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Note

1-Aryl-6,7-dichloro-3-β-D-erythrofuranosylpyrazolo[3,4-*b*]quinoxaline *C*-nucleoside analogues ☆

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The synthesis of *C*-nucleosides has received considerable attention because of the diverse biological properties of such naturally occurring analogues as showdomycin, formycin, and oxazinomycin [2]. We have been interested recently in the synthesis for biological evaluation of *C*-nucleoside analogues having different substituents at the base moiety [3–6]. Substitution at the base moiety by chlorine and/or fluorine atoms is of interest because of the stability of the carbon–halogen bond in biological systems [7]. Here a series of 1-aryl-6,7-dichloro-3-β-D-erythrofuranosylpyrazolo[3,4-*b*]quinoxaline analogues have been prepared and their structures and anomeric configurations were determined by NMR spectroscopy and mass spectrometry.

Condensation of 4,5-dichloro-*o*-phenylenediamine, D-*glycero*-D-*gulo*-heptose, and the corresponding arylhydrazine derivatives (**1–4**) in a conventional manner [3–6], gave the corresponding acyclic *C*-nucleoside analogues; 1-aryl-6,7-dichloro-3-(D-*arabino*-tetritol-1-yl)pyrazolo[3,4-*b*]quinoxalines (**5–8**), in good yield (85–90%). The ^{1}H NMR spectra of compounds **5–8** showed a common spectral pattern comparable to that of unsubstituted pyrazolo[3,4-*b*]quinoxaline analogues [8]. The polyhydroxyalkyl chain showed three doublets corresponding to three secondary hydroxyl groups and one triplet

☆ Part VI; for Part V, see ref. [1].

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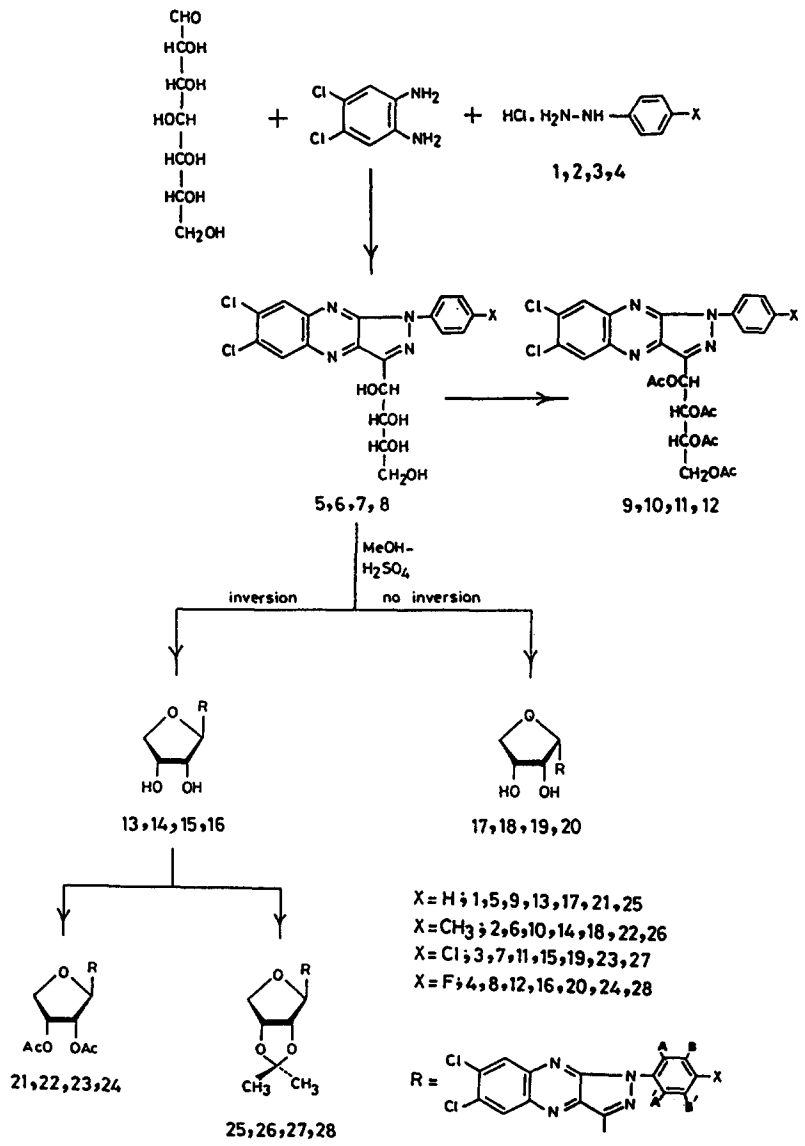
corresponding to a primary hydroxyl group, which disappeared on deuteration (see Experimental).



The coupling constants for the D-*arabino*-polyhydroxyalkyl side-chain protons showed similar values for compounds **5–8** and for the unsubstituted 1-phenyl-3-(D-*arabino*-tetritol-1-yl)pyrazolo[3,4-*b*]quinoxaline [3,8], indicating the same population of the planar zig-zag conformation of the D-*arabino* side chain, which is not affected by

substitution at the base moiety. Acetylation of compounds **5–8** afforded the corresponding tetra-*O*-acetyl derivatives (**9–12**), whose ^{1}H NMR spectra showed four high-field peaks (*O*-acetyl). The coupling constants of the polyacetoxyalkyl side-chain protons are close to those for compounds **5–8**, indicating similar population of the planar zig-zag conformation.

Dehydrative cyclization of the polyhydroxyalkyl chain for compounds **5–8** was effected by refluxing the compounds with 8–15% methanolic sulfuric acid solution for 48–60 h (depending upon the aryl residue), to give the corresponding *C*-nucleoside analogues, 1-aryl-6,7-dichloro-3-β-D-erythrofuranosylpyrazolo[3,4-*b*]quinoxalines **13–16**, as the preponderant anomers. The minor α-anomers (**17–20**) were detected by TLC as faint spots.

The structures of the *C*-nucleoside analogues **13–16** were determined by ^{1}H NMR spectroscopy. The erythrofuranosyl part of these compounds showed two doublets exchangeable by deuteration, corresponding to the two secondary hydroxyl groups in accord with 1′,4′-cyclization.

The ^{1}H NMR spectra of deuterium-exchanged compounds **13–16** showed the low-field anomeric doublet, having $J_{1',2'}$ 6.8–7.3 Hz. These large coupling constants make the anomeric assignment uncertain [9–11]. Acetylation of compounds **13–16** gave the respective diacetates, (**21–24**) two *O*-acetyl signals. The anomeric-proton doublets (δ 5.509–5.644) for compounds **21–24** had $J_{1',2'}$ values (6.2–6.8 Hz) that cannot be used to define the anomeric configuration. However, the corresponding isopropylidene derivatives (**25–28**) showed the anomeric protons as singlets at δ 5.782–5.821. These zero values for $J_{1',2'}$ indicates the H-1′,2′ *trans* arrangement, that is, the β-D configuration of the furanosyl group formed. In addition, the Δδ values (0.201–0.203) for the difference of the δ values for the two methyl signals of the 2,2-dimethyldioxolane ring for compounds **25–28** are consistent [12–15] with the β configuration. The multiplicity of the H-4′ signals for compounds **25–28**, which appeared as multiplets and not as triplets, confirms [16,17] the β-configuration for these compounds.

The ^{13}C NMR spectrum of the isopropylidene derivative **25** showed the two methyl signals at δ 25.735 and 27.175 having ^{13}C Δδ 1.44. It is known [18] that methyl signals in *O*-isopropylidene derivatives of nucleosides occur at δ 25.5 ± 0.2 and 27.5 ± 0.2 for β anomers and 24.9 ± 0.3 and 26.3 ± 0.2 for α anomers. The chemical shifts of the two methyl signals for compound **25** are therefore in accord with the β configuration. In addition, the ^{13}C Δδ value for these two methyl groups is known [18] to be 1.25 ± 0.2 ppm for β-anomers and 1.90 ± 0.2 for α anomers. The value found for compound **25** (1.44) is also consistent with the β configuration.

Dehydrative cyclization of compounds **5–8** proceeds stereoselectively to produce mainly the β anomers (**13–16**), which have the *trans* relationship between the 1-aryl-6,7-dichloropyrazolo[3,4-*b*]quinoxaline base moiety and the 2′-OH group. This observation is general for the dehydration of D-*arabino*-pyrazolo[3,4-*b*]quinoxaline analogues and the β anomer is obtained by inversion of configuration at C-1′ of the precursor acyclic analogues. The dehydrative cyclization process takes place through an alkenic intermediate [3] that is cyclized from the stereo-favoured direction giving the β anomers (**13–16**) as the preponderant isomers; the α anomers **17–20** are less favoured.

The mass spectra of compounds **14–16** showed the corresponding molecular-ion

peaks. Compounds **14** and **16** having two chlorine atoms showed the expected molecular ion peaks M, M + 2 and M + 4, due to the chlorine isotopes; compound **15** has three chlorine atoms and showed the isotopic molecular ion peaks M, M + 2, M + 4, and M + 6. The fragment BCHOH, characteristic of the fragmentation of *C*-nucleoside analogues [19,20], was shown as the base peak for compounds **14–16**.

1. Experimental

General procedures.—Melting points were determined with a Fisher–Johns apparatus and are uncorrected. Evaporations were performed under diminished pressure below 60°C Thin-layer chromatography (TLC) was conducted on silica gel (Kieselgel G, Merck) with solvent **A**, 10:1 $CHCl_3$–MeOH, or solvent **B**, 3:1 benzene–EtOH. IR spectra were recorded with a Perkin–Elmer 1430 instrument and UV absorption spectra with a Perkin–Elmer Lambda 48 instrument. ^{1}H NMR spectra were recorded with a Bruker 200 MHz or Jeol EX 400 MHz spectrometer using Me_4Si as the internal standard. ^{13}C NMR spectra were recorded with a Bruker 200 MHz instrument at 50 MHz or Jeol EX 400 MHz instrument at 100.4 MHz. Mass spectra were recorded with an AEI MS 902 spectrometer. Combustion analyses were performed in the Department of Chemistry, Cairo University, Cairo, Egypt.

*Preparation of 1-aryl-6,7-dichloro-3-(*D-arabino-*tetritol-1-yl)pyrazolo[3,4-*b*]quinoxalines* (**5–8**).—General procedure — A solution of D-*glycero*-D-*gulo*-heptose [21] (0.001 mmol) in water (100 mL) was heated with a solution of 4,5-dichloro-*o*-phenylenediamine (1 μmol) in EtOH (3–5 mL), arylhydrazine hydrochloride (**1–4**) (5 μmol), and AcOH (4 μmol) in a sealed flask for 8–10 h in a boiling water-bath. The flask was cooled, opened, and the yellow precipitate was filtered off, washed successively with water, 50% MeOH, and diethyl ether, and dried. It was then recrystallized from 1-propanol. The following compounds were prepared in this manner.

*6,7-Dichloro-1-phenyl-3-(*D-arabino-*tetritol-1-yl)pyrazolo[3,4-*b*]quinoxaline* (**5**).—Phenylhydrazine hydrochloride (**1**) (7 g), gave **5** (1.9 g, 57.8%), mp 229–231°C; R_f 0.25 (solvent A); ν_{max}^{KBr}3390, 3263 (OH), 1598, 1565 (C=N), 1502, and 753 cm^{-1} (Ph); $\lambda_{max}^{1,4-dioxane}$373, 344, and 425 nm (log ϵ 4.8, 4.3, and 3.9); ^{1}H NMR data (400 MHz; Glc.nu$_2$ Me_2SO-d_6): δ 3.482 (q, 1 H, $J_{3',4''}$ 5.9 $J_{4',4''}$ 10.7 Hz, H-4″), 3.674–3.731 (m, 2 H, H-3′, H-4′), 4.111–4.155 (m, 1 H, H-2′), 4.381 (t, 1 H, 4′-OH), 4.679 (d, 1 H, $J_{3'}$, OH 6.8 Hz, 3′-OH), 4.780 (d, 1 H, $J_{2',OH}$ 4.8 Hz, 2′-OH) 5.431 (d, 1 H, $J_{1',OH}$ 7.3 Hz), 5.571 (q, 1 H, $J_{1',2'}$ 2.9 Hz, $J_{1',OH}$ 7.3 Hz H-1′) 7.379 (t, 1 H, *J* 7.3 Hz *para* proton), 7.634 (t, 2 H, *J* 7.3 Hz *meta* protons), 8.385 (d, 2 H, *J* 7.3 Hz *ortho* protons) 8.541 (s, 1 H, H-8), and 8.609 (s, 1 H, H-5); after addition of CD_3CO_2D the four hydroxyl-proton signals disappeared; δ 3.482 (q, 1 H, $J_{3',4''}$ 5.9, $J_{4',4''}$ 10.7 Hz), 3.676–3.745 (m, 2 H, $J_{3',4'}$ 2.9 H, H-3′, H-4′) 4.140 (q, 1 H, H-2′, $J_{1',2'}$ 2.9, $J_{2',3'}$ 8.3 Hz), and 5.574 (d, 1 H, $J_{1',2'}$ 2.9 Hz, H-1′).

Anal. Calcd for $C_{19}H_{16}Cl_2N_4O_4$: C, 52.43; H, 3.71; N, 12.87. Found: C, 52.30; H, 3.90; N, 12.60.

*6,7-Dichloro-3-(*D-arabino-*tetritol-1-yl)-1-*p-*tolylpyrazolo[3,4-*b*]quinoxaline* (**6**).—*p*-Tolylhydrazine hydrochloride (**2**) (3.8 g) gave **6** (0.7 g, 85.4%), mp 255–256°C, ν_{max}^{KBr}3393, 3258 (OH), 1606, 1554 (C=N), and 1517 cm^{-1} (*para*-disubstituted ben-

zene); $\lambda_{max}^{1,4-dioxane}$276, 344, and 431 nm (log ϵ 4.9, 4.2, and 3.8); ^{1}H NMR data (400 MHz; Me_2SO-d_6): δ 2.503 (s, 3 H, tolyl CH_3), 3.417–3.466 (m, 1 H, H-4″ $J_{3',4''}$ 5.4, $J_{4',4''}$ 10.7 Hz), 3.654–3.688 (m, 2 H, H-4′, H-3′, $J_{3',4'}$ 3.4 Hz), 4.114–4.135 (m, 1 H, H-2′), 4.369 (t, 1 H, 4′-OH, $J_{4'',OH}$ 4.9, $J_{4',OH}$ 9.8 Hz), 4.677 (d, 1 H, 3′-OH, $J_{3',OH}$ 6.8 Hz), 4.767 (d, 1 H, 2′-OH, $J_{2',OH}$ 4.8 Hz), 5.416 (d, 1 H, 1″-OH, J 7.3 Hz), 5.551 (dd, 1 H, H-1′, $J_{1',2'}$ 2.9, $J_{1',OH}$ 7.3 Hz), 7.442 (d, 2 H, H-B, H-B′, J 8.3 Hz), 8.256 (d, 2 H, H-A, H-A′, J 8.3 Hz), 8.576 (s, 1 H, H-8), and 8.641 (s, 1 H, H-5); after addition of CD_3CO_2D the four hydroxyl-proton signals disappeared: δ 3.450–3.476 (m, 1 H, H-4″, $J_{3',4''}$ 5.4, $J_{4',4''}$ 10.3 Hz), 3.662–3.686 (m, 2 H, H-4′, H-3′, $J_{3',4'}$ 3.4 Hz), 4.266 (dd, 1 H, H-2′, $J_{1',2'}$ 2.9, $J_{2',3'}$ 8.3 Hz), and 5.701 (d, 1 H, H-1′, $J_{1',2'}$ 2.9 Hz).

Anal. Calcd for $C_{20}H_{18}Cl_2N_4O_4$: C, 53.47; H, 4.04; N, 12.47. Found: C, 53.30; H, 4.20; N, 12.30.

*6,7-Dichloro-1-*p*-chlorophenyl-3-(*D*-arabino-tetritol-1-yl)pyrazolo[3,4-*b*]quinoxaline* (**7**).—*p*-Chlorophenylhydrazine hydrochloride (**3**) (4.3 g), gave **7** (0.7 g, 84.3%), mp 263–265°C; ν_{max}^{KBr}3282 (OH), 1590, 1557 (C=N), and 1495 cm^{-1} (*para*-disubstituted benzene); $\lambda_{max}^{1,4-dioxane}$278, 344, and 224 nm (log ϵ 4.9, 4.3, and 3.9); ^{1}H NMR data (400 MHz; Me_2SO-d_6): δ 3.461–3.488 (m, 1 H, H-4″), 3.675–3.733 (m, 2 H, H-4′, H-3′), 4.104–4.147 (m, 1 H, H-2′), 4.404 (t, 1 H, 4′-OH, $J_{4'',OH}$ 5.4 Hz), 4.679 (d, 1 H, 3′-OH, $J_{3',OH}$ 6.3 Hz), 4.807 (d, 1 H, 2′-OH, $J_{2',OH}$ 4.9 Hz), 5.464 (d, 1 H, 1′-OH, $J_{1',OH}$ 7.3 Hz), 5.569 (dd, 1 H, H-1′, $J_{1',2'}$ 2.9 Hz), 7.670 (d, 2 H, H-B, H-B′), J 8.8 Hz), 8.404 (d, 2 H, H-A, H-A′, J 8.8 Hz), 8.506 (s, 1 H, H-8), and 8.590 (s, 1 H, H-5); after addition of CD_3CO_2D the four hydroxyl-proton signals disappeared: δ 3.474 (q, 1 H, H-4″, $J_{3',4''}$ 5.9, $J_{4',4''}$ 10.7 Hz), 3.679–3.724 (m, 2 H, H-4′, H-3′, $J_{1',2'}$ 2.9 Hz), 4.121 (dd, 1 H, H-2′, $J_{1',2'}$ 2.9, $J_{2',3'}$ 8.3 Hz), 5.567 (d, 1 H, H-1′ $J'_{,2'}$ 2.9 Hz).

Anal. Calcd for $C_{19}H_{15}Cl_3N_4O_4$: C, 48.59; H, 3.22; N, 11.93. Found: C, 48.30; H, 3.50; N, 11.80.

*6,7-Dichloro-1-*p*-fluorophenyl-3-(*D*-arabino-tetritol-1-yl)pyrazolo[3,4-*b*]quinoxaline* (**8**).—*p*-Fluorophenylhydrazine hydrochloride (**4**) (3.9 g), gave **8** (0.75 g, 90.4%), mp 246–248°C; ν_{max}^{KBr}3392, 3257 (OH), 1605, 1558 (C=N), 1512 (*para*-disubstituted benzene), and 1286, 1232 cm^{-1} (C–F); $\lambda_{max}^{1,4-dioxane}$270, 344, and 424 nm (log ϵ 4.7, 4.3, and 3.9); ^{1}H NMR data (400 MHz; Me_2SO-d_6): δ 3.438–3.494 (m, 1 H, H-4″), 3.668–3.773 (m, 2 H, H-4′, H-3′), 4.098–4.140 (m, 1 H, H-2′), 4.389 (t, 1 H, 4′-OH, $J_{4'',OH}$ 5.4, $J_{4',OH}$ 4.9 Hz), 4.682 (d, 1 H, 3′-OH, $J_{3',OH}$ 6.4 Hz), 4.793 (d, 1 H, 2′-OH, $J_{2',OH}$ 4.9 Hz), 5.444 (d, 1 H, 1′-OH, $J_{1',OH}$ 7.3 Hz), 5.563 (dd, 1 H, H-1′, $J_{1',2'}$ 2.9, $J_{1'-OH}$ 7.3 Hz), 7.484 (t, 2 H, H-B, H-B′, J 7.3, 8.3 Hz), 8.352–8.396 (m, 2 H, H-A, H-A′), 8.536 (s, 1 H, H-8), and 8.613 (s, 1 H, H-5); after addition of CD_3CO_2D the four hydroxyl-proton signals disappeared: δ 3.449–3.491 (m, 1 H, H-4″, $J_{3',4''}$ 4.4, $J_{4',4''}$ 10.7 Hz), 3.663–3.713 (m, 2 H, H-4′, H-3′, $J_{3',4'}$ 2.9 Hz), 4.112–4.133 (m, 1 H, H-2′ $J_{2',3'}$ 8.3 Hz), and 5.559 (d, 1 H, H-1′, $J_{1',2'}$ 2.9 Hz).

Anal. Calcd for $C_{19}H_{15}Cl_2N_4O_4F$: C, 50.35; H, 3.34; N, 12.36. Found: C, 50.30; H, 3.10; N, 12.10.

Acetylation of compounds **5–8**. *General procedure.*—A solution of the 1-aryl-6,7-dichloro-3-(D-*arabino*-tetritol-1-yl)pyrazolo[3,4-*b*]quinoxaline (0.1 g) was acetylated with 1:1 pyridine–Ac_2O (6 mL) for 24 h at room temperature the solution was poured on to crushed ice and the acetate obtained was filtered off, washed with water, and dried.

6,7-Dichloro-1-phenyl-3-(1,2,3,4-tetra-O-*acetyl*-D-arabino-*tetritol-1-yl)pyrazolo[3,4-b]quinoxaline* (**9**).—Compound **5** gave **9** (0.12 g, 87%), recrystallized from Me.OH as yellow needles, mp 163–165°C. TLC showed one spot, R_F 0.81 (solvent A); ν_{max}^{KBr}1744 (OAc), 1596 (C = N), and 1499, 752 cm^{-1} (Ph); ^1H NMR data (400 MHz; $CDCl_3$): δ 1.957 (s, 3 H, OAc), 2.048 (s, 3 H, OAc), 2.141 (s, 3 H, OAc), 2.251 (s, 3 H, OAc), 4.297 (dd, 1 H, H-4″, $J_{3',4''}$ 5.4, $J_{4',4''}$ 12.2 Hz), 4.392 (dd, 1 H, H-4′, $J_{3',4'}$ 2.4 Hz), 5.460–5.500 (m, 1 H, H-3′), 6.035 (q, 1 H, H-2′, $J_{1',2'}$ 2.9, $J_{2',3'}$ 8.3 Hz), 6.856 (d, 1 H, H-1′, $J_{1',2'}$ 2.9 Hz), 7.332 (t, 1 H, *para* proton), 7.584 (t, 2 H, *meta* protons), 8.379 (d, 2 H, *ortho* protons, *J* 6.8 Hz), 8.449 (s, 1 H, H-8), and 8.456 (s, 1 H, H-5).

Anal. Calcd. for $C_{27}H_{24}Cl_2N_4O_8$: C, 53.74; H, 4.01; N, 9.28. Found: C, 53.70; H, 3.87; N, 9.40.

6,7-Dichloro-3-(1,2,3,4-tetra-O-*acetyl*-D-arabino-*tetritol-1-yl)-1*-p-*tolylpyrazolo[3,4-b]quinoxaline* (**10**).—Compound **6** (0.1 g) gave **10** (0.13 g, 94.9%), mp 169–171°C (MeOH); ν_{max}^{KBr}1745 (OAc), 1613 1566 (C=N), and 1510 cm^{-1} (*para*-disubstituted benzene); ^1H NMR data (200 MHz; $CDCl_3$): δ 1.956 (s, 3 H, OAc), 2.045 (s, 3 H, OAc), 2.136 (s, 3 H, OAc), 2.242 (s, 3 H, OAc), 2.445 (s, 3 H, tolyl CH_3), 4.313 (dd, 1 H, H-4″, $J_{3',4''}$ 4.9, $J_{4',4''}$ 12.9 Hz), 4.367 (dd, 1 H, H-4′, $J_{3',4'}$ 3.4 Hz), 5.473–5.514 (m, 1 H, H-3′), 6.029 (dd, 1 H, H-2′, $J_{1',2'}$ 3.4, $J_{2',3'}$ 8.3 Hz), 6.819 (d, 1 H, H-1′, $J_{1',2'}$ 3.4 Hz), 7.337 (d, 2 H, H-B, H-B′), 8.192 (d, 2 H, H-A, H-A′), 8.449 (s, 1 H, H-8), and 8.382 (s, 1 H, H-5).

Anal. Calcd for $C_{28}H_{27}Cl_2N_4O_8$: C, 54.38; H, 4.37; N, 9.0 6. Found: C, 54.10; H, 4.20; N, 8.90.

6,7-Dichloro-1-p-*chlorophenyl-3-)1,2,3,4-tetra*-O-*acetyl*-D-arabino-*tetritol-1-yl)pyrazolo[3,4*-b*]quinoxaline* (**11**).—Compound **7** (0.1 g) gave **11** (0.13 g, 96.2%), mp 203–205°C (MeOH); ν_{max}^{KBr}1743 (OAc), 1607, 1564 (C=N), and 1216 cm^{-1} (*para*-disubstituted benzene); $\lambda_{max}^{1,4-dioxane}$276,, 345, and 426 nm (log ϵ 4.9, 4.5, and 4.1); ^1H NMR data (400 MHz; $CDCl_3$): δ 1.952 (s, 3 H, OAc), 2.048 (s, 3 H, OAc), 2.145 (s, 3 H, OAc), 2.253 (s, 3 H, OAc), 4.260 (dd, 1 H, H-4″, $J_{3',4'}$ 4.9, $J_{4',4''}$ 12.2 Hz), 4.393 (dd, 1 H, H-4′, $J_{3',4'}$ 2.9 Hz), 5.455–5.495 (m, 1 H, H-3′), 6.021 (dd, 1 H, H-2′, $J_{1',2'}$ 3.4, $J_{2',3'}$ 8.3 Hz), 6.801 (d, 1 H, H-1; $J_{1',2'}$ 3.4 Hz), 7.532 (d, 2 H, H-B, H-B′, *J* 9.3 Hz), 8.362 (s, 1 H, H-8), 8.368 (d, 2 H, H-A, H-A′, *J* 9.3 Hz), and 8.443 (s, 1 H, H-5).

Anal. Calcd for $C_{27}H_{23}Cl_3N_4O_8$: C, 50.84; H, 3.63; N, 8.78. Found: C, 50.60; H, 3.40; N, 8.60.

6,7-Dichloro-1-p-*fluorophenyl-3-(1,2,3,4-tetra*-O-*acetyl*-D-arabino-*tetritol-1-yl)pyrazolo[3,4*-b*]quinoxaline* (**12**).—Compound **8** (0.1 g) gave **12** (0.13 g, 95.6%), mp 193–195°C (MeOH); ν_{max}^{KBr}1746 (OAc), 1564 (C=N), 1512 (*para*-disubstituted benzene) and 1215 cm^{-1} (C–F); $\lambda_{max}^{1,4-dioxane}$369, 345, and 424 nm (log ϵ 4.8, 4.2, and 3.9); ^1H NMR data (400 MHz; $CDCl_3$): δ 1.955 (s, 3 H, OAc), 2.048 (s, 3 H, OAc), 2.142 (s, 3 H, OAc), 2.250 (s, 3 H, OAc), 4.259 (dd, 1 H, H-4″, $J_{3',4'}$ 4.9, $J_{4',4''}$ 12.7 Hz), 4.392 (dd, 1 H, H-4′, $J_{3',4'}$ 2.4 Hz), 5.452–5.493 (m, 1 H, H-3′), 6.024 (dd, 1 H, H-2′, $J_{2',3'}$ 7.8 Hz), 6.804 (d, 1 H, H-1′, $J_{1',2'}$ 3.4 Hz), 7.256 (t, 2 H, H-B, H-B′), 8.324–8.346 (m, 2 H, H-A, H-A′), 8.358 (s, 1 H, H-8), and 8.448 (s, 1 H, H-5).

Anal. Calcd. for $C_{27}H_{23}Cl_2N_4O_8F$: C, 52.19; H, 3.73; N, 9.02. Found: C, 52.30; H, 3.50; N, 8.80.

Dehydrative cyclization of **5–8**. *General procedure.*—Suspensions of compounds

5–8 were refluxed with 8–15% methanolic H_2SO_4 for 48–75 h with TLC monitoring. Two more-mobile spots were produced in the ratio of 1:4, corresponding to the anomeric α- and β-*C*-nucleoside analogues respectively. The solution was poured into hot water, and the MeOH was evaporated off under diminished pressure. The resultant yellow precipitate was filtered off, washed with water, dried, and recrystallized from MeOH to afford the major β isomer as yellow crystals. The minor isomer (less mobile spot), tentatively assigned as the α anomer, was not isolated and remained in the mother liquor.

*6,7-Dichloro-3-β-*D*-erythrofuranosyl-1-phenylpyrazolo[3,4-*b*]quinoxaline* (**13**).—Compound **5** (0.5 g) in 8% methanolic H_2SO_4 (250 mL) was refluxed for 60 h TLC revealed the absence of the starting material and formation of two more mobile spots, R_f 0.42 and 0.55 (solvent A), in the ratio 1:4. Conventional processing gave a yellow precipitate; yield 0.35 g (74.47%), recrystallized as yellow needles, mp 208–210°C TLC showed one spot, R_f 0.55 (solvent A); ν_{max}^{KBr}3885 (OH), 1597, 1560 (C=N) and 1499, 751 cm^{-1} (Ph); ^1H NMR data (400 MHz; Me_2SO-d_6): δ 3.866 (dd, 1 H, H-4″, $J_{3',4''}$ 2.9, $J_{4',4''}$ 9.3 Hz), 4.354 (dd, 1 H, H-4′, $J_{3',4''}$ 4.4 Hz), 4.421–4.430 (m, 1 H, H-3′), 4.823–4.866 (m, 1 H, H-2′), 5.177 (d, 1 H, 3′-OH, $J_{3'\text{-OH}}$ 3.9 Hz), 5.210 (d, 1 H, H-1′, $J_{1',2'}$ 6.8 Hz), 5.311 (d, 1 H, 2′-OH, *J* 6.4 Hz), 7.410 (t, 1 H, *para* proton, *J* 7.8 Hz), 7.635 (t, 2 H, *meta* protons, *J* 8.3, 7.8 Hz), 8.320 (d, 2 H, *ortho* protons, *J* 7.8 Hz), 8.540 (s, 1 H, H-8), and 8.609 (s, 1 H, H-5); after addition of CD_3CO_2D the two hydroxyl protons disappeared: δ 3.867 (dd, 1 H, H-4″, $J_{3',4''}$ 2.9, $J_{4',4''}$ 9.3 Hz), 4.369 (dd, 1 H, H-4′, $J_{3',4'}$ 4.4 Hz), 4.413–4.443 (m, 1 H, H-3′, $J_{2',3'}$ 4.8 Hz), 4.843 (q, 1 H, H-2′, $J_{1',2'}$, 6.8, $J_{2',3'}$ 4.8 Hz), and 5.214 (d, 1 H, H-1′, $J_{1',2'}$ 6.8 Hz).

Anal. Calcd for $C_{19}H_{14}Cl_2N_4O_3$: C, 54.69; H, 3.38; N, 13.43. Found: C, 54.30; H, 3.40; N, 13.20.

*6,7-Dichloro-3-β-*D*-erythrofuranosyl-1-*p*-tolylpyrazolo[3,4-*b*]quinoxaline* (**14**).—A suspension of compound **6** (0.3 g) in 8% methanolic H_2SO_4 (200 mL) was boiled under reflux for 48 h and treated as for compound **13**. TLC showed two spots, R_f 0.42 and 0.44 (solvent B), in the ratio 1:4. The major isomer gave yellow needles; yield 0.23 g (79.3%), mp 251–252°C, depressed when admixed with **6**. TLC showed one spot, R_f 0.44 (solvent B); ν_{max}^{KBr}3240 (OH), 1606, 1558 (C=N), and 1513 cm^{-1} (*para*-disubstituted benzene). $\lambda_{max}^{1,4-dioxane}$269, 345, and 431 nm (log ϵ 4.6, 4.1, and 3.9); ^1H NMR data (400 MHz; Me_2SO-d_6): δ 2.62 (s, 3 H, tolyl CH_3), 3.973 (dd, 1 H, H-4″, $J_{3',4''}$ 2.9, $J_{4',4''}$ 9.3 Hz), 4.459 (dd, 1 H, H-4′, $J_{3',4'}$ 4.4 Hz), 4.533–4.551 (m, 1 H, H-3′), 4.932–4.976 (m, 1 H, H-2′), 5.241 (d, 1 H, 3′-OH, $J_{3',OH}$ 4.4 Hz), 5.319 (d, 1 H, H-1′, $J_{1',2'}$ 6.8 Hz), 5.371 (d, 1 H, 2′-OH, $J_{2',OH}$ 6.4 Hz), 7.541 (d, 2 H, H-B, H-B′, *J* 8.4 Hz), 8.284 (d, 2 H, H-A, H-A′, *J* 8.4 Hz), 8.649 (s, 1 H, H-8), and 8.719 (s, 1 H, H-5). After addition of CD_3CO_2D the two hydroxyl protons disappeared: δ 2.510 (s, 3 H, tolyl CH_3), 3.857 (dd, 1 H, H-4″, $J_{3',4''}$ 2.9, $J_{4',4''}$ 9.3 Hz), 4.344 (dd, 1 H, H-4′, $J_{3',4'}$ 4.4, $J_{4'',4'}$ 9.3 Hz), 4.424–4.453 (m, 1 H, H-3′), 4.838 (dd, 1 H, H-2′, $J_{1',2'}$ 7.3, $J_{2',3'}$ 4.5 Hz), and 5.213 (d, 1 H, H-1′, $J_{1',2'}$ 7.3 Hz); mass spectral data (selected ions): *m/z* 434 (7, M + 4), 433 (8, M + 3), 432 (29, M + 2), 431 (11, M + 1), 430 (44, M), 412 (3, M − H_2O), 398(7), 397(8), 396(12), 395 (5, M − H_2 − OH), 394 (8, M − $2H_2O$), 383(12), 381(9), 379(12), 374(9), 373 (22, BH_2CH_2CHOH; where B = 6,7-dichloro-1-*p*-tolylpyrazolo[3,4-*b*]quinoxaline), 372 (16, $BHCH_2CHOH$), 371 (37, $BHCH_2CHO$,

370 (11, BCH_2CHO), 369 (11, BCH_2CO), 367(10), 361(12), 360(18), 359 (63, BH_2CHOH), 358 (30, BHCHOH), 357 (100, BCHOH), 356(13, BCHO), 355(9, BCO), 344(6), 343(11), 342(9), 341(13), 331(9), 330(8), 329 (21, BH_2), 328 (10, BH), 327 (18, B), 326 (5, B-H), 316(5), 315(11), 314 (7, $BH_2 - CH_3$), 313 (12, $BH - CH_3$), 312 (3, $B - CH_3$), 304 (10), 303(5), 302 (15, $BH_2 - HCN$), 301 (4, BH – HCN), 300 (8, B – HCN), 103(8), 91 (42, p-$CH_3C_6H_4$), 90(9), 89(9), 85(7), 77 (11, Ph), 65(27), 61(18), 60(21), 57(28), 56(9), and 55(13).

Anal. Calcd for $C_{20}H_{16}Cl_2N_4O_3$: C, 55.70; H, 3.74; N, 12.99. Found: C, 55.40; H, 4.00; N, 12.70.

6,7-Dichloro-1-p-*chlorophenyl-3-β*-D-*erythrofuranosylpyrazolo[3,4*-b*]quinoxaline* (**15**).—A suspension of **7** (0.4 g) in 15% methanolic H_2SO_4 (500 mL) was refluxed for 75 h. TLC showed two spots, R_f 0.39 and 0.48 (solvent B), in the ratio 1:4. The major product, yield 0.25 g (65.81%), was recrystallized from MeOH as yellow needles, mp 230–232°C; R_f 0.48. ν_{max}^{KBr}3374 (OH), 1608, 1555 (C = N), and 1514 cm^{-1} (*para*-disubstituted benzene); ^1H NMR data (400 MHz; Me_2SO-d_6): δ 3.859 (dd, 1 H, H-4″, $J_{3',4''}$ 2.9, $J_{4',4''}$ 9.3 Hz), 4.345 (dd, 1 H, H-4′, $J_{3',4''}$ 4.4 Hz), 4.417–4.446 (m, 1 H, H-3′), 4.798–4.840 (m, 1 H, H-2′), 5.174 (d, 1 H, 3′-OH, $J_{3',OH}$ 6.8 Hz), 5.201 (d, 1 H, H-1′, $J_{1',2'}$ 6.8 Hz), 5.260 (d, 1 H, 2′-OH, $J_{2',OH}$ 7.3 Hz), 7.703 (d, 2 H, H-B, H-B′, J 8.8 Hz), 8.376 (d, 2 H, H-A, H-A′, J 8.8 Hz), 8.565 (s, 1 H, H-8), and 8.639 (s, 1 H, H-5); after addition of CD_3CO_2D the two hydroxyl protons disappeared: δ 3.859 (dd, 1 H, H-4″, $J_{3',4''}$ 2.9, $J_{4',4''}$ 9.3 Hz), 4.340 (dd, 1 H, H-4′, $J_{3',4'}$ 4.4 Hz), 4.409–4.417 (m, 1 H, H-3′), 4.817 (q, 1 H, H-2′, $J_{1',2'}$ 7.3, $J_{2',3'}$ 4.9 Hz), and 5.200 (d, 1 H, H-1′, $J_{1',2}$ 7.3 Hz); mass spectral data (selected ions): m/z 456 (2, M + 6), 455 (3, M + 5), 454 (15, M + 4), 453 (9, M + 3), 452 (42, M + 2), 451 (11, M + 1), 450 (41, M), 432 (4, $M - H_2O$), 418(10), 417 (8), 416(23), 415 (6, $M - H_2O - OH$), 414 (20, $M - 2\ H_2O$), 405(8), 403(10), 401(7), 399(7), 395(6), 394(6), 393(19, BH_2CH_2CHOH; where B = 6,7-dichloro-1-*p*-chlorophenylpyrazolo[3,4-*b*]quinoxaline), 392 (10, $BHCH_2CHOH$), 391 (22, $BHCH_2CHO$), 390 (8, BCH_2CHO), 389 (7, BCH_2CO), 387(5), 382(8), 381 (32), 380(21), 379 (98, BH_2CHOH), 378 (27, BHCHOH), 377 (100, BCHOH), 376 (6, BCHO), 375 (5, BCO), 364(5), 363(8), 362(5), 361(7), 352(6), 351(11), 350(6), 349 (14, BH_2), 348 (4, BH), 347 (8, B), 324(8), 322 (9, BH_2 – HCN), 320 (2, B – HCN), 315(12), 314(7), 313(15), 289(5), 288(5), 287(9), 158(7), 137(5), 125(6), 111 (25, p-ClC_6H_4), 77 (3, Ph), and 55(8).

Anal. Calcd for $C_{19}H_{13}Cl_3N_4O_3$: C, 50.52; H, 2.90; N, 12.40. Found: C, 50.30; H, 2.60; N, 12.20.

6,7-Dichloro-3-β-D-*erythrofuranosyl-1*-p-*fluorophenylpyrazolo[3,4*-b*]quinoxaline* (**16**).—A suspension of **8** (0.1 g) in 8% methanolic H_2SO_4 (100 mL) was refluxed for 48 h. TLC showed two spots, R_f 0.45 and 0.55 (solvent A), in the ratio 1:4. The yellow precipitate, yield 85 mg (89%), was recrystallized as yellow needles, mp 220–222°C; R_f 0.55; ν_{max}^{KBr}3401 (OH), 1619, 1556 (C=N), 1509 (*para*-disubstituted benzene), and 1226 cm^{-1} (C–F); ^1H NMR data (400 MHz; Me_2SO-d_6): δ 3.875 (dd, 1 H, H-4″, $J_{3',4''}$ 2.4, $J_{4',4''}$ 8.8 Hz), 4.343–4.496 (m, 2 H, H-3′, H-4′), 4.840–4.853 (m, 1 H, H-2′), 5.177 (d, 1 H, 3′-OH, $J_{3',OH}$ 4.4 Hz), 5.217 (d, 1 H, H-1′, $J_{1',2'}$ 6.8 Hz), 5.306 (d, 1 H, 2′-OH, $J_{2',OH}$ 7.8 Hz), 7.510 (t, 2 H, H-B, H-B′), 8.314–8.349 (m, 2 H, H-A, H-A′), 8.558 (s, 1 H, H-8), and 8.639 (s, 1 H, H-5); after addition of CD_3CO_2D, the two hydroxyl protons

disappeared: δ 3.875 (dd, 1 H, H-4″, $J_{3',4''}$ 2.4, $J_{4',4'}$ 9.3 Hz), 4.358 (dd, 1 H, H-4′, $J_{3',4'}$ 4.4 Hz), 4.419–4.448 (m, 1 H, H-3′), 4.843 (1, 1 H, H-2′, $J_{1',2'}$ 7.3, $J_{2',3'}$ 6.8 Hz), and 5.217 (d, 1 H, H-1′, $J_{1',2'}$ 7.3 Hz); mass spectral data (selected ions): *m/z* 438 (6, M + 4), 437 (6, M + 3), 436 (26, M + 2), 435 (9, M + 1), 434 (39,M), 416 (2, M − H_2O), 400(5), 399 (3, M − H_2O − OH), 398 (4, M − 2 H_2O), 387(6), 383(6), 377(12, BH_2CH_2CHOH; where B = 6,7-dichloro-1-*p*-fluorophenylpyrazolo[3,4-*b*]quinoxaline), 376 (8, $BHCH_2CHOH$), 375 (22, $BHCH_2CHO$), 374 (7, BCH_2CHO), 373 (7, BCH_2CO), 371(5), 365(12), 364(14), 363 (64, BH_2CHOH), 262 (27, BHCHOH), 361 (100, BCHOH), 360 (12, BCHO), 359 (5, BCO), 348(4), 347(8), 346(7), 345(11), 335(8), 334(8), 333 (21, BH_2), 332 (8, BH), 331 (19, B), 308(7), 307(5), 306 (12, BH_2 − HCN), 305 (4, BH − HCN), 304 (2, B − HCN), 271(5), 160(5), 158(6), 121(5), 109(8), 103(7), 95 (31, C_6H_4-*p*-F), 77 (1, Ph), 69(9), 61(11), 57(15), and 55(6).

Anal. Calcd for $C_{19}H_{13}Cl_2N_4O_3F$: C, 52.43; H, 3.01; N, 12.87. Found: C, 52.50; H, 3.10; N, 12.70.

*6,7-Dichloro-3-(2,3-di-*O*-acetyl-β-*D*-erythrofuranosyl)-1-phenylpyrazolo [3,4-b]quinoxaline* (**21**).—Conventional acetylation of **13** (0.1 g) with pyridine (2 mL) and Ac_2O (2 mL) for 24 h at room temperature gave 0.11 g (92%) of **21**, recrystallized from MeOH as yellow needles, mp 172–174°C, ν_{max}^{KBr}1744 (OAc), 1595, 1560 (C=N), and 1503, 753 cm^{-1} (Ph); ^1H NMR data (400 MHz; $CDCl_3$): δ 2.081 (s, 3 H, OAc), 2.199 (s, 3 H, OAc), 4.183 (dd, 1 H, H-4″, $J_{3',4''}$ 3.4, $J_{4',4''}$ 10.3 Hz), 4.639 (dd, 1-H, H-4′, $J_{3',4'}$ 4.9 Hz). 5.644 (d, 1 H, H-1′, $J_{1',2'}$ 6.8 Hz), 5.843–5.877 (m, 1 H, H-3′), 6.225 (q, 1 H, H-2′, $J_{1',2'}$ 6.8, $J_{2',3'}$ 5.4 Hz), 7.370 (t, 1 H, *para* proton), 7.581 (t, 2 H, *meta* protons), 8.370 (s, 1 H, H-8), 8.390 (d, 2 H, *ortho* protons), and 8.451 (s, 1 H, H-5).

Anal. Calcd for $C_{23}H_{18}Cl_2N_4O_5$: C, 55.11; H, 3.62; N, 11.18. Found: C, 54.71; H, 3.62; N, 10.91.

*6,7-Dichloro-3-(2,3-di-*O*-acetyl-β-*D*-erythrofuranosyl-1-yl)-1-*p*-tolylpyrazolo-[3,4-b]quinoxaline* (**22**).—Compound **14** (0.03 g) gave **22** (0.03 g, 88.6%), mp 177–179°C (MeOH); ν_{max}^{KBr}1744 (OAc), 1609, 1562 (C=N), and 1517 cm^{-1} (*para*-disubstituted benzene); ^1H NMR data (400 MHz; $CDCl_3$): δ 2.078 (s, 3 H, OAc), 2.192 (s, 3 H, OAc), 2.442 (s, 3 H, tolyl CH_3), 4.177 (dd, 1 H, H-4″, $J_{3',4''}$ 3.4, $J_{4',4''}$ 10.3 Hz), 4.636 (dd, 1 H, H-4′, $J_{3',4'}$ 4.9 Hz), 5.640 (d, 1 H, H-1′, $J_{1',2'}$ 6.8 Hz), 5.844–5.877 (m, 1 H, H-3′), 6.222 (q, 1 H, H-2′, $J_{1',2'}$ 6.8, $J_{2',3'}$ 5.4 Hz), 7.366 (d,2 H, H-B, H-B′, *J* 8.3 Hz), 8.203 (d, 2 H, H-A, H-A′, *J* 8.3 Hz), 8.352 (s, 1 H, H-8), and 8.435 (s, 1 H, H-5).

Anal. Calcd for $C_{24}H_{20}Cl_2N_4O_5$: C, 55.94; H, 3.91; N, 10.87. Found: C, 55.60; H, 3.70; N, 10.70.

*6,7-Dichloro-1-*p*-chlorophenyl-3-(2,3-di-*O*-acetyl-β-*D*-erythrofuranosyl)-pyrazolo[3,4-b]quinoxaline* (**23**).—Compound **15** (0.05 g) was treated as for compound **21**, and gave **23** (0.05 g, 84.7%), mp 190–192°C (MeOH); ν_{max}^{KBr}1750 (OAc), 1607 (C = N), and 1517 cm^{-1} (*para*-disubstituted benzene); ^1H NMR data (400 MHz; $CDCl_3$): δ 2.079 (s, 3 H, OAc), 2.197 (s, 3 H, OAc), 4.180 (dd, 1 H, H-4″, $J_{3',4''}$ 3.4, $J_{4',4''}$ 10.3 Hz), 4.631 (dd, 1 H, H-4′, $J_{3',4'}$ 4.9 Hz), 5.618 (d, 1 H, H-1′, $J_{1',2'}$ 6.3 Hz), 5.833–5.866 (m, 1 H, H-3′), 6.208 (q, 1 H, H-2′, $J_{1',2'}$ 6.3, $J_{2',3'}$ 4.3 Hz), 7.536 (d, 2 H, H-B, H-B′, *J* 8.4 Hz), 8.371 (s, 1 H, H-8), 8.390 (d, 2 H, H-A, H-A′, *J* 8.4 Hz), and 8.451 (s, 1 H, H-5).

Anal. Calcd for $C_{23}H_{17}Cl_3N_4O_5$: C, 51.56; H, 3.19; N, 10.46. Found: C, 51.60; H, 3.20; N, 10.50.

*6,7-Dichloro-3-(2,3-di-*O*-acetyl-β-*D*-erythrofuranosyl)-1-*p*-fluorophenylpyrazolo[3,4-*b*]quinoxaline* (**24**).—Compound **16** (0.03 g) gave **24** (0.03 g, 97.2%), mp 188–190°C (MeOH); ν_{max}^{KBr} 1744 (OAc), 1608, 1561 (C=N), 1517 (*para*-disubstituted benzene) and 1242 cm^{-1} (C–F); ^{1}H NMR data (200 MHz; Me_2SO-d_6): δ 2.035 (s, 3 H, OAc), 2.150 (s, 3 H OAc), 4.066 (dd, 1 H, H-4″), 4.411–4.681 (m, 1 H, H-4′), 5.509 (d, 1 H, H-1′, $J_{1',2'}$ 6.2 Hz), 5.734–5.758 (m, 1 H, H-3′), 6.038 (t, 1 H, H-2′), 7.474 (t, 2 H, H-B, H-B′), 8.270 (t, 2 H, H-A, H-A′), 8.511 (s, 1 H, H-8), and 8.586 (s, 1 H, H-5).

Anal. Calcd for $C_{23}H_{17}Cl_2N_4O_5F$: C, 53.19; H, 3.29; N, 10.79. Found: C, 53.10; H, 3.10; N, 10.50%.

*6,7-Dichloro-3-(2,3-*O*-isopropylidene-β-*D*-erythrofuranosyl)-1-phenylpyrazolo[3,4-b]quinoxaline* (**25**).—A solution of **13** (0.05 g) in dry acetone (50 mL) was treated with *p*-toluenesulfonic acid (0.15 g), with stirring. After 2 h, TLC showed the reaction to be complete giving one spot, R_f 0.81 (solvent A). The mixture was poured into ice-cold $NaHCO_3$ solution, and the resulting precipitate was filtered off, washed with water, and dried; yield 51 mg (95%). Recrystallization from MeOH gave yellow needles, mp 183–185°C, ^{1}H NMR data (200 MHz; $CDCl_3$): δ 1.443 and 1.644 (2 s, 6 H, CMe_2, Δδ 0.201), 4.122–4.179 (m, 2 H, H-4″, H-4′), 5.214–5.233 (m, 1 H, H-3′), 5.521 (d, 1 H, H-2′, $J_{2',3'}$ 6.2 Hz), 5.801 (s, 1 H, H-1′), 7.362 (t, 1 H, *para* proton), 7.556 (t, 2 H, *meta* protons), 8.336 (s, 1 H, H-8), 8.334–8.367 (m, 2 H, *ortho* protons), and 8.413 (s, 1 H, H-5). ^{13}C NMR spectral data (50 MHz; $CDCl_3$): δ 25.735 (isopropylidene CH_3), 27.175 (isopropylidene CH_3); (^{13}C Δδ 1.44), 74.098, 80.039, 82.413, and 84.435 (C-1′, C-2′, C-3′, and C-4′), 113.520 (acetonide C), 120.621 (*ortho* carbons), 126.880 (*para* carbon), 129.761 (C-8, *meta* carbons), 131.132 (C-5), and 133.172, 133.700, 136.745, 139.228, 140.275, 140.668, 143.033, 144.720 (8, quaternary carbons).

Anal. Calcd for $C_{22}H_{18}Cl_2N_4O_3$: C, 57.78; H, 3.97; N, 12.25. Found: C, 57.62; H, 3.93; N, 12.10.

*6,7-Dichloro-3-(2,3-*O*-isopropylidene-β-*D*-erythrofuranosyl)-1-*p*-tolylpyrazolo[3,4-b]quinoxaline* (**26**).—Acetonation of **14** (0.05 g) as described for **13** gave **26** (0.045 g, 90%), mp 198–200°C (MeOH); ^{1}H NMR data (400 MHz; $CDCl_3$): δ 1.457 and 1.659 (2 s, 6 H, CMe_2, Δδ 0.202), 2.453 (s, 3 H, tolyl CH_3), 4.159 (dd, 1 H, H-4″, $J_{3',4''}$ 3.9 Hz, $J_{4',4''}$ 10.7 Hz), 4.201–4.227 (m, 1 H, H-4′), 5..218–5.242 (m, 1 H, H-3′), 5.540 (d, 1 H, H-2′, $J_{2',3'}$ 5.4 Hz), 5.821 (s, 1 H, H-1′), 7.381 (d, 2 H, H-B, H-B′, *J* 8.3 Hz), 8.203 (d, 2 H, H-A, H-A′, *J* 8.3 Hz), 8.370 (s, 1 H, H-8), and 8.449 (s, 1 H, H-5); ^{13}C NMR data (100.4 MHz; Me_2SO-d_6): δ 20.609 (tolyl CH_3), 24.796 (isopropylidene CH_3), 26.406 (isopropylidene CH_3); (^{13}C Δδ 1.61), 78.618, 78.947, 79.020, 79.276 (C-1′, C-2′, C-3′, and C-4′), 111.756 (isopropylidene C), and 120.150–135.896 (aromatic carbons).

Anal. Calcd for $C_{23}H_{20}Cl_2N_4O_3$: C, 58.59; H, 4.25; N, 11.89. Found: C, 58.30; H, 4.30; N, 12.10.

*6,7-Dichloro-1-*p*-chlorophenyl-3-(2,3-*O*-isopropylidene-β-*D*-erythrofuranosyl)pyrazolo[3,4-b]quinoxaline* (**27**).—Acetonation of **15** (0.05 g) as described for **13** gave **27** (0.05 g, 95.6%), mp 201–203°C (MeOH); R_f 0.73 (solvent A); ^{1}H NMR data (400 MHz; $CDCl_3$): δ 1.458 and 1.660 (2 s, 6 H, CMe_2), Δδ 0.202),

4.155 (dd, 1 H, H-4″, $J_{3',4''}$ 3.9, $J_{4',4''}$ 10.7 Hz), 4.219–4.252 (m, 1 H, H-4′), 5.226–5.251 (m, 1 H, H-3′), 5.531 (d, 1 H, H-2′, $J_{2',3'}$ 6.4 Hz), 5.814 (s, 1 H, H-1′), 7.546 (d, 2 H, H-B, H-B′, *J* 8.4 Hz), 8.372 (s, 1 H, H-8), 8.373 (d, 2 H, H-A, H-A′, *J* 8.4 Hz), and 8.451 (s, 1 H, H-5).

Anal. Calcd for $C_{22}H_{17}Cl_3N_4O_3$: C, 53.73; H, 3.48; N, 11.39. Found: C, 53.40; H, 3.30; N, 11.20.

*6,7-Dichloro-3-(2,3-*O*-isopropylidene-β-*D*-erythrofuranosyl)-1-*p*-fluorophenylpyrazolo[3,4-*b*]quinoxaline* (**28**).—Acetonation of **16** (0.05 g) as described for **13** gave **28** (0.05 g, 90.9%), mp 180–182°C (MeOH); R_f 0.78 (solvent A); ν_{max}^{KBr} 1625, 1559 (C = N), 1610, (*para*-disubstituted benzene) and 1391 cm^{-1} (CMe_2); ^1H NMR spectral data (200 MHz; $CDCl_3$): δ 1.436 and 1.638 (2 s, 6 H, CMe_2, Δδ 0.202), 3.994–4.296 (m, 2 H, H-4″, H-4′), 5.106–5.280 (m, 1 H, H-3′), 5.503 (d, 1 H, H-2′, $J_{2',3'}$ 6.1 Hz), 5.782 (s, 1 H, H-1′), 7.250 (t, 2 H, H-B, H-B′), 8.282–8.325 (m, 2 H, H-A, H-A′), 8.333 (s, 1 H, H-8), and 8.423 (s, 1 H, H-5).

Anal. Calcd for $C_{22}H_{17}Cl_2N_4O_3F$: C, 55.59; H, 3.60; N, 11.79. Found: C, 55.20; H, 3.40; N, 11.52.

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