C-Nucleosides. 11.† Synthesis of Quinoxaline *C*-Nucleosides through Condensation of 1,2-Diaminobenzenes with 6-Hydroxy-6-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-2,6-dihydropyran-3-one

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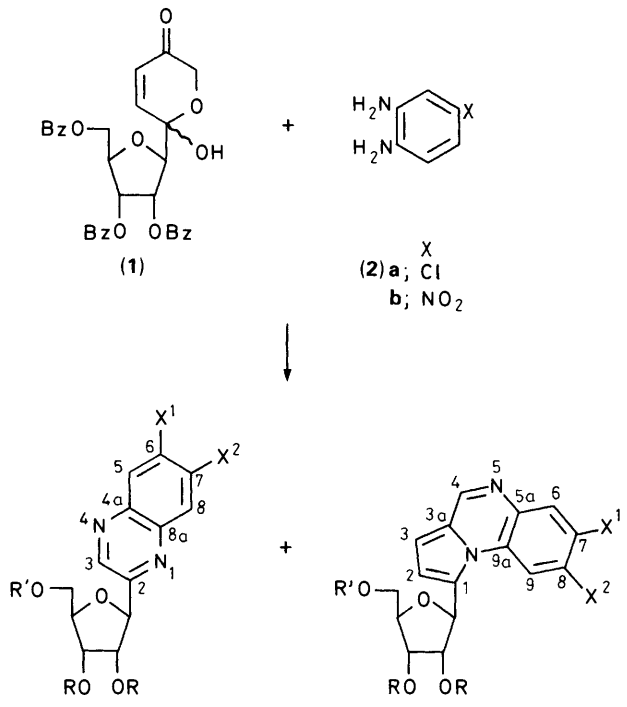
The synthesis of 6- and 7-substituted-2-(β-D-ribofuranosyl)quinoxaline and 7- and 8-substituted-1-(β-D-ribofuranosyl)pyrrolo[1,2-*a*]quinoxaline from 6-hydroxy-6-(2,3,5-tri-*O*-benzoyl-β-D- ribofuranosyl)-2,6-dihydropyran-3-one (**1**) is described. Treatment of (**1**) with 1,2-diamino-4-chlorobenzene (**2a**) afford three compounds, the 6- and 7-chloroquinoxalines (**3a**) and (**3b**) and the 7-chloropyrrolo[1,2-*a*]quinoxaline (**4a**) in 23, 43, and 9% yield, respectively. The position of the substituent in products (**3a**) and (**3b**) was determined by comparison of these ^{1}H n.m.r. spectra with those of the corresponding *N*-oxides (**5a**), (**6a**), and (**5b**), (**6b**), prepared by oxidation of compounds (**3a**) and (**3b**) with *m*-chloroperbenzoic acid. The position of the substituent in (**4a**) was confirmed by ^{1}H–^{13}C long-range COSY experiment with corresponding deblocked pyrrolo[1,2-*a*]quinoxaline (**4c**). Treatment of compound (**1**) with 1,2-diamino-4-nitrobenzene (**2b**) afforded two compounds, the 6-nitroquinoxaline (**3c**) and the 8-nitropyrrolo[1,2-*a*]quinoxaline (**4b**). Deprotection of compounds (**3a—c**), (**4a, b**), (**5a, b**), and (**6a, b**) with methanolic sodium hydroxide afforded (**3d—f**), (**4c, d**), (**5c, d**), and (**6c, d**), respectively.

In a recent report from our laboratory, we described the preparation of a functionalized *C*-glycoside, 6-hydroxy-6-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-2,6-dihydropyran-3-one (**1**), and its utilization in the synthesis of quinoxaline and pyrrole *C*-nucleosides.[1] We have investigated a convenient and general synthesis of quinoxaline derivatives through condensation of 1,2-diaminobenzenes with compound (**1**). It was of interest to examine whether 6-substituted quinoxaline *C*-nucleosides or the corresponding 7-isomers would be obtained on treatment of 1,2-diamino-4-substituted benzenes with compound (**1**). The key synthetic intermediate pyranulose (**1**) can be obtained readily from 2-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)furan by our previously published procedure.[1]

Treatment of 1,2-diamino-4-chlorobenzene (**2a**) with pyranulose (**1**) in chloroform under reflux gave a mixture of 6-chloro-2-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)quinoxaline (**3a**), 7-chloro-2-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)quinoxaline (**3b**), and 7-chloro-1-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-pyrrolo[1,2-*a*]quinoxaline (**4a**) in 23, 43, and 9% yield, respectively (Scheme 1). The position of the substituent in compounds (**3a**) and (**3b**) was determined by comparison of their ^{1}H n.m.r. spectra with those of the corresponding *N*-oxides (**5a**), (**6a**), and (**5b**), (**6b**), prepared by oxidation of (**3a**) and (**3b**) with *m*-chloroperbenzoic acid (MCPBA). The ratios of 1-oxide (**5a**)/4-oxide (**6a**) and 1-oxide (**5b**)/4-oxide (**6b**) were ~1:3, respectively. The position of the N–O group in these *N*-oxides was also determined by analysis of the ^{1}H n.m.r. spectra of the corresponding *N*-oxides. In ^{1}H n.m.r. spectra, the signals for the proton adjacent to the *N*-oxide underwent an upfield shift relative to the parent quinoxaline, whereas the signals due to the proton at the *peri*-position to the *N*-oxide were displaced downfield.[2] The signal of 3-H of 4-oxide (**6a**) at δ 8.61 occurs at higher field than that of (**3a**) at δ 9.06, and 3-H of 1-oxide (**5a**) shifted to δ 9.04. These data indicate that (**5a**) and (**6a**) are the 1-oxide and 4-oxide, respectively. The spectra of compounds (**5a**) and (**6a**) contained doublets at δ 8.47 (*J* 9.4 Hz) and 8.51 (*J* 2.0 Hz), which could be assigned to 8-H and 5-H at the position *peri* to the *N*-oxide. These coupling constants indicated that the chloro group was located at the 6-position. As summarized in Table 1, (**5b**) and (**6b**) are the 1-oxide and 4-oxide, respectively. The chloro group was located at the 7-position as follows. The position of the substituent in the pyrrolo[1,2-*a*]quinoxaline (**4a**) was confirmed by a ^{1}H–^{13}C long-range COSY experiment with the corresponding deblocked pyrrolo[1,2-*a*]quinoxaline (**4c**). In ^{1}H–^{13}C long-range experiments of (**4c**), a correlation was observed between 9-H at δ 8.46 (*J* 9.1 Hz) and C-5a and C-7 at δ_C 137.93 and 129.06. Other long-range correlations are shown by arrows in the Figure. This data indicated that the chloro group was located at the 7 position. Coupling constants for the ^{1}H n.m.r. spectra are given in Table 2.

Next, the reaction between 1,2-diamino-4-nitrobenzene (**2b**) and the pyranulose (**1**) afforded 6-nitro-2-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)quinoxaline (**3c**) in 40% yield without formation of the 7-nitroquinoxaline isomer, and small amounts of 8-nitro-1-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)pyrrolo-[1,2-*a*]quinoxaline (**4b**). In order to determine the position of nitro group, we attempted to prepare the corresponding *N*-oxide compound. However, attempted *N*-oxidation of (**3c**) with MCPBA resulted in the recovery of unchanged starting material. The ^{1}H–^{13}C long-range COSY spectrum of compound (**3c**) exhibited a correlation between 8-H at δ 8.09 (*J* 9.2 Hz) and C-4a at δ_C 141.25. Other long-range correlations are shown by arrows in the Figure. Hence, the nitro group was located at C-6. The position of the nitro group in (**4b**) was confirmed by a ^{1}H–^{13}C COSY experiment with the corresponding deblocked pyrrolo[1,2-*a*]quinoxaline (**4d**). The spectrum of compound (**4d**) contained a doublet at low field δ 9.60 (*J* 2.3 Hz, 9-H).[3] This coupling constant indicated that the nitro group was located at C-8. This positionally selective synthesis of compounds (**3c**) and (**4b**) most probably proceeds *via* preferential reaction of C-5 and C-3 in the pyranulose with the more basic amino group in (**2b**) (Scheme 2). The preponderant product (**3b**) would result from preferential reaction at C-5 in the pyranulose by the more basic amino group in (**2a**).

† Part 10. I. Maeba, K. Kitaori, and C. Ito, *J. Org. Chem.*, 1989, **54**, 3927.



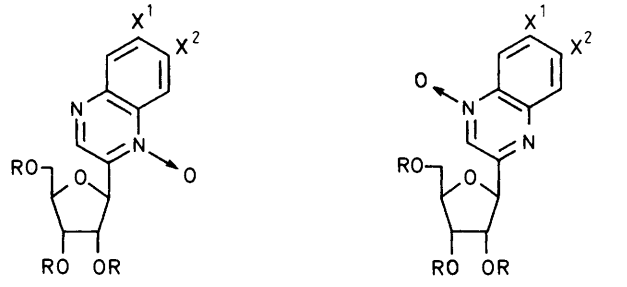
(1)

(2) a; X = Cl
b; X = NO_2

	X^1	X^2	R′	R
(3)a;	Cl	H	Bz	Bz
b;	H	Cl	Bz	Bz
c;	NO_2	H	Bz	Bz
d;	Cl	H	H	H
e;	H	Cl	H	H
f;	NO_2	H	H	H
g;	Cl	H	H	R = CMe_2
h;	H	Cl	H	R = CMe_2
i;	NO_2	H	H	R = CMe_2

	X^1	X^2	R′	R
(4)a;	Cl	H	Bz	Bz
b;	H	NO_2	Bz	Bz
c;	Cl	H	H	H
d;	H	NO_2	H	H
e;	Cl	H	H	R = CMe_2
f;	H	NO_2	H	R = CMe_2

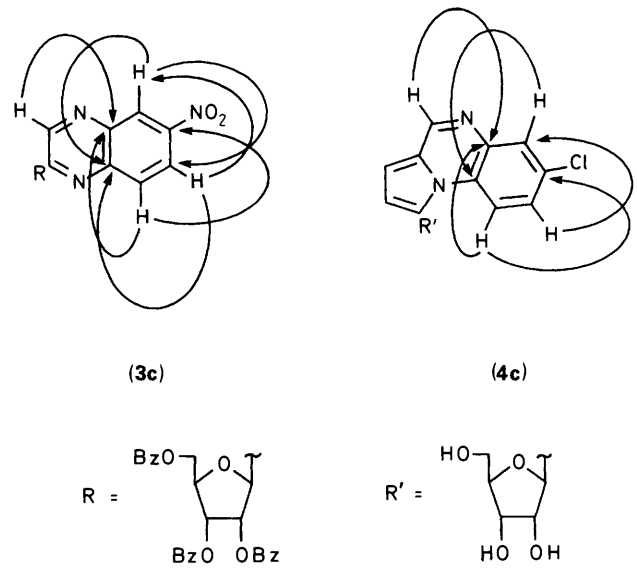
Scheme 1.



	X^1	X^2	R
(5)a;	Cl	H	Bz
b;	H	Cl	Bz
c;	Cl	H	H
d;	H	Cl	H

	X^1	X^2	R
(6)a;	Cl	H	Bz
b;	H	Cl	Bz
c;	Cl	H	H
d;	H	Cl	H

Deprotection of compounds (**3a**—**c**), (**4a, b**), (**5a, b**), and (**6a, b**) with methanolic sodium hydroxide afforded products (**3d**—**f**), (**4c, d**), (**5c, d**), and (**6c, d**), respectively. The assignments of anomeric configurations of compounds (**3d**—**f**) and (**4c, d**) were made on the basis of the difference in the chemical shifts of the two methyl signals of the corresponding 2,3-*O*-isopropylidene derivatives (**3g**—i) and (**4e, f**). The ^1H n.m.r. chemical-shift



(3c) (4c)

Figure The ^1H–^{13}C long-range COSY experiments with compounds (**3c**) and (**4c**)

differential value ($\Delta\delta$) of the methyl groups in the isopropylidene derivatives is indicative of β stereochemistry in accordance with the Imbach's rule (< 0.15 and > 0.15 p.p.m. for the α and β anomers)[4] (see Experimental Section). Deoxygenation of *N*-oxides (**5c**), (**6c**), (**5d**), and (**6d**) with triphenylphosphine in methanol gave (**3d**) and (**3e**), respectively. This showed that the β-ribofuranoside configuration had been preserved during the reaction sequence.

Experimental

M.p.s were determined on a Yanagimoto apparatus and are uncorrected. Mass spectra were taken on a Hitachi M-80 instrument by direct insertion at 70 eV; fast-atom bombardment (f.a.b.) mass spectra were run on a JMS-HX 110 using nitrobenzyl alcohol. ^1H N.m.r. spectra were measured with a JNM-GX-270 and a GX-400 (JEOL) spectrometer, with tetramethylsilane as internal standard. ^{13}C N.m.r. spectra were recorded on a JEOL JNM-FX-100 Fourier transform spectrometer operating at 25.00 MHz, with tetramethylsilane as internal standard. Elemental analysis were determined by the analytical centre of this faculty. Analytical t.l.c. was performed on glass plates coated with a 0.5-mm layer of silica gel GF_{254} (Merck). The compounds were detected by u.v. light (254 nm). Column chromatography was performed on silica gel C-200 (74—149 μm, Wakogel).

*6-Chloro- and 7-Chloro-2-(2,3,5-tri-*O*-benzoyl-*β*-*D*-ribofuranosyl)quinoxaline* (**3a**) *and* (**3b**) *and 7-Chloro-1-(2,3,5-tri-*O*-benzoyl-*β*-*D*-ribofuranosyl)pyrrolo*[1,2-a]*quinoxaline* (**4a**).—A solution of the pyranulose (**1**) (825 mg, 1.48 mmol) and 1,2-diamino-4-chlorobenzene (**2a**) (253 mg, 1.77 mmol) in chloroform (10 ml) was heated under reflux for 5 h, and then the solvent was evaporated off under reduced pressure. T.l.c. (chloroform–methanol, 9:1) showed that the light yellow syrup contained three major components (R_F 0.15, 0.17, and 0.18). The mixture was separated by preparative t.l.c. (p.l.c.) with chloroform as developer (× 6).

Compound (**3a**) (212 mg, 23%); R_F 0.18; syrup (Found: C, 66.8; H, 4.3; N, 4.4. $C_{34}H_{25}ClN_2O_7$ requires C, 67.05; H, 4.14; N, 4.60%); $\delta_C(CDCl_3)$ 63.83 (C-5′), 72.66, 75.59, 80.73, 82.55 (C-1′, -2′, -3′, and -4′), 128.24—133.50 (C-5, -7, -8, and -Ar), 136.08 (C-

Table 1. ^{1}H N.m.r. chemical shifts (δ) of certain *C*-nucleosides

Compound	Solvent[a]	1′-H	2′-H	3′-H	4′-H	5′-Ha	5′-Hb	3-H	Other
(3a)	A	5.62(d)	6.20(t)	5.99(t)	4.88(m)	4.63(dd)	4.88(m)	9.06(s)	7.26—8.10(m, 5-H, 7-H, 8-H, Ar-H)
(3b)	A	5.62(d)	6.19(t)	6.02(t)	4.87(m)	4.62(dd)	4.87(m)	9.04(s)	7.37—8.11(m, 5-H, 6-H, 8-H, Ar-H)
(3c)	A	5.66(d)	5.97(t)	6.22(t)	4.93(m)	4.64(dd)	4.93(m)	9.23(s)	7.26—8.02(m, Ar-H), 8.09(d, 8-H) 8.48(dd, 7-H), 8.94(d, 5-H)
(3d)	B	5.35(d)	4.31(t)	4.19(t)	4.13(q)	3.77(dd)	3.91(dd)	9.14(s)	7.84(dd, 7-H), 8.06(d, 8-H) 8.09(d, 5-H)
(3e)	C	5.09(d)	4.31(t)	4.19(t)	4.14(q)	3.77(dd)	3.91(dd)	9.23(s)	7.79(dd, 6-H), 8.14(d, 5-H), 8.15(apparent s, 8-H)
(df)	B	5.13(d)	4.34(t)	4.15(m)		3.78(dd)	3.91(dd)	9.33(s)	8.28(d, 8-H), 8.59(dd, 7-H), 8.97(d, 5-H)
(5a)	A	5.86(d)	6.02(dd)	5.81(dd)	4.86(m)	4.71(m)	4.86(m)	9.04(s)	7.26—8.10(m, Ar-H), 7.68(dd, 7-H), 8.15(d, 5-H), 8.47(d, 8-H)
(5b)	A	5.87(d)	6.01(dd)	5.82(t)	4.87(m)	4.71(dd)	4.87(m)	9.01(s)	7.20—7.61, 7.90—8.11(m, 5-H, Ar-H), 7.77(dd, 6-H), 8.53(d, 8-H)
(5c)	E	5.48(3)	4.31(t)	4.21(t)	4.11(q)	3.91(dd)	4.05(dd)	9.27(s)	7.84(dd, 7-H), 8.15(d, 5-H), 8.53(d, 8-H)
(5d)	B	4.98(d)	4.27(t)	4.13(m)		3.75(dd)	3.90(dd)	8.88(s)	7.89(dd, 6-H), 8.11(d, 5-H), 8.53(d, 8-H)
(6a)	A	5.47(d)	6.15(t)	5.89(t)	4.85(m)	4.64(dd)	4.85(m)	8.61(s)	7.29—7.68, 7.95—8.09(m, 8-H, Ar-H), 7.71(dd, 7-H), 8.51(d, 5-H)
(6b)	A	5.45(d)	6.12(t)	5.91(t)	4.87(m)	4.63(dd)	4.87(m)	8.57(s)	7.33—8.07(m, Ar-H), 7.64(dd, 6-H), 7.92(d, 8-H), 8.44(d, 5-H)
(6c)	C	4.85(d)	5.06(dd)	5.30(t)	4.12(m)	3.96(m)		8.90(s)	7.96(dd, 7-H), 8.14(d, 8-H), 8.43(d, 5-H)
(6d)	B	4.88(d)	4.18(t)	3.87(m)		3.67(dd)	3.78(dd)	8.77(s)	7.70(dd, 6-H), 8.04(d, 8-H), 8.40(d, 5-H)

Compound	Solvent[a]	1′-H	2′-H	3′-H	4′-H	5′-Ha	5′-Hb	2-H, 3-H[b]	H-4	Other
(4a)	A	5.88(d)	6.35(dd)	5.99(dd)	4.88(q)	4.60(dd)	4.78(dd)	6.86(d), 7.02(d)	9.04(s)	7.29—8.02(m, 6-H, 8-H, Ar-H),
(4b)	A	5.92(d)	6.38(dd)	6.00(dd)	5.01(q)	4.65(dd)	4.85(dd)	6.97(d), 7.12(d)	8.86(s)	8.42(d, 9-H) 7.26—8.09(m, 6-H, Ar-H), 8.31(dd, 7-H), 9.54(d, 9-H)
(4c)	C	5.19(d)	4.39(t)	4.03(m)		3.17—3.49(m)		7.02(d), 7.13(d)	8.90(s)	7.66(dd, 8-H), 7.92(d, 6-H), 8.46(d, 9-H)
(4d)	D	5.30(d)	4.35—4.91(m)	4.30(m)		3.83(apparent d)		7.18(d), 7.24(d)	8.89(s)	8.05(d, 6-H), 8.32(dd, 7-H), 9.60(d, 9-H)

[a] A = $CDCl_3$; B = CD_3OD; C = $(CD_3)_2SO$; D = $CDCl_3$–CD_3OD (1 : 1). [b] The designated assignment can be reversed.

6), 140.17, and 142.69 (C-4a and -8a), 144.85 (C-3), 152.46 (C-2), and 165.39 (C=O).

Compound (**3b**) (385 mg, 43%); R_F 0.17; syrup (Found: C, 66.8; H, 4.2; N, 4.3%); $\delta_C(CDCl_3)$ 63.71 (C-5′), 72.66, 75.59, 80.79, 82.43 (C-1′, -2′, -3′, and -4′), 128.41—133.44 (C-5, -6, -8, and -Ar), 136.08 (C-7), 140.87, and 141.87 (C-4a and -8a), 144.15 (C-3), 153.16 (C-2), and 165.33, and 166.03 (C=O).

Compound (**4a**) (80 mg, 9%); R_F 0.15; foam (Found: C, 67.8; H, 4.4; N, 4.5. $C_{37}H_{27}ClN_2O_7 \cdot \frac{1}{2}H_2O$ requires C, 67.73; H, 4.30, N, 4.27%); $\delta_C(CDCl_3)$ 63.89 (C-5′), 72.72, 73.60, 75.23, 80.62 (C-1′, -2′, -3′, and -4′), 107.76 and 114.31 (C-2 and -3), 118.18 (C-9), 127.54—129.70 (C-3a, -9a, and -Ar), 130.64 (C-7), 133.21 and 133.62 (C-6 and -8), 138.13 and 138.18 (C-1 and -5a), 146.78 (C-4), and 165.21 and 166.03 (C=O).

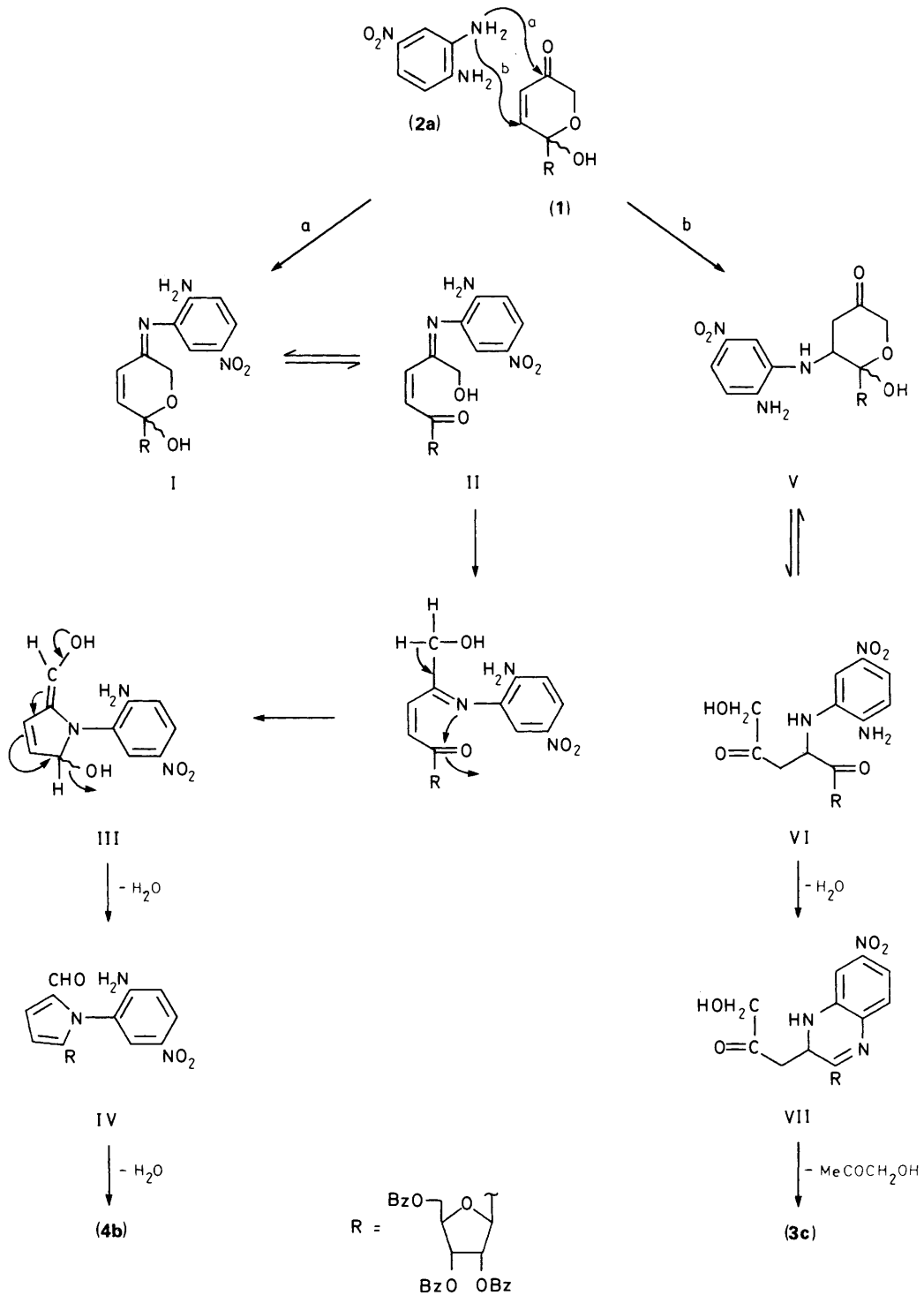
6-*Nitro*-2-(2,3,5-*tri*-O-*benzoyl*-β-D-*ribofuranosyl*)*quinoxaline* (**3c**) *and* 8-*Nitro*-1-(2,3,5-*tri*-O-*benzoyl*-β-D-*ribofuranosyl*)*pyrrolo*[1,2-a]*quinoxaline* (**4b**).—A solution of the pyranulose (**1**) (494 mg, 0.89 mmol) and 1,2-diamino-4-nitrobenzene (**2b**) (163 mg, 1.06 mmol) in toluene (10 ml) was heated at 90 °C for 4 h, and then the solvent was evaporated off under reduced pressure. T.l.c. (chloroform–methanol, 99 : 1) showed that the light yellow syrup contained two major components (R_F 0.37 and 0.45). The mixture was separated by p.l.c. with hexane–ethyl acetate (3 : 1) as developer (× 3).

Compound (**3c**) (89 mg, 16%); R_F 0.45; yellow foam (Found: C, 63.4; H, 4.2; N, 6.2. $C_{34}H_{25}N_3O_9 \cdot \frac{3}{2}H_2O$ requires C, 63.15; H, 4.36; N, 6.45%) $\delta_C(CDCl_3)$ 63.63 (C-5′), 72.58 (C-2′), 75.50 (C-3′), 81.00 (C-4′), 82.49 (C-1′), 123.65 (C-7), 125.74 (C-5), 128.39—134.60 (C-Ar), 131.20 (C-8), 141.25 (C-4a), 143.95 (C-8a), 146.21 (C-3), 148.01 (C-6), 155.63 (C-2), and 165.35, 165.42, and 166.03 (C=O).

Compound (**4b**) (140 mg, 43%); R_F 0.37; yellow foam (Found: C, 63.4; H, 4.2; N, 6.2. $C_{37}H_{27}N_3O_9 \cdot \frac{1}{2}H_2O$ requires C, 63.15; H, 4.36; N, 6.50%); $\delta_C(CDCl_3)$ 63.94 (C-5′), 72.31, 73.13, 74.83, and 81.08 (C-1′, -2′, -3′, and -4′), 109.28 and 115.19 (C-2 and -3), 113.85 (C-9), 119.93 (C-7), 128.53—133.62 (C-1, -3a, -6, -9a, and -Ar), 141.02 and 141.46 (C-8 and -5a), 148.71 (C-4), and 165.21, 166.03, and 166.50 (C=O).

6-*Chloro*-2-(2,3,5-*tri*-O-*benzoyl*-β-D-*ribofuranosyl*)*quinoxaline* 1-*Oxide* (**5a**) *and* 4-*Oxide* (**6a**).—To a solution of compound (**3a**) (60 mg, 0.1 mmol) in dichloromethane (5 ml) at 0 °C was added MCPBA (81.7 mg, 0.4 mmol), and the mixture was kept at room temperature for 48 h. The solvent was evaporated off under reduced pressure. T.l.c. (benzene–methanol, 99 : 1) showed that the residue contained two major components (R_F 0.36 and 0.35). The mixture was separated by p.l.c. with benzene–methanol (99 : 1) as developer (× 5).

Compound (**5a**) (12 mg, 19%); R_F 0.36; foam (Found: C, 65.0; H, 4.1; N, 4.3. $C_{34}H_{25}ClN_2O_8$ requires C, 65.33; H, 4.03; N, 4.48%); $\delta_C(CDCl_3)$ 63.63 (C-5′), 71.90, 73.90, 78.69, and 79.27



Scheme 2.

(C-1′, -2′, -3′, and -4′), 120.22 (C-8), 128.47—133.50 (C-2, -5, -7, and -Ar), 136.08 (C-6), 142.69 and 144.85 (C-4a and -8a), 145.91 (C-3), and 165.21 (C=O).

Compound (**6a**) (37 mg, 55%); R_F 0.35; foam (Found: C, 65.5; H, 4.1; N, 4.55%); $\delta_C(CDCl_3)$ 63.53 (C-5′), 72.43, 75.47, 80.79, and 82.08 (C-1′, -2′, -3′, and -4′), 120.28 (C-5), 128.18—133.50 (C-3, -7, -8, and -Ar), 135.37 (C-6), 138.13, and 145.32 (C-4a and -8a), 156.44 (C-2), and 165.21, 165.39, and 166.15 (C=O).

7-*Chloro*-2-(2,3,5-*tri*-O-*benzyol*-β-D-*ribofuranosyl*)*quinoxaline* 1-*Oxide* (**5b**) *and* 4-*Oxide* (**6b**).—The same procedure was used as for the reaction of (**3a**) with MCPBA, but with substrate (**3b**).

Compound (**5b**) (17%); R_F 0.32; foam (Found: C, 65.4; H, 4.4; N, 4.2%); $\delta_C(CDCl_3)$ 63.42 (C-5′), 71.96, 73.95, 78.63, and 79.39 (C-1′, -2′, -3′, and -4′), 118.23 (C-8), 128.47—133.44 (C-2, -5, -6, and -Ar), 137.01 (C-7), 139.12, and 143.86 (C-4a and -8a), 144.79 (C-3), and 165.21, and 166.21 (C=O).

Compound (**6b**) (46%); R_F 0.31; foam (Found: C, 64.6; H, 4.3; N, 4.3. $C_{34}H_{25}ClN_2O_8 \cdot \frac{1}{3}H_2O$ requires C, 64.71; H, 4.15; N,

Table 2. ^{1}H N.m.r. coupling constants (Hz) of certain *C*-nucleosides

Compound	1′, 2′	2′, 3′	3′, 4′	4′, 5′a	4′, 5′b	5′a, 5′b	5, 6	5, 7	6, 8	7, 8
(3a)	4.7	4.7	4.7	3.7	*a*	11.8		*a*		*a*
(3b)	5.0	5.0	5.0	3.7	*a*	8.1	*a*		*a*	
(3c)	4.7	4.7	4.7	3.7	*a*	12.1		2.6		9.2
(3d)	5.3	5.3	5.3	3.7	3.0	12.1		2.4		9.1
(3e)	5.3	5.3	5.3	4.0	3.3	12.1	9.1		2.4	
(3f)	5.7	5.7	*a*	4.0	3.0	11.8		2.4		9.4
(5a)	3.7	5.7	7.4	*a*	*a*	*a*		2.4		9.4
(5b)	3.7	3.7	3.7	4.0	*a*	11.4	8.7		2.4	
(5c)	3.4	3.4	3.4	3.4	3.4	8.1		2.0		9.4
(5d)	5.4	5.4	5.4	4.0	3.0	12.4	9.1		2.3	
(6a)	4.7	4.7	4.7	3.4	*a*	11.8		2.0		9.1
(6b)	4.7	4.7	4.7	3.7	*a*	11.4	9.4		2.4	
(6c)	4.7	4.0	4.7	*a*	*a*	*a*		2.4		9.1
(6d)	5.0	5.0	*a*	4.4	3.2	11.4	9.4		2.0	

Compound	1′, 2′	2′, 3′	3′, 4′	4′, 5′a	4′, 5′b	5′a, 5′b	2, 3	6, 7	6, 8	7, 9	8, 9
(4a)	7.1	5.7	4.0	3.7	3.3	12.1	4.3		*a*		9.0
(4b)	7.7	4.4	4.0	4.4	3.3	12.1	4.3	8.7		2.4	
(4c)	7.0	4.3	*a*	*a*	*a*	*a*	4.0		2.4		9.1
(4d)	7.7	*a*	*a*	*a*	*a*	*a*	4.0	9.0		2.3	

[a] Unresolved.

4.43%); δ_C($CDCl_3$) 63.59 (C-5′), 72.37, 75.47, 80.67, and 82.08 (C-1′, -2′, -3′, and -4′), 118.23 (C-5), 128.41—133.50 (C-3, -6, -8, and -Ar), 136.60 (C-7), 138.30, and 143.45 (C-4a and -8a), 155.32 (C-2), and 165.70, 165.39, and 166.15 (C=O).

General Deoxygenation Procedure.—A solution of a quinoxaline *N*-oxide and triphenylphosphine in methanol was heated under reflux for 3 h, and then the solvent was evaporated off under reduced pressure. The residue was purified by p.l.c with di-isopropyl ether–methanol (93:7) as developer, to give the corresponding deoxygenated *C*-nucleoside. Identification was confirmed by comparison of i.r. and ^{1}H n.m.r. spectra with those of the deoxygenated *C*-nucleosides.

General Deprotection Procedure.—Sufficient methanolic sodium hydroxide was added to the protected *C*-nucleoside in absolute methanol. The mixture was kept at room temperature for 5 h, rendered neutral with acetic acid, and evaporated. The residue was purified by p.l.c. to afford the free *C*-nucleoside.

6-*Chloro*-2-(β-D-*ribofuranosyl*)*quinoxaline* (**3d**). This compound (61%) was obtained from the tri-*O*-benzoate (**3a**), as crystals m.p. 178—181 °C (from methanol) (Found C, 52.4; H, 4.1; N, 9.8. $C_{13}H_{13}ClN_2O_4$ requires C, 52.61; H, 4.42; N, 9.44%); δ_C(CD_3OD) 61.40 (C-5′), 71.14, 76.58, 83.95, and 85.30 (C-1′, -2′, -3′, and -4′), 127.59, 130.58, and 130.81 (C-5, -7, and -8), 134.03 (C-6), 139.30 and 141.69 (C-4a and -8a), 145.56 (C-3), and 156.38 (C-2).

7-*Chloro*-2-(β-D-*ribofuranosyl*)*quinoxaline* (**3e**). This compound (71%) was obtained from the tri-*O*-benzoate (**3b**), as crystals m.p. 145—147 °C (from methanol) (Found: C, 52.8; H, 4.3; N, 9.6%); δ_C(CD_3OD) 61.31 (C-5′), 71.14, 76.76, 84.01, and 85.24 (C-1′, -2′, -3′, and -4′), 127.42, 130.34, and 130.70 (C-5, -6, and -8), 134.56 (C-7), 140.00, and 140.99 (C-4a and -8a), 144.91 (C-3), and 156.96 (C-2).

6-*Nitro*-2-(β-D-*ribofuranosyl*)*quinoxaline* (**3f**). This compound (25%) was obtained from the tri-*O*-benzoate (**3c**), as pale yellow crystals m.p. 253—255 °C (from methanol) (Found: C, 50.9; H, 4.35; N, 14.0. $C_{13}H_{13}N_3O_6$ requires C, 50.81; H, 4.26; N, 13.68%).

7-*Chloro*-1-(β-D-*ribofuranosyl*)*pyrrolo*[1,2-a]*quinoxaline* (**4c**). This compound (97%) was obtained from the tri-*O*-benzoate (**4a**), as needles m.p. 196—199 °C (from methanol) (Found: C, 51.9; H, 5.4; N, 7.4. $C_{16}H_{15}ClN_2O_4 \cdot 2H_2O$ requires C, 51.83; H, 5.17; N, 7.56%) δ_C[$(CD_3)_2SO$] 61.68 (C-5′), 71.05 (C-3′), 73.75 (C-2′), 75.55 (C-1′), 85.31 (C-4′), 107.89, and 114.53 (C-2 and -3), 119.07 (C-9), 127.32 (C-9a), 127.42 (C-3a), 127.64 (C-8), 128.30 (C-6), 129.06 (C-7), 131.26 (C-1), 137.93 (C-5a), and 147.12 (C-4).

8-*Nitro*-1-(β-D-*ribofuranosyl*)*pyrrolo*[1,2-a]*quinoxaline* (**4d**). This compound (30%) was obtained from the tri-*O*-benzoate (**4b**), as yellow needles m.p. 254—255 °C (from methanol) (Found: C, 53.0; H, 4.8; N, 11.6. $C_{16}H_{15}N_3O_6 \cdot H_2O$ requires C, 52.89; H, 4.72; N, 11.57%); δ_C[$(CD_3)_2SO$)] 61.54 (C-5′), 70.84 (C-3′), 73.45 (C.2′), 74.94 (C-1′), 85.97 (C-4′), 109.38, and 115.16 (C-2 and -3), 113.95 (C-9), 119.71 (C-7), 127.55 (C-3a), 127.83 (C-9a), 130.22 (C-6), 131.92 (C-1), 141.14 (C-5a), 145.18 (C-8), and 148.94 (C-4).

6-*Chloro*-2-(β-D-*ribofuranosyl*)*quinoxaline* 1-*Oxide* (**5c**). This compound (84%) was obtained from the tri-*O*-benzoate (**5a**), as crystals m.p. 165—166 °C (from methanol) {Found: $[M + H]^+$ (f.a.b.), 313.0542. $C_{13}H_{14}ClN_2O_5$ requires $M + H$, 313.0591}.

6-*Chloro*-2-(β-D-*ribofuranosyl*)*quinoxaline* 4-*Oxide* (**6c**). This compound (88%) was obtained from the tri-*O*-benzoate (**6a**), as crystals m.p. 204—206 °C (from methanol) {Found: $[M + H]^+$ (f.a.b.), 313.0584. $C_{13}H_{14}ClN_2O_5$ requires $M + H$, 313.0591}.

7-*Chloro*-2-(β-D-*ribofuranosyl*)*quinoxaline* 1-*Oxide* (**5d**). This compound (82%) was obtained from the tri-*O*-benzoate (**5b**), as crystals m.p. 182—183 °C (from methanol) {Found: $[M + H]^+$ (f.a.b.), 313.0577. $C_{13}H_{14}ClN_2O_5$ requires $M + H$, 313.0591}.

7-*Chloro*-2-(β-D-*ribofuranosyl*)*quinoxaline* 4-*Oxide* (**6d**). This compound (87%) was obtained from the tri-*O*-benzoate (**6b**), as crystals m.p. 144—146 °C (from benzene–hexane, 1:1) {Found: $[M + H]^+$ (f.a.b.), 313.0583. $C_{13}H_{14}ClN_2O_5$ requires $M + H$, 313.0591}.

General Acetonization Procedure.—To a solution of a deprotected *C*-nucleoside in acetone was added acetone containing toluene-*p*-sulphonic acid monohydrate and the mixture was kept at room temperature for 2 h. The reaction mixture was neutralized with sodium hydrogen carbonate and stirred for 15 min. The solid was collected by filtration and thoroughly washed with acetone. The filtrate and washings were combined, and evaporated under reduced pressure to give a syrup, which

was purified by p.l.c. with chloroform–methanol (97:3) as developer.

6-*Chloro*-2-(2,3-O-*isopropylidene*-β-D-*ribofuranosyl*)-*quinoxaline* (**3g**). This compound (49%) was obtained from the deprotected nucleoside (**3d**), as a foam; R_F 0.32 (chloroform–methanol, 97:3); $\delta_H(CDCl_3)$ 1.39 and 1.67 (6 H, each s, isopropylidene Me), 3.75 (1 H, m, 5′-H_a), 4.02 (1 H, dd, *J* 2.3 and 12.1 Hz, 5′-H_b), 4.22 (1 H, q, 4′-H), 4.96 (2 H, m, 2′- and 3′-H), 5.35 (1 H, d, *J* 3.0 Hz, 1′-H), 7.75 (1 H, dd, *J* 2.3 and 9.1 Hz, 7-H), 8.02 (1 H, d, *J* 9.1 Hz, 8-H), 8.14 (1 H, d, *J* 2.3 Hz, 5-H), and 8.92 (1 H, s, 3-H).

7-*Chloro*-2-(2,3-O-*isopropylidene*-β-D-*ribofuranosyl*)-*quinoxaline* (**3h**). This compound (52%) was obtained from the deprotected nucleoside (**3e**), as a foam; R_F 0.32 (chloroform–methanol, 97:3); $\delta_H(CDCl_3)$ 1.39 and 1.67 (6 H, each s, isopropylidene Me), 3.72 (1 H, m, 5′-H_a), 4.02 (1 H, dd, *J* 3.7 and 12.4 Hz, 5′-H_b), 4.22 (1 H, q, 4′-H), 4.96 (2 H, m, 2′- and 3′-H), 5.35 (1 H, d, *J* 4.3 Hz, 1′-H), 7.74 (1 H, dd, *J* 2.0 and 9.1 Hz, 6-H), 8.06—8.09 (2 H, m, 5- and 8-H), and 8.90 (1-H, s, 3-H).

6-*Nitro*-2-(2,3-O-*isopropylidene*-β-D-*ribofuranosyl*)*quinoxaline* (**3i**). This compound (56%) was obtained from the deprotected nucleoside (**3f**), as a foam; R_F 0.30 (chloroform–methanol, 99:1); $\delta_H(CDCl_3)$ 1.92 and 2.12 (6 H, each s, isopropylidene Me), 4.03—4.45 (3 H, m, 4′-H and 5′-H_2), 4.62—4.92 (2 H, m, 2′-and 3′-H), 5.20 (1 H, d, *J* 4.7 Hz, 1′-H), 8.64 (1-H, d, *J* 9.6 Hz, 8-H), 8.96 (1 H, dd, *J* 2.3 and 9.6 Hz, 7-H), 9.33 (1 H, d, *J* 2.3 Hz, 5-H), and 9.66 (1 H, s, 3-H).

7-*Chloro*-1-(2,3-O-*isopropylidene*-β-D-*ribofuranosyl*)*pyrrolo*-[1,2-a]*quinoxaline* (**4e**). This compound (43%) was obtained from the deprotected nucleoside (**4c**), as a foam; R_F 0.33 (chloroform); $\delta_H(CDCl_3)$ 1.37 and 1.55 (6 H, each s, isopropylidene Me), 3.18—3.50 (2 H, m, 5′-H_2), 4.14 (2 H, m, 3′- and 4′-H), 4.90 (1 H, m, 2′-H), 5.37 (1 H, d, *J* 6.0 Hz, 1′-H), 7.12 and 7.24 (2 H, each d, *J* 4.0 Hz, 2- and 3-H), 7.47 (1 H, dd, *J* 2.0 and 8.1 Hz, 8-H), 7.93 (1 H, d, *J* 2.0 Hz, 6-H), 8.42 (1 H, d, *J* 8.1 Hz, 9-H), and 8.92 (1 H, s, 4-H).

8-*Nitro*-1-(2,3-O-*isopropylidene*-β-D-*ribofuranosyl*)*pyrrolo*-[1,2-a]*quinoxaline* (**4f**). This compound (47%) was obtained from the deprotected nucleoside (**4d**), as a foam; R_F 0.33 (chloroform); $\delta_H(CDCl_3)$ 1.39 and 1.55 (6 H, each s, isopropylidene Me), 3.18—3.51 (4 H, m, 3′- and 4′-H, and 5′-H_2), 4.19 (1 H, m, 2′-H), 5.35 (1 H, d, *J* 6.9 Hz, 1′-H), 7.22 and 7.35 (2 H, each d, *J* 4.0 Hz, 2-and 3-H), 8.09 (1 H, d, *J* 8.7 Hz, 6-H), 8.34 (1 H, dd, *J* 2.7 and 8.7 Hz, 7-H), 9.07 (1 H, s, 4-H), and 9.40 (1 H, d, *J* 2.7 Hz, 9-H).

References

1 I. Maeba, T. Takeuchi, T. Iijima, and H. Furukawa, *J. Org. Chem.*, 1988, **53**, 1401.
2 S. N. Mannore, J. L. Bose, A. A. Thaker, and M. S. Wadia, *Indian J. Chem.*, 1975, **13**, 609.
3 J. Cobb and G. W. H. Cheeseman, *Mag. Reson. Chem.*, 1986, **24**, 231.
4 J.-L. Imbach and B. L. Kam, *J. Carbohydr. Nucleosides, Nucleotides*, 1974, **1**, 271.

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