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3-β-D-ERYTHROFURANOSYL-6,7-DIMETHYL-1-*p*-TOLYL- AND -1-(*p*-CHLOROPHENYL)-PYRAZOLO[3,4-*b*]QUINOXALINE *C*-NUCLEOSIDE ANALOGS*

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ABSTRACT

The *C*-nucleoside analogs 3-β-D-erythrofuranosyl-6,7-dimethyl-1-*p*-tolylpyrazolo[3,4-*b*]quinoxaline (**5**) and 1-(*p*-chlorophenyl)-3-β-D-erythrofuranosyl-6,7-dimethylpyrazolo[3,4-*b*]quinoxaline (**7**) were prepared by the dehydrative cyclization of the polyhydroxyalkyl chain of 6,7-dimethyl-3-(D-*arabino*-tetritol-1-yl)-1-*p*-tolylpyrazolo[3,4-*b*]quinoxaline and 1-(*p*-chlorophenyl)-6,7-dimethyl-3-(D-*arabino*-tetritol-1-yl)-1-*p*-tolylpyrazolo[3,4-*b*]quinoxaline, respectively. The structure and anomeric configuration of compounds **5** and **7**, as well as of their 2′,3′-isopropylidene acetals were determined by n.m.r. spectroscopy. The mass spectra and biological activity are discussed.

INTRODUCTION

The chemistry of *C*-nucleosides has received considerable attention recently, owing to the biological activity of such naturally occurring analogs as showdomycin, formycin, and oxazinomycin[2]. The biological importance of these compounds has prompted the exploration of routes leading to the synthesis of *C*-nucleoside analogs. The synthetic members of this class of compound are not so common as *N*-nucleoside analogs, owing to the difficulty in preparing *C*-nucleosides from anomerically functionalized *C*-glycosyl compounds. The synthesis of *C*-nucleosides by the dehydrative cyclization of the polyhydroxyalkyl chain of saccharide heterocyclic analogs has been used[3–5] as a route for the facile synthesis of these compounds, but, in the past, lack of knowledge about the anomeric configuration of the products militated against the extensive use of this reaction for *C*-nucleoside synthesis.

Pyrazolo[3,4-*b*]quinoxaline derivatives are of biological interest[6], but the saccharide analogs have not been thoroughly investigated, although the carbohydrate residue strongly modifies the solubility properties of the aglycon and introduces further chiral centers, and thus contributes to the biological activity. In the present

*C-Nucleoside Pyrazolo[3,4-*b*]quinoxaline Analogs, Part IV. For Part III, see ref. 1.

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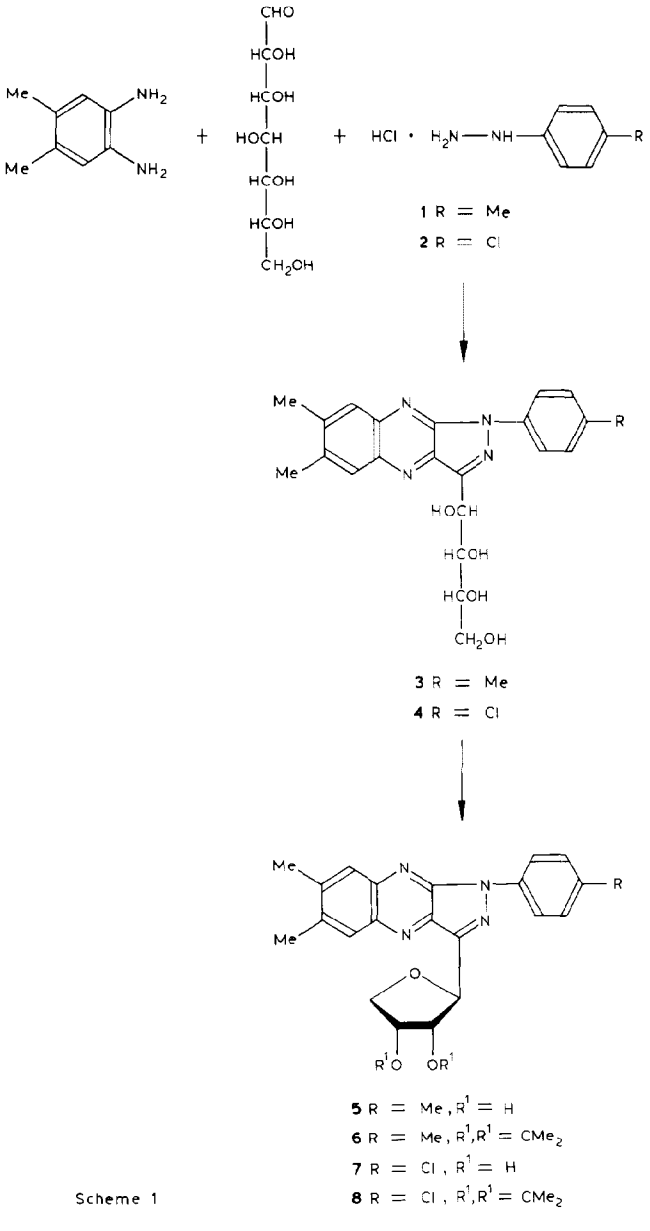
work, two types of saccharide pyrazolo[3,4-*b*]quinoxaline substituted in the pyrazole were prepared, and converted into the corresponding *C*-nucleoside analogs. The anomeric configuration and the biological activity of these compounds were studied.



Scheme 1

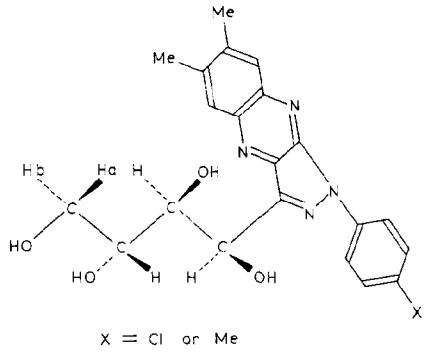
DISCUSSION

Condensation of 4,5-dimethyl-*o*-phenylenediamine, D-*glycero*-D-*gulo*-heptose, and *p*-tolylhydrazine hydrochloride (**1**) afforded 6,7-dimethyl-3-(D-*arabino*-tetritol-1-yl)-1-*p*-tolylpyrazolo[3,4-*b*]quinoxaline (**3**) in a one-step reaction. Treatment of **3** with boiling methanolic sulfuric acid solution under reflux gave the *C*-nucleoside analog, namely, 3-β-D-erythrofuranosyl-6,7-dimethyl-1-*p*-tolylpyrazolo[3,4-*b*]quinoxaline (**5**) (see Scheme 1). Its ^{1}H-n.m.r. spectrum showed the anomeric proton as a doublet at δ 5.19 ($J_{1',2'}$ 6.9 Hz), but the anomeric configuration could not be ascertained[7] from this large value of the coupling constant. However, the isopropylidene derivative **6** showed the anomeric proton as a singlet at δ 5.82, shifted farther downfield than the rest of the sugar protons. The zero value of the coupling constant ($J_{1',2'}$) is in agreement[7] with a *trans* arrangement between H-1 and H-2 of the β-D-erythrofuranosyl group formed.

Additional evidence for the β-D configuration was obtained from the value of the difference ($\Delta\delta$) between the chemical shifts of the methyl signals of the 2,2-dimethyldioxolane ring; the difference 0.20 (1.656 − 1.456) between the chemical shifts of the two methyl protons of **6** is consistent[8,9] with the β-D configuration. The high-negative specific rotation of **5** ($[\alpha]_D^{20}$ − 121.5°) confirms[10] the β-D configuration for **5**, and illustrates the inversion at C-1′ of compound **3** during the dehydrative cyclization process.

Condensation of 4,5-dimethyl-*o*-phenylenediamine, D-*glycero*-D-*gulo*-heptose, and (*p*-chlorophenyl)hydrazine hydrochloride (**2**) afforded 1-(*p*-chlorophenyl)-6,7-dimethyl-3-(D-*arabino*-tetritol-1-yl)pyrazolo[3,4-*b*]quinoxaline (**4**). Treatment of compound **4** with boiling methanolic sulfuric acid solution under reflux gave the *C*-nucleoside analog, namely, 1-(*p*-chlorophenyl)-3-β-D-erythrofuranosyl-6,7-dimethylpyrazolo[3,4-*b*]quinoxaline (**7**), whose ^{1}H-n.m.r. spectrum showed the anomeric proton as a doublet at δ 5.20 having $J_{1',2'}$ 7.2 Hz. The anomeric configuration of **7** could not be ascertained[7] from this large value of the coupling constant. However, the isopropylidene acetal **8** showed the anomeric proton as a singlet at δ 5.80, in agreement[7] with a *trans* arrangement of H-1′ and H-2′, that is, the β-D configuration. The difference $\Delta\delta$ = 0.199 (1.661 −1.462) between the two methyl signals of the 2,2-dimethyldioxolane ring of compound **8** confirmed the β-D configuration. Similarly, the high-negative value of the specific rotation of compound **7** ($[\alpha]_D^{20}$ −108°) confirmed[10] the β-D configuration for compound **7**, and the inversion at C-1′ of compound **4** during the dehydration process.

The dehydrative cyclization of polyhydroxyalkylpyrazolo[3,4-*b*]quinoxalines is a stereospecific process, giving the favored β isomer having a *trans* arrangement between the bulky, base moiety and the 2-hydroxyl group of the furanosyl group formed. This steric requirement may be the reason for the preponderance of the β isomer from the dehydrative cyclization of heterocyclic polyhydroxyalkyl analogs having the D-*arabino* configuration, with inversion of the configuration at C-1′. Substitution on the base moiety did not change the steric course of the reaction.



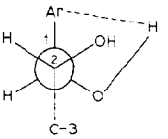
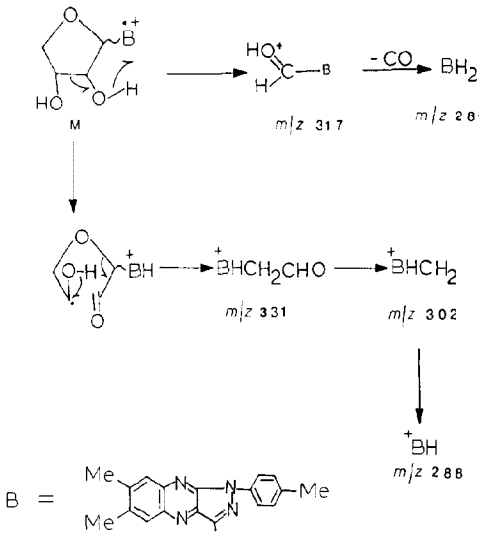


Fig 1

The ^{1}H-n.m.r. spectra of compounds **3** and **4** showed an identical pattern for the D-*arabino*-glycerol-1-yl sidechain. The small coupling constants for the protons on C-1′ and C-2′ ($J_{1',2'}$ 2.3–2.8 Hz) indicated a *gauche* relationship, whereas H-2′ and H-3′ showed large coupling constants ($J_{2',3'}$ 8.0–8.1 Hz), indicating the anti-parallel disposition. These values are in agreement[11] with the favored, planar zig-zag conformation for the D-*arabino* configuration (see Fig. 1).

The mass spectrum of compound **3** showed the molecular-ion peaks, M and (M + 1), at *m/z* 408 and 409, respectively. The fragment at *m/z* 347 (BCHOH-CHOH) is obtained by cleavage of C-2′–C-3′ of the polyhydroxyalkyl chain attached to the base (B). The abundant peaks at *m/z* 317 and 318, corresponding to the ions BCHOH and BCH_2OH, are formed by McLafferty rearrangement of the molecular ion, which is characteristic for the fragmentation of heterocyclic, polyhydroxyalkyl derivatives[12]. The peak at *m/z* 317 was the base peak. The peaks corresponding to the base moiety (B) or its protonated forms BH and BH_2 were at *m/z* 287, 288 and 289, respectively. The protonated-base fragments BH and BH_2 are formed by rearrangements of hydrogen from the sugar hydroxyl groups to the heteroatoms through the unshared electrons[13], and are of major importance in identifying the base moiety and its substituents.

The mass spectrum of the *C*-nucleoside analog **5** showed the molecular-ion peaks, M and (M + 1), at *m/z* 390 and 391, respectively. The peak at *m/z* 317, corresponding to the fragment BCHOH, was the base peak; it demonstrates the presence of the carbon–carbon linkage between the carbohydrate and the base moiety that is characteristic of *C*-nucleosides[13–15]. Further elimination of CO from this ion gives an additional path to the BH_2 ion (see Scheme 2). Another characteristic ion for *C*-nucleosides was shown at *m/z* 331, corresponding to the fragment $BHCH_2CHO$ that is formed by fragmentation of the O–C-1′ and C-2′–C-3′ bonds. Further fragmentation gives an additional path to the BH ion.



Scheme 2

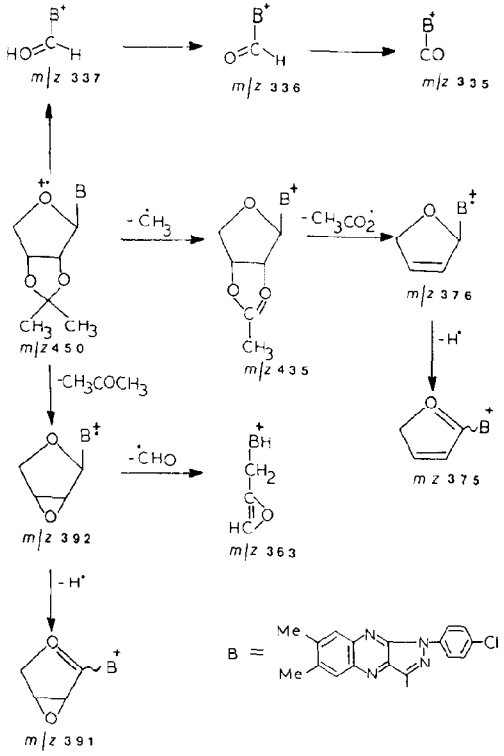
The mass spectrum of compound **4** showed the molecular ion M at *m/z* 428 and 430 in the ratio of 3:1 for the isotopes ^{35}Cl and ^{37}Cl. The peak at *m/z* 367, corresponding to the fragment BCHOHCHOH, is obtained by cleavage of C-2′–C-3′ of the polyhydroxyalkyl chain. The fragment[12] BCHOH, obtained by cleavage of C-1′–C-2′ by McLafferty rearrangement, was at *m/z* 337, as the base peak. The fragments $BHCH_2CHO$ and BCH_2CHO were at *m/z* 351 and 350, respectively. The fragments containing the base moiety, B, BH, and BH_2 were shown at *m/z* 307, 308, and 309, respectively.

The mass spectrum of the isopropylidene acetal **8** showed molecular-ion fragments (having the isotope ratio of the chlorine) at *m/z* 450 and 452. Loss of a methyl radical from the isopropylidene group gives the tertiary carbonium ion (M $- CH_3$) at *m/z* 435, stabilized by two adjacent oxygens atom; further elimination of acetic acid gives the ion at *m/z* 375 (see Scheme 3). The elimination of acetone from the isopropylidene group gives the 2′,3′-epoxide ion at *m/z* 392, which, by loss of a CHO group, gives the ion at *m/z* 363. The peaks BCHOH and BCHO, characteristic for the carbon–carbon linkage, were shown as base peaks at *m/z* 337 and 336, respectively.

Biological activity

Compounds **3**, **4**, **5**, and **7** were tested *in vitro* against KB cells (a human epidermoid carcinoma of the nasopharynx; cell culture). Compound **3** was active at a dilution of 100 μg/mL, and **4** was active at dilutions of 100 μg/mL and 10 μg/mL. The *C*-nucleoside analogs **5** and **7** were active at 100 μg/mL dilution. Tests for

biological activity *in vivo* of compound **3** against mouse leukemia P388 indicated toxicity. The *C*-nucleoside analog **5** was inactive against L-1210 lymphoid leukemia (LE).



Scheme 3

EXPERIMENTAL

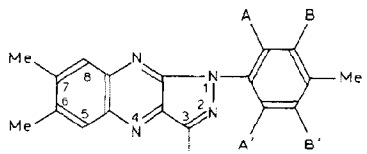
General. — Evaporations were performed under diminished pressure below 60°. T.l.c. was conducted on silica gel (Kieselgel G, Merck) with 3:1 benzene–ethanol. I.r. absorption spectra were recorded with a Unicam SP 1025 instrument. ^{1}H-N.m.r. spectra were recorded with a Nicolet 470-MHz instrument, using internal tetramethylsilane as the reference. Mass spectra were recorded with a Finnigan 6100 Data system gas chromatograph–e.i.-c.i. mass spectrometer. Combustion analyses were performed in the Department of Chemistry, Purdue University. The *in vitro*, KB biological tests were conducted by the Cell Culture Laboratory of the Purdue University Cancer Center. The compounds were tested as suspensions in dilute, aqueous dimethyl sulfoxide. The *in vivo* leukemia 3PS31 and LE tests were obtained through the screening program of the Drug Evaluation Branch, Division

TABLE I

CHEMICAL SHIFTS (δ) AND FIRST-ORDER COUPLING-CONSTANTS (IN HZ) FOR COMPOUNDS **3**, **5**, AND **6**

Protons	**3**	**5**	**6**
Sugar protons			
H-1′	[a]5.54dd	[a]5.19d	[b]5.82s
	$J_{1',2'}$ 2.3	$J_{1',2'}$ 6.9	
	$J_{1',OH}$ 7.2	[c]5.20	
	[c]5.6d	$J_{1',2'}$ 6.9	
	$J_{1',2'}$ 2.8		
H-2′	[a]4.13m	[a]4.91dd	5.56d
	[c]5.15dd	J 6.2	$J_{2',3'}$ 6.0
	$J_{2',3'}$ 8.1	[c]4.91t	
		J 5.1, 6.0	
H-3′		[a]4.46m	5.26t
	3.71m	[c]4.46m	
H-4′	$J_{3',4'}$ 3.0	4.35dd	
		$J_{3',4'}$ 4.4	4.17m
H-4″	[a]3.47m	3.87dd	$J_{3',4'}$ 0
	[c]3.49q	$J_{3',4''}$ 2.2	$J_{3',4''}$ 3.5
	$J_{3',4''}$ 5.8	$J_{4',4''}$ 9.2	$J_{4',4''}$ 10.7
	$J_{4',4''}$ 10.5		
OH	5.31d	5.26d	
	J 7.2	J 6.4	
	4.77d	5.13d	
	J 5.1	J 3.9	
CMe_2	4.47d		1.656
	J 6.5		1.456
	4.37t		$\Delta\delta$ 0.200
	J 5.5, 5.2		
Protons of the base[d]			
H-5	8.30s	8.23s	8.25s
H-8	8.29s	8.22s	8.23s
CH_3-6	2.52s	2.48s	2.53s
CH_3-7	2.50s	2.47s	2.52s
ar-CH_3	2.398s	2.395s	2.431s
H-A	8.03s	7.99s	8.01s
H-A′	7.98s	7.93s	7.93s
H-B	7.44s	7.43s	7.36s
H-B′	7.42s	7.41s	7.34s

[a]In dimethyl sulfoxide. [b]In $CDCl_3$. [c]CD_3CO_2D added. [d]6,7-Dimethyl-1-*p*-tolylpyrazolo[3,4-*b*]-quinoxaline:



of Cancer Treatment, National Cancer Institute, National Institutes of Health, Bethesda, Maryland 20205.

*6,7-Dimethyl-3-(*D-arabino-*tetritol-1-yl)-1-*p-*tolylpyrazolo[3,4-*b]*quinoxaline* (**3**). — A solution of D-*glycero*-D-*gulo*-heptose[16] (5 g) in water (200 mL) was heated with 4,5-dimethyl-*o*-phenylenediamine (3.2 g), (*p*-tolylphenyl)hydrazine hydrochloride (**1**; 20 g), and acetic acid (5 mL) in a sealed flask for 10 h in a boiling-water bath. The flask was cooled and opened, and the yellow precipitate was filtered off, washed successively with water, 50% ethanol, and ether, and dried; yield 3.5 g (36%). Recrystallization from propyl alcohol gave yellow needles, m.p. 248–250°, $[\alpha]_D^{20}$ −32.7° (*c* 1.1, pyridine); R_F 0.28; ν_{max}^{KBr} 3420, 3300 (OH), 1620, 1560 (C=N), and 1530 (*p*-disubstituted benzene); mass-spectral data (selected ions): *m/z* 409 (1, M + 1), 408 (4. M), 347 (2, BCHOHCHOH), 331 (2, $BHCH_2CHO$), 319 (4, BH_2CHOH), 318 (24, BHCHOH), 317 (100, BCHOH), 289 (15, BH_2), 288 (9, BH), 287 (18, B), 285 (B − H), 274 (6, $BH_2 - CH_3$), 273 (14, $BH - CH_3$), 272 (8, $B - CH_3$), 262 (23, BH − CN), 260 (B − HCN), 246 (5), 91 (10), 77 (5, Ph), and 44 (18); for ^{1}H-n.m.r.-spectral data, see Table I.

Anal. Calc. for $C_{22}H_{24}N_4O_4$: C, 64.69; H, 5.92; N, 13.92. Found: C, 64.85; H, 6.08; N, 13.69.

*3-β-*D-*Erythrofuranosyl-6,7-dimethyl-1-*p-*tolylpyrazolo[3,4-*b]*quinoxaline* (**5**). — A suspension of **3** (1.8 g) in 8% methanolic sulfuric acid solution (300 mL) was boiled under reflux, with stirring, for 48 h, whereby complete dehydration was obtained (one spot, R_F 0.55). The solution was diluted with hot water, the methanol was evaporated under diminished pressure, and the yellow precipitate obtained was collected, washed with water until neutral, and dried; yield, 1.2 g (71%). It was recrystallized from methanol–benzene to give yellow needles, m.p. 240–242° (mixed m.p. with **3**, 228–230°), $[\alpha]_D^{20}$ −121.5° (*c* 1.3, pyridine); ν_{max}^{KBr} 3420 (OH), 1560, 1595 (C=N), and 1520 cm^{-1} (*p*-disubstituted benzene); mass-spectral data (selected ions); *m/z* 391 (5, M + 1), 390 (17, M), 373 (2, M − OH), 331 (15, $BHCH_2CHO$), 319 (4, BH_2CHOH), 318 (17, BHCHOH), 317 (100, BCHOH), 316 (3, BCHO), 315 (4, BCO), 302 (3, $BHCH_2$), 289 (8, BH_2), 288 (5, BH), 287 (12, B), 274 (5, $BH_2 - CH_3$), 273 (10, $BH - CH_3$), 272 (2, $B - CH_3$), 263 (4, BH_2 − CN), 262 (17, BH_2 − HCN), 260 (4, B − HCN), 144 (3), 91 (25), and 77 (11, Ph); for ^{1}H-n.m.r.-spectral data, see Table I.

Anal. Calc. for $C_{22}H_{22}N_4O_3$: C, 67.68; H, 5.68; N, 14.35. Found: C, 67.52; H, 5.73; N, 14.20.

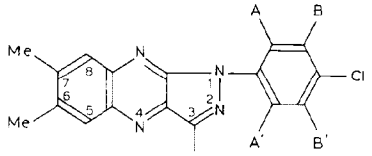
*3-(2,3-*O-*Isopropylidene-β-*D-*erythrofuranosyl)-6,7-dimethyl-1-*p-*tolylpyrazolo[3,4-*b]*quinoxaline* (**6**). — A solution of **5** (50 mg) in dry acetone (50 mL) was treated with *p*-toluenesulfonic acid (150 mg), with stirring. After 24 h, t.l.c. showed the reaction to be complete (one spot, R_F 0.76). The mixture was poured into an ice-cold solution of sodium hydrogencarbonate, and the resulting precipitate was filtered off, washed with water, and dried; yield 50 mg (91%). It was recrystallized from methanol–chloroform, to give yellow needles, m.p. 194–195°, $[\alpha]_D^{20}$ −64.2° (*c* 1.2, chloroform); for ^{1}H-n.m.r.-spectral data, see Table I.

TABLE II

CHEMICAL SHIFTS (δ) AND FIRST-ORDER COUPLING-CONSTANTS (IN HZ) FOR COMPOUNDS **4**, **7**, AND **8**

Protons	**4**	**7**	**8**
Sugar protons			
H-1′	[a]5.56dd	[a]5.19dd	[b]5.80s
	[c]5.57d	*J* 6.9	
	$J_{1',2}$ 2.81	[c]5.20d	
		J 7.2	
H-2′	[a]4.15m	[a]4.90dd	5.54d
	[c]4.16dd	$J_{2',3'}$ 5.0	$J_{2',3'}$ 6.0
	$J_{2',3'}$ 8.0		
H-3′		4.47m	5.26m
H-4′	3.72m	4.36dd	
	$J_{3',4'}$ 3.0	$J_{3',4'}$ 4.5	4.18m
H-4″	[a]3.47m	3.87dd	$J_{3',4'}$ 0
	[c]3.49q	$J_{3',4''}$ 2.3	$J_{3',4''}$ 3.6
	$J_{3',4''}$ 5.9		$J_{4',4''}$ 10.6
	$J_{4',4''}$ 11.0		
OH	5.37d	5.28d	
	J 7.4	*J* 6.4	
CMe_2	4.80d	5.15d	1.661s
	J 5.4	*J* 4.3	1.462s
	4.73d		$\Delta\delta$ 0.199
	J 6.5		
	4.4m		
Protons of the base[d]			
H-5	8.47s	8.40s	8.43s
H-8	8.46s	8.38s	8.41s
CH_3-6	2.50s	2.45s	2.55s
CH_3-7	2.49s	2.44s	2.53s
H-A	8.01s	7.94s	8.01s
H-A′	7.96s	7.87s	7.94s
H-B	7.67s	7.68s	7.52s
H-B′	7.65s	7.66s	7.50s

[a]In dimethyl sulfoxide. [b]In $CDCl_3$. [c]CD_3CO_2D added. [d]1-(*p*-Chlorophenyl)-6,7-dimethylpyrazolo[3,4-*b*]quinoxaline:



Anal. Calc. for $C_{25}H_{26}N_4O_3$: C, 69.75; H, 6.09; N, 13.01. Found: C, 69.66; H, 6.22; N, 12.90.

*1-(*p*-Chlorophenyl)-6,7-dimethyl-3-(*D*-arabino-tetritol-1-yl)pyrazolo[3,4-*b*]-quinoxaline* (**4**). — A solution of D-*glycero*-D-*gulo*-heptose (2 g), 4,5-dimethyl-*o*-phenylenediamine (1.3 g), (*p*-chlorophenyl)hydrazine hydrochloride (**2**, 9 g), and

acetic acid (3 mL) in water (200 mL) was treated as for compound **3**; yield 2.1 g (43%). It was recrystallized from propyl alcohol, to give yellow needles, m.p. 264–266°, $[\alpha]_D^{20}$ −31.4° (*c* 1.02, pyridine); R_F 0.24; ν_{max}^{KBr} 3440, 3320 (OH), 1605, and 1580 cm^{-1} (C=N); mass-spectral data (selected ions): *m/z* 430 (1.6, M), 428 (4.8, M), 367 (7, BCHOHCHOH), 351 (6, $BHCH_2CHO$), 350 (10, BCH_2CHO), 340 (15), 339 (44, BH_2CHOH), 338 (57, BHCHOH), 337 (100, BCHOH), 336 (22, BCHO), 335 (11, BCO), 309 (BH_2), 308 (14, BH), 307 (25, B), 293 (6, BH − CH_3), 282 (19, BH − CN), 274 (14), 273 (48, BH − Cl), 115 (18), 111 (15), 91 (20), 77 (15, Ph), 43 (83, CH_3CO), and 41 (16); for ^{1}H-n.m.r.-spectral data, see Table II.

Anal. Calc. for $C_{21}H_{21}ClN_4O_4$: C, 58.81; H, 4.94; N, 13.06. Found: C, 58.85; H, 4.97; N, 12.76.

1-(p-Chlorophenyl)-3-β-D-erythrofuranosyl-6,7-dimethylpyrazolo[3,4-b]-quinoxaline (**7**). — A suspension of **4** (1 g) in 8% methanolic sulfuric acid solution (240 mL) was boiled for 50 h under reflux, with stirring, and monitoring of the reaction by t.l.c.; complete dehydration was found after 48 h (only one spot, R_F 0.57). The solution was diluted with hot water, the methanol evaporated, and the yellow precipitate filtered off, washed with water, and dried; yield 0.5 g (53%). It was recrystallized from methanol to give yellow needles, m.p. 261–263° (mixed m.p. with **4**, 238–240°), $[\alpha]_D^{20}$ −108° (*c* 1.2, pyridine); ν_{max}^{KBr} 3400 (OH), and 1595, 1650 cm^{-1} (C=N); for ^{1}H-n.m.r.-spectral data, see Table II.

Anal. Calc. for $C_{22}H_{22}ClN_4O_3$: C, 67.68; H, 5.68; N, 14.35. Found: C, 67.52; H, 5.73; N, 14.20.

1-(p-Chlorophenyl)-3-(2,3-O-isopropylidene-β-D-erythrofuranosyl)-6,7-dimethylpyrazolo[3,4-b]quinoxaline (**8**). — Compound **7** (50 mg) was dissolved in dry acetone and treated with *p*-toluenesulfonic acid (150 mg) as described for compound **6**; the yellow precipitate obtained was recrystallized from methanol–chloroform, to give yellow needles, m.p. 205–207°; mass-spectral data (selected ions): *m/z* 453 (5, M + 3), 452 (11, M^{37}), 451 (10, M^{35} + 1), 450 (31, M^{35}), 435 (9, M − CH_3), 394 (9), 393 (26, M + 1 − CH_3COCH_3), 392 (25, M − CH_3COCH_3), 391 (59, M − CH_3COO), 367 (7, M − CH_3 − CH_3COO), 375 (15, M − CH_3 − CH_3COOH), 365 (33), 364 (29), 363 (84, M − CH_3COCH_3 − CHO), 352 (16), 351 (20, $BHCH_2CHO$), 350 (48, BCH_2CHO), 349 (20), 347 (10), 339 (39, BH_2CHOH), 338 (45, BHCHOH), 337 (99.8, BCHOH), 336 (100, BCHO), 335 (34, BCO), 334 (17), 309 (BH_2), 308 (19, BH), 307 (71, B), 282 (13, BH − CN), 281 (6, B − CN), 280 (15, B − HCN), 274 (21, BH_2 − Cl), 273 (97, BH − Cl), 272 (26, B − Cl), 156 (23), 116 (19), 111 (15, C_6H_4Cl), and 77 (14, Ph); for ^{1}H-n.m.r.-spectral data, see Table II.

Anal. Calc. for $C_{24}H_{23}ClN_4O_3$: C, 63.93; H, 5.14; N, 12.42. Found: C, 63.73; H, 5.26; N, 12.47.

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