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Cyclodehydration of 3-(D-*manno*-pentitol-1-yl)pyrazoles: synthesis of 3-(D-arabinofuranosyl)pyrazoles

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ABSTRACT

Several 3-(D-*manno*-pentitol-1-yl)pyrazoles were cyclodehydrated by treatment with boiling aqueous 10% trifluoroacetic acid. The products were α,β-mixtures of 3-(D-arabinofuranosyl)pyrazoles in which the β anomer was the major component. The structures and configurations of these *C*-nucleoside analogues were assigned on the basis of their analytical and spectral data, and those of the triacetates.

INTRODUCTION

The acid-catalysed cyclodehydration of polyhydroxyalkyl chains attached to heterocycles is a reaction that has been used widely in the synthesis of *C*-nucleoside analogues[1–14]. When the polyhydroxyalkyl chain is bonded to π-electron-rich heterocycles, 1′,4′- and/or 1′,5′-anhydro derivatives are obtained, depending on the reaction conditions and on the length of the polyhydroxyalkyl chain[3–6]. When the heterocycle is π-electron-deficient, C-1′ is not usually involved in the cyclisation process and 2′,5′-anhydro derivatives are formed[7–10]. Treatment[11] of 3(5)-(D-*manno*-pentitol-1-yl)pyrazole (**1**) with hydrochloric acid gave no cyclised product; this behaviour was explained in terms of (*a*) the basicity of the pyrazole ring which, on protonation, precludes the development of a cationic center on C-1′, and (*b*) the D-*manno* configuration of the sugar chain, which is one of the most unfavorable for cyclisation[12,13]. Pentahydroxypentyl derivatives of imidazole also failed to undergo cyclodehydration on treatment with acids[14].

The therapeutic importance of D-arabinonucleosides[15] and of *C*-glycosylpyrazoles[16,17] prompted a study of the conditions for ring closure in polyhydroxyalkylpyrazoles. The syntheses of some new 3-(D-arabinofuranosyl)pyrazoles by cyclodehydration of the corresponding 3-(D-*manno*-pentitol-1-yl) derivatives of pyrazole[11] (**1**) and substituted 1-methylpyrazoles[18] are now reported.

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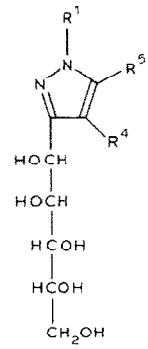
RESULTS AND DISCUSSION

On treatment with boiling aqueous 10% trifluoroacetic acid for 2–4 days, the 3-(D-*manno*-pentitol-1-yl) derivatives of 1-methyl-5-phenylpyrazole (**2**) and 1,4-dimethyl-5-(*p*-tolyl)pyrazole (**3**) reacted completely (t.l.c.) and gave α,β-mixtures of the corresponding 3-(D-arabinofuranosyl)pyrazoles **4** and **5** in good yields. The respective α,β-ratios, determined by ^{1}H-n.m.r. spectroscopy, were 15:85 and 40:60, and the isomers were isolated by chromatography.

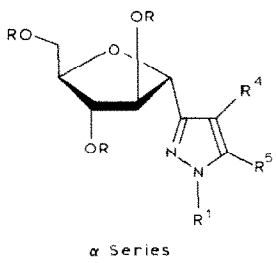
In contrast, treatment of **2** and **3** with 2M hydrochloric acid for several hours gave mixtures of four products which could not be resolved. When boiling ethanolic trifluoroacetic acid was used for several hours, only two products were formed ($\sim$50%) in each reaction; **4**β and **5**β preponderated, some starting material remained, and prolongation of the reaction led to complex mixtures.



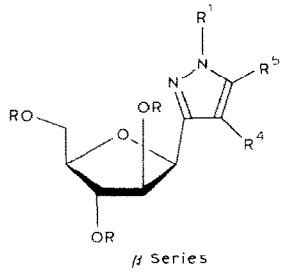
1 $R^1 = R^4 = R^5 = H$

2 $R^1 = Me, R^4 = H, R^5 = Ph$

3 $R^1 = R^4 = Me, R^5 = p\text{-}C_6H_4\text{—}Me$



α Series



β Series

4 $R = H, R^1 = Me, R^4 = H, R^5 = Ph$

5 $R = H, R^1 = R^4 = Me, R^5 = p\text{-}C_6H_4\text{—}Me$

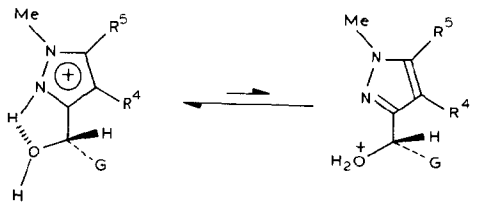
6 $R = Ac, R^1 = Me, R^4 = H, R^5 = Ph$

7 $R = Ac, R^1 = R^4 = Me, R^5 = p\text{-}C_6H_4\text{—}Me$

8 $R = R^1 = R^4 = R^5 = H$

Treatment of 3(5)-(D-*manno*-pentitol-1-yl)pyrazole (**1**) with aqueous trifluoroacetic acid, as described for **2** and **3**, gave only 24% of **8**β, and 26% of **1** was recovered. Prolongation of the reaction led to extensive decomposition. Therefore, the cyclodehydration seems to be favoured by the presence of alkyl or aryl substituents on the pyrazole ring.

Pyrazole is a stronger base than pyrrole, but much weaker than imidazole[19]. The attachment of a polyhydroxyalkyl group at C-3 allows the formation of an intramolecularly hydrogen-bonded pyrazolium cation **9** in equilibrium with a small amount of the oxonium ion **10**. The displacement of water by HO-4′ in an internal S_N2 process that leads to the β epimer may compete with the formation of the cation on C-1′ which, by an S_N1 mechanism, would lead to an α,β-mixture.



9 10

With the imidazole analogues, the equilibrium should be even more displaced towards **9** and cyclodehydration is not possible[14].

In the gas phase, *N*-methylation increases the intrinsic basicity of the azoles, but, in aqueous solution, an opposite effect, due to solvation phenomena, is observed frequently and the derived azolium cations are solvated to a lesser extent than the parent compounds[20]. In aqueous solution, *C*-aryl substituents cause a slight decrease in the basicity of the pyrazole ring[20]. Thus, 1-methylpyrazole[21] and 1-methyl-3,5-diphenylpyrazole[22] are weaker bases than pyrazole. In consequence, in aqueous media, **2** and **3** should be weaker bases than **1**, which would explain their easier cyclodehydration.

The expulsion of water *via* HO-4′ is preferred kinetically in comparison with HO-5′, and may constitute the driving force of the reaction.

The structures of **4** and **5** were assigned on the basis of analytical and spectral data. Compounds **4β** and **5β** each consumed ~1 mol of periodate consistent with either a 1′,4′- or a 2′,5′-anhydro ring. The ^{1}H-n.m.r. spectra (Table I) of **4** and **5** contain signals (2 d and a t) consistent with two secondary hydroxyl groups and one primary hydroxyl group. These data, together with the doublet for H-1′, indicated that the ring closure had occurred between C-1′ and C-4′. Treatment of **4** and **5** with acetic anhydride and pyridine afforded the triacetates **6** and **7**, the ^{1}H-n.m.r. spectra of which (Table I) confirmed the proposed structures. Thus, the resonance for H-4′ in **6** and **7** appeared at higher field than those for H-2′ and H-3′, indicating the absence of an acyloxy group on C-4′.

The resonance for H-1′ appeared at higher field for **4α** and **5α** than for **4β** and **5β**, and the values of $J_{1',2'}$ (5–7 Hz) for the *α* anomers of **4–7** were higher than those (3.5–4 Hz) for the *β* anomers. These data are consistent with those reported[11,23–25] for D-arabinofuranosyl *C*-nucleosides. The resonances for H-2′ in **4–7** were at lower field in the *α* anomers ($\Delta\delta$ ~0.32 p.p.m.), which could be attributed to the anisotropic effect of the heterocyclic ring.

The ^{13}C-n.m.r. data for **4–7** are recorded in Table II. For the *α* anomers, C-1′ resonated at higher field than for *β* anomers. The literature data for different epimeric pairs are inconsistent[23].

The mass spectra of the *α* and *β* forms of **4** and **5** showed fragmentation patterns that differed only in the relative intensities of the most abundant peaks. The base peaks for **4α** and **5α** (*m/z* 201 and 229, respectively) corresponded to the fragment $[BCH_2CHOH]^+$, where **B** is the heterocycle, and those for **4β** and **5β** (*m/z* 187 and 215, respectively) corresponded to $[B + 30]^+$, *i.e.*, the heterocycle plus a protonated formyl

TABLE I

^{1}H-N.m.r. data[a] (δ in p.p.m. and J in Hz) for **4–7** at 200 MHz

Compound	*H-1*	*H-2*	*H-3*	*H-4*	*H-5*	*H-5'*	*OH*	*OAc*	*N-Me*	R^4	R^5
4α[b]	4.68d $J_{1,2}$6.7	4.25dd $J_{2,3}$ 5.9	3.96dd $J_{3,4}$ 6.5	3.86m	3.65dd	3.56dd	4.84t 5.37d 5.45d		3.91s	6.50s	7.6–7.7m
4β[b]	4.89d $J_{1,2}$3.4	3.95dd $J_{2,3}$1.9	3.85dd $J_{3,4}$2.5	3.72m	3.58	3.51m	4.90d 4.98t 5.27d		3.78s	6.36s	7.4–7.5m
5α[b]	4.73d $J_{1,2}$7.6	4.43dd $J_{2,3}$6.3	3.96dd $J_{3,4}$7.2	3.85m	3.70	3.50m	4.46d 4.81t 5.25d		3.77s	2.06s	2.49s 7.3–7.5m
5β[b]	4.80d $J_{1,2}$3.6	4.06dd $J_{2,3}$1.8	3.87dd $J_{3,4}$2.3	3.70		3.50m	4.85d 4.92t 5.13d		3.69s	1.97s	2.35s 7.2–7.3m
6α[c]	5.17d $J_{1,2}$4.8	5.65dd $J_{2,3}$3.1	5.24dd $J_{3,4}$4.2	4.50		4.30m		2.08s 2.12s 2.13s	3.86s	6.37s	7.3–7.5m
6β[c]	5.26d $J_{1,2}$3.6	5.43dd $J_{2,3}$1.2	5.12dd $J_{3,4}$3.1	4.17m	4.41dd	4.31dd		2.01s 2.11s 2.14s	3.84s	6.35s	7.4–7.5m
7α[c]	5.16d $J_{1,2}$5.6	5.85dd $J_{2,3}$3.6	5.26dd $J_{3,4}$4.0	4.50		4.30m		2.10s 2.11s 2.12s	3.71s	2.01s	2.41s 7.1–7.3m
7β[c]	5.30d $J_{1,2}$4.1	5.48dd $J_{2,3}$1.5	5.18dd $J_{3,4}$4.1	4.05m	4.51dd	4.34dd		2.03s 2.10s 2.14s	3.69s	1.98s	2.42s 7.2–7.3m

[a] Internal Me_4Si. [b] In $(CD_3)_2SO$. [c] In $CDCl_3$. [d] HO-5'

TABLE II

^{13}C-N.m.r. data (δ in p.p.m.[a]) for **4–7** at 50.3 MHz

Compound	*C-1′–C-4′*	*C-5′*	*N-CH$_3$*	*C-3*	*C-4*	*C-5*	*Aromatic-5* i	o,m	p	p-C$_6$H$_4$-CH$_3$	*CH$_3$-4*	*AcO* *CH$_3$*	*CO*
4α[b]	83.7 81.6 78.8 77.3	61.9	37.7	151.1	104.5	143.9	130.4	128.2 128.6	128.8				
4β[b]	86.1 78.6 78.2 78.0	62.3	37.5	148.4	106.4	142.3	130.5	129.0 128.4	128.6				
5α[b]	83.3 80.0 77.8 77.3	62.0	37.3	148.1	112.5	141.5	138.3	129.8	127.1	21.2	8.7		
5β[b]	86.7 78.9 78.1 77.9	62.2	37.6	148.7	111.6	140.9	137.5	128.2	127.1	20.7	8.5		
6α[c]	80.9 80.2 78.9 78.5	63.2	37.4	157.6	104.1	148.2		128.5				20.8 20.7 20.7	170.6 170.1 169.8
6β[c]	83.2 82.9 79.1 78.7	63.4	37.3	153.6	106.3	149.5	130.2	128.8 128.2	128.1			21.3 21.2 20.9	170.3 169.9 169.7
7α[c]	80.1 79.6 78.5 77.5	62.9	37.1	145.3	112.9	142.0	138.2	129.4 129.2	127.0	21.2	8.2	21.2 20.8 20.7	170.6 170.3 169.9
7β[c]	83.4 82.8 79.5 78.9	63.1	37.6	144.9	112.3	143.5	137.8	129.6	128.0	20.9	8.4	21.4 21.3 20.8	170.5 170.2 169.8

[a] Internal Me_4Si. [b] In $(CD_3)_2SO$. [c] In $CDCl_3$.

group. All these peaks are characteristic for *C*-nucleosides[26]. The *C*-glycoside structure was also indicated by the weak $[B + 1]^+$ and $[B + 2]^+$ peaks that, for *N*-nucleosides, are abundant.

The new *C*-nucleosides followed the general rule, namely, that, in the D-series, the α anomers are more dextrorotatory than the β anomers.

EXPERIMENTAL

General methods. — Solvents were evaporated *in vacuo* at $<40°$. Melting points were determined with a Gallenkamp MFB-595 apparatus and are uncorrected. Optical rotations were measured with a Perkin–Elmer 241 MC polarimeter. Analytical t.l.c. was performed on Alugram Sil G/UV_{254} (MN), preparative t.l.c. on PSC-60 F_{254} (Merck), and column chromatography on Silica Gel 60 (Merck, 63–200 μm). I.r. spectra were recorded with a Perkin–Elmer 299 spectrophotometer and u.v. spectra with a Hitachi 150–20 spectrophotometer. N.m.r. spectra were recorded with a Varian XL-200 spectrometer; $J_{H,H}$ values were measured directly from the spectra and assignments were confirmed by deuteration and/or double-resonance experiments. The chemical shifts of ^{13}C resonances are relative to that of internal Me_4Si. The resonances were assigned from "off-resonance" spectra and the multiplicities from APT spectra. The ^1H- and ^{13}C-n.m.r. data are given in Tables I and II, respectively. The e.i.-mass spectra were obtained at 70 eV, using a MS-80 RFA Kratos instrument with an ion-source temperature of 200°.

3-(α-D-Arabinofuranosyl- and β-D-arabinofuranosyl)-1-methyl-5-phenylpyrazole (**4α** and **4β**). — A solution of 1-methyl-3-(D-*manno*-pentitol-1-yl)-5-phenylpyrazole[18] (**2**; 0.500 g, 1.62 mmol) in water (25 mL) containing trifluoroacetic acid (2.5 mL) was boiled for 4 days under reflux and then concentrated to dryness. Ethanol was evaporated several times from the residue until the trifluoroacetic acid had been removed. Column chromatography (dichloromethane–methanol, 10:1) of the residue gave a mixture (0.366 g, 78%) of **4α** and **4β** in the ratio 15:85, which was crystallised from ethyl acetate to give **4β** (0.249 g). Preparative t.l.c. (dichloromethane–methanol, 4:1) of the material in the mother liquor gave more **4β** (total 0.303 g, 64%), R_f 0.60 (dichloromethane–methanol, 6:1), m.p. 136–137°, $[\alpha]_D^{22}$ −17° (*c* 1, pyridine); λ_{max}^{MeOH} 240 nm; ν_{max} 3350 (OH), 1490, 1470 (C=C, C=N aromatic), 950 cm^{-1} (pyrazole ring bending). Mass spectrum: *m/z* 292 (<1%, $[M + 2]^+$), 291 (2, $[M + 1]^+$), 290 (9, M^+), 201 (44, $[BCH_2CHOH]^+$), 187 (100, $[BCHOH]^+$), 171 (15, $[BCH_2]^+$), 159 (6, $[B + 2]^+$), 158 (2, $[B + 1]^+$).

Anal. Calc. for $C_{15}H_{18}N_2O_4$: C, 62.06; H, 6.25; N, 9.65. Found: C, 62.50; H, 5.98; N, 9.27.

Compound **4α**, R_f 0.56, was isolated as a colorless syrup (0.049 g, 10%), $[\alpha]_D^{25}$ +34° (*c* 1, pyridine); λ_{max}^{MeOH} 240 nm; ν_{max} 3300 (OH), 1490, 1465 (C=C, C=N aromatic), 920 cm^{-1} (pyrazole ring bending). Mass spectrum: *m/z* 292 (<1, $[M + 2]^+$), 291 (2, $[M + 1]^+$), 290 (9, M^+), 201 (100, $[BCH_2CHOH]^+$), 187 (93, $[BCHOH]^+$), 171 (20, $[BCH_2]^+$), 159 (7, $[B + 2]^+$), 158 (3, $[B + 1]^+$).

Anal. Found: C, 62.22; H, 6.09; N, 9.58.

3-(α-D-Arabinofuranosyl- and β-D-arabinofuranosyl)-1,4-dimethyl-5-(p-tolyl)pyrazole (**5α** and **5β**). — A solution of 1,4-dimethyl-3-(D-*manno*-pentitol-1-yl)-5-(*p*-tolyl)-pyrazole[18] (**3**; 0.400 g, 1.19 mmol) in water (20 mL) containing trifluoroacetic acid (2 mL) was boiled for 2 days under reflux, then worked-up as described above. Column chromatography (dichloromethane–methanol, 10:1) of the product gave a mixture (0.306 g, 81%) of **5α** and **5β** in the ratio 40:60. Preparative t.l.c. (dichloromethane–methanol, 4:1) gave **5β** (0.164 g, 43%), R_f 0.63 (dichloromethane–methanol, 6:1), m.p. 152–153° (from ether), $[\alpha]_D^{22}$ −4.3° (*c* 1, pyridine); λ_{max}^{MeOH} 241 nm; ν_{max} 3340 (OH) 1500, 1470 (C=C, C=N aromatic), 940 cm^{-1} (pyrazole ring bending). Mass spectrum: *m/z* 320 (<1, $[M + 2]^+$), 319 (1, $[M + 1]^+$), 318 (7, $[M]^+$), 229 (63, $[BCH_2CHOH]^+$), 215 (100, $[BCHOH]^+$), 199 (18, $[BCH_2]^+$), 187 (5, $[B + 2]^+$), 186 (3, $[B + 1]^+$).

Anal. Calc. for $C_{17}H_{22}N_2O_4$: C, 64.13; H, 6.97; N, 8.80. Found: C, 63.82; H, 7.13; N, 8.52.

Compound **5α** was also isolated as a colorless syrup (0.106 g, 30%), R_f 0.58, $[\alpha]_D^{25}$ +59° (*c* 1, pyridine); λ_{max}^{MeOH} 241 nm; ν_{max} 3350 (OH), 1490, 1460 (C=C, C=N, aromatic), 920 cm^{-1} (pyrazole ring bending). Mass spectrum: *m/z* 319 (1, $[M + 1]^+$), 318 (4, $[M]^+$), 229 (100, $[BCH_2CHOH]^+$), 215 (62, $[BCHOH]^+$), 199 (19, $[BCH_2]^+$), 187 (5, $[B + 2]^+$), 186 (3, $[B + 1]^+$).

Anal. Found: C, 64.04; H, 7.01; N, 8.53.

Acetylation of **4** *and* **5**. — Compounds **4α**, **4β**, **5α**, and **5β** (0.050 g each) were acetylated[27] with acetic anhydride (0.5 mL) in pyridine (0.5 mL) for 48 h at 0°. The products were purified by preparative t.l.c. (ether–hexane, 7:1) or crystallisation.

1-Methyl-5-phenyl-3-(2,3,5-tri-*O*-acetyl-α-D-arabinofuranosyl)pyrazole (**6α**; 60 mg, 84%), $[\alpha]_D^{25}$ +55° (*c* 1, chloroform); ν_{max} 1740 (C=O), 1490, 1465 (C=C, C=N, aromatic), 1230 (C=O), 915 cm^{-1} (pyrazole ring bending).

Anal. Calc. for $C_{21}H_{24}N_2O_7$: C, 60.57; H, 5.81; N, 6.72. Found: C, 60.60; H, 5.96; N, 6.57.

1,4-Dimethyl-5-(*p*-tolyl)-3-(2,3,5-tri-*O*-acetyl-α-D-arabinofuranosyl)pyrazole (**7α**; 62 mg, 89%), $[\alpha]_D^{25}$ +56° (*c* 1, chloroform); ν_{max} 1745 (C=O), 1510, 1450 (C=C, C=N, aromatic), 1230 (C–O), 920 cm^{-1} (pyrazole ring bending).

Anal. Calc. for $C_{23}H_{28}N_2O_7$: C, 62.15; H, 6.35; N, 6.30. Found: C, 61.88; H, 6.42; N, 6.22.

1-Methyl-5-phenyl-3-(2,3,5-tri-*O*-acetyl-β-D-arabinofuranosyl)pyrazole (**6β**; 53 mg, 74%), m.p. 102–104° (from methanol), $[\alpha]_D^{22}$ +12.5° (*c* 1, chloroform); ν_{max} 1735 (C=O), 1475, 1495 (C=C, C=N, aromatic), 1230 (C–O), 935 cm^{-1} (pyrazole ring bending).

Anal. Calc. for $C_{21}H_{24}N_2O_7$: C, 60.57; H, 5.81; N, 6.72. Found: C, 60.89; H, 5.45; N, 6.92.

1,4-Dimethyl-5-(*p*-tolyl)-3-(2,3,5-tri-*O*-acetyl-β-D-arabinofuranosyl)pyrazole (**7β**; 50 mg, 72%), m.p. 81–83° (from methanol), $[\alpha]_D^{22}$ +23° (*c* 1, chloroform); ν_{max} 1740 (C=O), 1470, 1500 (C=C, C=N, aromatic), 930 cm^{-1} (pyrazole ring bending).

Anal. Calc. for $C_{23}H_{28}N_2O_7$: C, 62.15; H, 6.35; N, 6.30. Found: C, 62.57; H, 6.37; N, 5.97.

*3(5)-β-*D-*Arabinofuranosylpyrazole* (**8β**). — A solution of 3(5)-(D-*manno*-pentitol-1-yl)pyrazole[11] (**1**; 0.10 g, 0.50 mmol) in water (5 mL) containing trifluoroacetic acid (0.5mL) was boiled for 2 days under reflux and then worked-up as described above. Column chromatography (ethyl acetate–acetone, 1:1) of the product gave, first, **8β** (0.022 g, 24%), the ^{1}H-n.m.r. data of which accorded with those reported[11]. Elution with dichloromethane–methanol (10:1) gave (**1**) (0.026 g).

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