-H^b), 3.31 (2 H, br s, $CONH_2$), 2.75 (1 H, ddd, J_{gem} 13.0, $J_{1',2'a}$ 7.9, $J_{2'a,3'}$ 6.4, 2'-H^a) and 2.05 (1 H, ddd, J_{gem} 13.0, $J_{1',2'b}$ 6.2, $J_{2'b,3'}$ 4.9, 2'-H^b); NOE (1'-H ↔ 3'-H, 4'-H ↔ 5-H) was observed; HRMS (FAB) [Found: (M + H), 239.1033. $C_{11}H_{15}N_2O_4$ requires *m/z*, 239.1032].

4-(2'-*Deoxy*-α-D-*ribofuranosyl*)*pyrimidine* **29VII-a** was an oil; ν_{max}(neat)/cm^{-1} 3600–3000, 1735, 1580, 1550, 1470, 1395, 1385, 1310, 1000, 895 and 865; δ_H($CDCl_3$ with CD_3OD) 9.13 (1 H, d, $J_{2,6}$ 1.3, 2-H), 8.74 (1 H, d, $J_{5,6}$ 5.1, 6-H), 7.57 (1 H, dd, $J_{5,6}$ 5.1, $J_{2,5}$ 0.9, 5-H), 5.16 (1 H, dd, $J_{1',2'a}$ 8.6, $J_{1',2'b}$ 4.6, 1'-H), 4.38 (1 H, ddd, $J_{2'a,3'}$ 6.4, $J_{2'b,3'}$ 3.8, $J_{3',4'}$ 3.3, 3'-H), 4.16 (1 H, td, $J_{4',5'a}$ 4.6, $J_{3',4'}$ 3.3, 4'-H), 3.71 (1 H, dd, J_{gem} 11.7, $J_{4',5'a}$ 4.6, 5'-H^a), 3.68–3.64 (1 H, m, 5'-H^b), 2.73 (1 H, ddd, J_{gem} 13.6, $J_{1',2'a}$ 8.6, $J_{2'a,3'}$ 6.4, 2'-H^a) and 2.16 (1 H, ddd, J_{gem} 13.6, $J_{1',2'b}$ 4.6, $J_{2'b,3'}$ 3.8, 2'-H^b); NOE (1'-H ↔ 3'-H) was observed: HRMS (FAB) [Found: (M + H), 197.0928. $C_9H_{13}N_2O_3$ requires *m/z*, 197.0926].

4-(2'-*Deoxy*-β-D-*ribofuranosyl*)*pyrimidine* **29VII-b** was an oil; δ_H($CDCl_3$ with CD_3OD) 9.16 (1 H, s, 2-H), 8.73 (1 H, d, $J_{5,6}$ 5.1, 6-H), 7.43 (1 H, dd, $J_{5,6}$ 5.1, $J_{2,5}$ 1.3, 5-H), 5.23 (1 H, dd, $J_{1',2'b}$ 9.2, $J_{1',2'a}$ 6.6, 1'-H), 4.49 (1 H, dd, $J_{3',4'}$ 3.1, $J_{2'a,3'}$ 2.4, 3'-H), 4.14 (1 H, td, $J_{4',5'}$ 3.5, $J_{3',4'}$ 3.1, 4'-H), 3.87 (1 H, dd, J_{gem} 12.1, $J_{4',5'a}$ 3.5, 5'-H^a), 3.72 (1 H, dd, J_{gem} 12.1, $J_{4',5'b}$ 3.5, 5'-H^b), 2.45 (1 H, br s, OH), 2.40 (1 H, ddd, J_{gem} 13.2, $J_{1',2'a}$ 6.6, $J_{2'a,3'}$ 2.4, 2'-H^a) and 2.19 (1 H, ddd, J_{gem} 13.2, $J_{1',2'b}$ 9.2, $J_{2'b,3'}$ 5.9, 2'-H^b); NOE (1'-H ↔ 4'-H, 5'-H ↔ 2-H) was observed.

2-(2'-*Deoxy*-β-D-*ribopyranosyl*)-4-*methylquinoline* **36I** had m.p. 147–148 °C; $[\alpha]_D^{24}$ +3.6 (*c* 0.27, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 3500–3100, 1595, 1225, 1100, 1055, 880 and 780; δ_H 8.05 (1 H, d, $J_{7,8}$ 8.5, 8-H), 7.99 (1 H, dd, $J_{5,6}$ 8.3, $J_{5,7}$ 1.4, 5-H), 7.71 (1 H, ddd, $J_{7,8}$ 8.5, $J_{6,7}$ 6.9, $J_{5,7}$ 1.4, 7-H), 7.55 (1 H, ddd, $J_{5,6}$ 8.3, $J_{6,7}$ 6.9, $J_{6,8}$ 1.1, 6-H), 7.51 (1 H, s, 3-H), 5.18 (2 H, dd and br s, $J_{1',2'b}$ 11.5, $J_{1',2'a}$ 2.5, 1'-H and 3'-OH), 4.43 (1 H, br d, $J_{3',4'}$ 2.8, 3'-H), 4.04 (1 H, dd, J_{gem} 9.9, $J_{4',5'a}$ 4.4, 5'-H^a), 3.97–3.88 (2 H, m, 4'-H and 5'-H^b), 2.97–2.85 (1 H, br s, 5'-OH), 2.72 (3 H, s, Me), 2.38 (1 H, ddd, J_{gem} 14.0, $J_{2'a,3'}$ 3.7, $J_{1',2'a}$ 2.5, 2'-H^a) and 1.96 (1 H, ddd, J_{gem} 14.0, $J_{1',2'b}$ 11.5, $J_{2'b,3'}$ 2.2, 2'-H^b); δ_C 161.4 (q, base C-2), 146.4 (q, base C-8a), 146.3 (q, base C-4), 129.8 (t, base C-8), 129.7 (t, base C-7), 127.6 (q, base C-4a), 126.3 (t, base C-5), 123.8 (t, base C-6), 119.1 (t, base C-3), 74.1 (t, C-1'), 67.1 (t, C-3'), 66.9 (s, C-5'), 66.3 (t, C-4'), 39.4 (s, C-2') and 18.9 (p, base Me); HRMS (FAB) [Found: (M + H), 260.1274. $C_{15}H_{18}NO_3$ requires *m/z*, 260.1286. Found: C, 69.1; H, 6.6; N, 5.2. $C_{15}H_{17}NO_3$ requires C, 69.48; H, 6.61; N, 5.40%].

2-(2'-*Deoxy*-β-D-*ribopyranosyl*)*benzothiazole* **36VI** had m.p. 137 °C; $[\alpha]_D^{24}$ +41.9 (*c* 0.34, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 3500–3000, 1510, 1330, 1175, 1090, 1055, 890, 765 and 735; δ_H 8.00 (1 H, dt, $J_{4,5}$ 8.3, $J_{4,7}$ 0.5, 4-H), 7.91 (1 H, ddd, $J_{6,7}$ 8.1, $J_{5,7}$ 1.3, $J_{4,7}$ 0.5, 7-H), 7.48 (1 H, ddd, $J_{4,5}$ 8.3, $J_{5,6}$ 7.1, $J_{5,7}$ 1.3, 5-H), 7.39 (1 H, ddd, $J_{6,7}$ 8.1, $J_{5,6}$ 7.1, $J_{4,6}$ 1.0, 6-H), 5.23 (1 H, dd, $J_{1',2'b}$ 10.8, $J_{1',2'a}$ 2.8, 1'-H), 4.31 (1 H, m, 3'-H), 4.00 (1 H, dd, J_{gem} 9.9, $J_{4',5'a}$ 4.2, 5'-H^a), 3.94–3.90 (1 H, m, 4'-H), 3.85 (1 H, t, $J_{gem} = J_{4',5'b}$ = 9.9, 5'-H^b), 2.59–2.05 (2 H, br s, 3'- and 5'-OH), 2.55 (1 H, ddd, J_{gem} 14.2, $J_{2'a,3'}$ 4.4, $J_{1',2'a}$ 2.8, 2'-H^a) and 2.09 (1 H, ddd, J_{gem} 14.2, $J_{1',2'b}$ 10.8, $J_{2'b,3'}$ 2.8, 2'-H^b); δ_C 173.7 (q, base C-2), 152.6 (q, base C-3a), 134.5 (q, base C-7a), 126.2 (t, base C-6), 125.1 (t, base C-5), 122.6 (t, base C-7), 121.9 (t, base C-4), 71.8 (t, C-1'), 66.9 (t, C-3'), 66.6 (s, C-5'), 66.2 (t, C-4') and 37.9 (s, C-2'); HRMS (FAB) [Found: (M + H), 252.0702. $C_{12}H_{14}NO_3S$ requires *m/z*, 252.0694. Found: C, 57.1; H, 5.1; N, 5.4. $C_{12}H_{13}NO_3S$ requires C, 57.35; H, 5.21; N, 5.58%].

4-(2'-*Deoxy*-β-D-*ribopyranosyl*)*pyrimidine* **36VII-a** had m.p. 135–137 °C; $[\alpha]_D^{24}$ +94.7 (*c* 0.35, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 3500–3000, 1580, 1470, 1390, 1100, 1050, 1000, 880, 770, 715 and 670; δ_H($CDCl_3$ with CD_3OD) 9.10 (1 H, d, $J_{2,6}$ 1.1, 2-H), 8.72 (1 H, d, $J_{5,6}$ 5.3, 6-H), 7.55 (1 H, dd, $J_{5,6}$ 5.3, $J_{2,5}$ 0.6, 5-H), 4.81 (1 H, dd, $J_{1',2'b}$ 11.5, $J_{1',2'a}$ 2.4, 1'-H), 4.19 (1 H, m, 3'-H), 3.93 (1 H, m, 5'-H^a), 3.79 (1 H, dd, $J_{4',5'b}$ 10.6, $J_{4',5'a}$ 3.1, 4'-H), 3.78–3.72 (1 H, m, 5'-H^b), 2.85 (2 H, br s, 3'- and 5'-OH), 2.35 (1 H, ddd, J_{gem} 14.1, $J_{2'a,3'}$ 3.8, $J_{1',2'a}$ 2.4, 2'-H^a) and 1.73 (1 H, ddd, J_{gem} 14.1, $J_{1',2'b}$ 11.5, $J_{2'b,3'}$ 2.6, 2'-H^b); δ_C($CDCl_3$ with CD_3OD) 170.4 (q, base C-4), 157.7 (t, base C-2,) 157.5 (t, base C-6), 118.0 (t, base C-5), 72.6 (t, C-1'), 66.9 (t, C-3'), 66.5 (t, C-4'), 66.4 (s, C-5') and 37.9 (s, C-2'); HRMS (FAB) [Found: (M + H), 197.0930. $C_9H_{13}N_2O_3$ requires *m/z*, 197.0925. Found: C, 55.4; H, 6.2; N, 14.0. $C_9H_{12}N_2O_3$ requires C, 55.09; H, 6.17; N, 14.28%].

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