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Synthesis of 3-(D-lyxofuranosyl)pyrazoles by trifluoroacetic acid-catalysed cyclodehydration of 3-(D-*galacto*-pentitol-1-yl)pyrazoles

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ABSTRACT

New 3-(D-*galacto*-pentitol-1-yl)pyrazole derivatives have been obtained by the reaction of D-galactose hydrazones and nitroalkenes. Cyclodehydration of the 1-methyl-3-(D-*galacto*-pentitol-1-yl)pyrazoles in trifluoroacetic acid at room temperature afforded good yields of 3-(α-D-lyxofuranosyl)-1-methyl derivatives. A β anomer was obtained only for the 5-(*p*-tolyl) derivative.

INTRODUCTION

We have described the preparation of 3-(D-arabinofuranosyl)pyrazoles by the cyclodehydration of the corresponding 3-(D-*manno*-pentitol-1-yl) derivatives with boiling aqueous 10% trifluoroacetic acid[1]. In the α,β-mixtures obtained, the β anomer was the major component. We now report on the application of this reaction to some new and known[2] 3-(D-*galacto*-pentitol-1-yl)pyrazoles.

RESULTS AND DISCUSSION

The reactions of D-galactose methylhydrazone (**1**) with 1-nitropropene and with 2-nitrobut-2-ene in 10:1 *N*,*N*-dimethylformamide–water at room temperature afforded the pyrazole derivatives **4** (79%) and **5** (88%), respectively. Similarly, with β-nitrostyrene, D-galactose benzylhydrazone (**2**) gave the 1-benzylpyrazole derivative **6** (85%), and D-galactose hydrazone (**3**) gave the pyrazole derivative **7** (77%). As in the previous study[2], loss of the nitro group took place and the regioselectivity was "normal" as indicated by the δ value (6.27–6.70) for the resonance of the pyrazole proton in compounds **4**, **6**, and **7**. As expected[2,3], the signal for H-1′ was the most downfield of those for the polyol chain. The chemical shifts of the ^{1}H and ^{13}C resonances for the remainder of the polyol chain accorded with previous findings[2–4]. For **7**, the signals of C-3 and C-5 were broadened as a consequence of tautomerism[5], and that of C-5′ was distinguished easily from the APT spectra[6] and was the most shielded of those in the polyol moiety.

Treatment of **5**, **8** (ref. 2), and **9** (ref. 2) severally with trifluoroacetic acid at room

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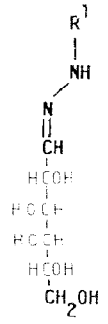
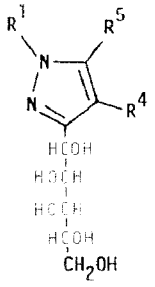


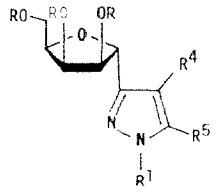
1 R^1 = Me
2 R^1 = Bn
3 R^1 = H



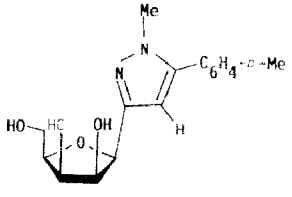
4 $R^1 = R^5$ = Me, R^4 = H
5 $R^1 = R^4 = R^5$ = Me
6 R^1 = Bn, R^4 = H, R^5 = Ph
7 $R^1 = R^4$ = H, R^5 = Ph
8 $R^1 = R^4$ = Me, R^5 = *p*-tolyl
9 R^1 = Me, R^4 = H, R^5 = *o*-tolyl

temperature for 24 h afforded the respective 3-(α-D-lyxofuranosyl)pyrazoles **10**–**12** in yields of 41–69%, but only one β compound (**13**, 14%). Similar treatment of **6** gave a complex mixture (presumably anomeric pyranoid and furanoid derivatives) which could not be resolved. Treatment of **7** with trifluoroacetic acid under reflux for 4 days, or aqueous or methanolic 10% trifluoroacetic acid under reflux for 2 days, resulted in only partial reaction. Thus, the absence of an N-1 substituent hinders the action of the acid catalyst, as observed[2] for the 3-(D-*manno*-pentitol-1-yl) analogues. The consumption of 1 mol of periodate by each of **10**–**13** confirmed the furanoid structures. Compound **11** was converted into the 2′,3′,5′-triacetate **14** and the 2′,3′-*O*-isopropylidene derivative **15**.

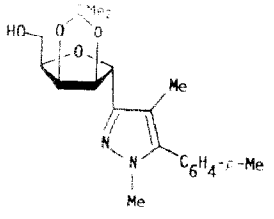
The structures and configurations of **7**–**13** were established by the n.m.r. data. In the ^{1}H-n.m.r. spectra (Table I), the hydroxyl protons of **10** gave broadened signals, but, for **11** and **12**, those for HO-2′ and HO-3′ (2 d) and HO-5′ (t) indicated the 1′,4′-anhydro structure, as did the lack of effect only on the H-1′ and H-4′ signals on deuterium exchange of **10**–**13**. Assignment of anomeric configurations was based on data for the pair **12** and **13**. Data[7] for D-lyxofuranosyl derivatives showed that the δ value for the



10 R = H, $R^1 = R^4 = R^5$ = Me
11 R = H, $R^1 = R^4$ = Me, R^5 = *p*-tolyl
12 R = H, R^1 = Me, R^4 = H, R^5 = *p*-tolyl
14 R = Ac, $R^1 = R^4$ = Me, R^5 = *p*-tolyl



13



15

H-1′ resonance should be lower for the α than for the β anomer (δ 4.71 for **12** and 4.88 for **13**), but the $J_{1',2'}$ values of 7.8 and 4.8 Hz for **12** and **13**, respectively, are outside the range established[8] for *cis* protons. Compound **12** was more dextrorotatory than **13**, in agreement with Hudson's rule[9]. The ^{1}H-n.m.r. spectra of **10** and **11** showed similarities with that of **12**. Thus, the respective $J_{1',2'}$ values (8.3 and 8.0 Hz) were higher than those expected for *cis* protons, and the δ values of H-2′ and H-3′ resonances were in the same order (H-2′ > H-3′) as for the α anomer **12** (*cf.* H-3′ > H-2′ for the β anomer **13**). The latter effect may be attributed to the anisotropy of the pyrazole ring. On this basis, the α configuration is assigned tentatively to **10** and **11**.

The ^{13}C-n.m.r. data for **10**–**15** (Table II) showed that, in comparison with the resonances for the pentitol-1-yl compounds, those of C-1′/4′ were shifted downfield, whereas that of C-5′ was at a higher field in accord with pentofuranosyl structures.

The mass spectra of **10**–**13** each contained a peak for M^+ (~5%), and a fragment for $(B + 30)^+$ (where B is the pyrazole residue and 30 is the mass of $CHOH^+$) was the base peak. The second peak in intensity (40–60%) had m/z $(B + 44)^+$ and was due to the ion $(B–CH_2–CHOH)^+$. These, and other, features are typical of *C*-nucleosides[10,11]. The derivatives **14** and **15** showed the expected fragmentations for these types of compounds[11–13].

The formation of furanoid derivatives only from **4**–**9** suggests the operation of kinetic control. The temperature necessary to effect cyclodehydration by using trifluoroacetic acid was much lower than those employed with dilute aqueous acid. Steric hindrance effects may account for the formation of the β-lyxosyl derivatives being disfavoured.

EXPERIMENTAL

General methods. — Solvents were evaporated *in vacuo* at <45°. Melting points were determined with a Gallenkamp MFB-595 apparatus and are uncorrected. Optical rotations were measured with a Perkin–Elmer 241 MC polarimeter. T.l.c. was performed on Alugram Sil G/UV_{254} (MN) and detection with u.v. light or iodine vapor or by charring with sulphuric acid. U.v. spectra were recorded with a Beckman DU-7 spectrophotometer and i.r. spectra (for films or KBr discs) with a Perkin–Elmer 299 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 ^{13}C-n.m.r. spectra (50.3 MHz) were recorded under proton-decoupled conditions and the multiplicities were assigned from APT spectra[6]. E.i.-mass spectra (70 eV) were obtained with a Kratos MS-80RFA instrument operated at an ionising current of 100 μA, an accelerating voltage of 4 kV, and a resolution of 1000 (10% valley definition). Consumption of periodate was determined by a method based on that of Fleury and Lange[14].

Prepartation of 3-(D-galacto-*pentitol-1-yl)pyrazoles* (**4**–**7**). — To a stirred solution of the D-galactose (alkyl)hydrazone (**1**–**3**, 10 mmol) in 10:1 *N*,*N*-dimethylformamide–water (~10 mL) was added nitroalkene (10 mmol) at room temperature. Each

TABLE I

^{1}H-N.m.r. data (200 MHz, internal Me_4Si) for **10–15**

Compound	*Chemical shifts (δ in p.p.m.)*													
	H-1'	*H-2'*	*H-3'*	*H-4'*	*H-5'a*	*H-5'b*	*HO-2'*	*HO-3'*	*HO-5'*	*N-Me*	R^4	R^5	*OAc*	*Ip*
10[a]	4.69	4.41	4.17	4.08	3.73	3.57	←4.8–5.1→			3.71	1.98	2.19		–
11[a]	4.79	4.54	4.21	4.13	←3.5–3.7→		5.06	4.91	4.66	3.76	2.03	2.49	–	
												7.37		
												7.44		
12[a]	4.71	4.36	←4.1–4.2→		3.75	3.63	5.11	4.92	4.68	3.88	6.45	2.46	–	
												7.35		
												7.49		
13[a]	4.88	4.18	4.43	4.01	←3.5–3.7→		←4.9–5.7→			3.89	6.51	2.47	–	–
												7.41		
												7.50		
14[b]	5.17	5.75	5.81	4.64	←4.2–4.3→		–	–	–	3.68	2.05[c]	2.40	1.99[c]	
												7.15	2.05[c]	
												7.25	2.13[c]	
15[a]	5.12	5.32	4.93	3.93	3.80	3.63		–	4.74	3.77	2.06	2.49	–	1.42
												7.39		1.55
												7.45		

	Coupling constants (J in Hz)									
	$J_{1',2'}$	$J_{2',3'}$	$J_{3',4'}$	$J_{4',5'}$	$J_{4',5'a}$	$J_{5'a,5'b}$	$J_{HO,2'}$	$J_{HO,3'}$	$J_{HO,5'}$	$J_{o,m}$
10	8.3	4.1	3.4	5.2	6.4	11.4				
11	8.0	4.3	3.5	5.4	6.1		4.3	7.3	5.6	7.8
12	7.8	4.2		4.8	6.4	11.4	3.9	7.3	5.8	8.1
13	4.8	4.8	6.5	4.0	5.1					8.2
14	5.9	4.8	4.8	6.2	6.2					8.3
15	0	5.9	3.8	5.5	6.6	11.4				8.4

[a] In $(CD_3)_2SO$. [b] In $CDCl_3$. [c] These assignments may be interchanged.

TABLE II

^{13}C-N.m.r. data (50.3 MHz, internal Me_4Si) (δ in p.p.m.) for **10–15**

Compound	*C-3*	*C-4*	*C-5*	*C-1′/4′*	*C-5′*	*N–CH₃*	*R*[d]	*R*[5]		*AcO*		*Isopropylidene*	
								CH₃	*Ar*	*CH₃*	*C=O*	*CH₃*	*Acetal C*
10[a]	147.9	112.3	137.9	81.5 76.8 76.2 72.1	61.0	36.5	8.6[c]	9.6[c]	–	–	–	–	–
11[a]	148.2	112.6	141.4	81.2 76.4 75.6 71.6	60.5	37.2	8.6	21.2	138.3 (*i*) 129.7 (*o,m*) 127.2 (*p*)	–	–	–	–
12[a]	151.3	104.2	144.1	81.3 77.2[b] 71.6	60.6	37.7	–	21.2	138.5 (*i*) 129.9 128.7 (*o,m*) 127.7 (*p*)	–	–	–	–
13[a]	149.3	106.5	143.4	80.3 77.1 72.5 72.2	60.5	37.7	–	21.2	138.3 (*i*) 129.9 128.6 (*o,m*) 127.8 (*p*)	–	–	–	–
14[b]	145.4	113.0	141.9	75.8 75.1 74.6 71.6	62.5	37.1	8.1	21.1[c]	138.2 (*i*) 129.4 129.2 (*o,m*) 126.9 (*p*)	20.7[c] 20.5[c] 20.4[c]	170.4 169.6 169.5	–	–
15[b]	146.6	112.8[c]	141.8	83.9 81.1 80.8 78.0	59.6	37.5	8.6	21.3	138.6 (*i*) 129.9 (*o,m*) 127.0 (*p*)	–	–	26.5 25.0	111.9[c]

[a] In $(CD_3)_2SO$. [b] In $CDCl_3$. [c] These assignments may be interchanged. [d] Double intensity.

reaction was monitored by t.l.c. (5:1 dichloromethane–methanol). After 48 h, the solvent was evaporated *in vacuo* (< 0.4 Torr), and the residue was washed successively with cold ethanol, ethyl acetate, and water, then crystallised and recrystallised from methanol.

The following compounds were prepared in this manner.

1,5-Dimethyl-3-(D-*galacto*-pentitol-1-yl)pyrazole (**4**; 1.94 g, 79%) [from D-galactose methylhydrazone[15] (**1**, 2.08 g) and 1-nitropropene[16] (0.87 g)], m.p. 172–173°, $[\alpha]_D^{25}$ +27° (*c* 1, pyridine); λ_{max}^{MeOH} 219 nm (ε 4300); ν_{max}^{KBr} 3300 (OH), 1545 (pyrazole C=N), 920 cm^{-1} (pyrazole ring bending). N.m.r. data: ^{1}H [$(CD_3)_2SO$ + D_2O], δ 6.27 (s, 1 H, H-4), 4.97 (d, 1 H, $J_{1',2'}$ 1.4 Hz, H-1'), 3.85 (s, 3 H, Me-1), 3.82 (m, 1 H, H-4'), 3.69 (m, 1 H, H-2'), 3.62 (dd, 1 H, $J_{2',3'}$ 9.1, $J_{3',4'}$ 1.1 Hz, H-3'), 3.52 (m, 2 H, H-5'a,5'b) 2.35 (s, 3 H, Me-5); ^{13}C [$(CD_3)_2SO$], δ 152.6 (s, C-3), 142.1 (s, C-5), 105.0 (d, C-4), 73.4, 70.5, 69.7, 67.0 (4 d, C-1',4'), 63.5 (t, C-5'), 35.8 (q, Me-1), 11.3 (q, Me-5) (Found: C, 48.70; H, 7.36; N, 11.22. $C_{10}H_{18}N_2O_5$ calc.: C, 48.77; H, 7.37; N, 11.38%).

1,4,5-Trimethyl-3-(D-*galacto*-pentitol-1-yl)pyrazole (**5**; 2.29 g, 88%) [from **1** (2.08 g) and 2-nitrobut-2-ene[17] (1.01 g)], m.p. 145–146°, $[\alpha]_D^{25}$ +14° (*c* 1, pyridine); λ_{max}^{MeOH} 230 nm (ε 5600); ν_{max}^{KBr} 3300 (OH), 1570 (pyrazole C=N), 920 cm^{-1} (pyrazole ring bending). N.m.r. data: ^{1}H [$(CD_3)_2SO$ + D_2O], δ 4.87 (d, 1 H, $J_{1',2'}$ 2.3 Hz, H-1'), 3.79 (m, 1 H, H-4'), 3.75 (s, 3 H, Me-1), 3.74 (m, 1 H, H-2'), 3.62 (dd, 1 H, $J_{2',3'}$ 8.6, $J_{3',4'}$ 1.3 Hz, H-3'), 3.50 (m, 2 H, H-5'a,5'b), 2.23 (s, 3 H, Me-5), 2.04 (s, 3 H, Me-4); ^{13}C [$(CD_3)_2SO$], δ 150.3 (s, C-3), 136.4 (s, C-5), 110.9 (s, C-4), 73.4, 70.3, 69.2, 65.9 (4 d, C-1',4'), 63.3 (t, C-5'), 36.1 (q, Me-1), 9.2 (q, Me-5), 8.5 (q, Me-4) (Found: C, 50.50; H, 7.82; N, 10.93. $C_{11}H_{20}N_2O_5$ calc.: C, 50.76; H, 7.75; N, 10.76%).

1-Benzyl-3-(D-*galacto*-pentitol-1-yl)-5-phenylpyrazole (**6**; 3.26 g, 85%) [from D-galactose benzylhydrazone[15] (**2**, 2.84 g) and β-nitrostyrene[18] (1.49 g)], m.p. 194–195°, $[\alpha]_D^{25}$ +14° (*c* 1, pyridine); λ_{max}^{MeOH} 241 nm (ε 12 400); ν_{max}^{KBr} 3300 (OH), 1600 (phenyl), 1545 (pyrazole C=N), 1490 (phenyl), 925 cm^{-1} (pyrazole ring bending). N.m.r. data: ^{1}H [$(CD_3)_2SO$ + D_2O], δ 7.6–7.0 (m, 10 H, 2 Ph), 6.50 (s, 1 H, H-4), 5.44 (s, 2 H, PhCH_2), 5.00 (d, 1 H, $J_{1',2'}$ 1.6 Hz, H-1'), 3.88 (m, 1 H, H-4'), 3.76 (m, 1 H, H-2'), 3.66 (dd, 1 H, $J_{2',3'}$ 9.2, $J_{3',4'}$ ~0 Hz, H-3'), 3.53 (m, 2 H, H-5'a,5'b); ^{13}C [$(CD_3)_2SO$], δ 155.1 (s, C-3), 143.9 (s, C-5), 138.2 (s, *ipso*-C of benzyl), 130.7 (s, *ipso*-C of Ph-5), 129.3, 128.9, 128.6, 127.7, 126.8 (5 d, *o*-, *m*-, and *p*-C of 2 Ph), 105.6 (d, C-4), 73.4, 70.3, 69.5, 67.1 (4 d, C-1',4'), 63.3 (t, C-5'), 52.7 (t, PhCH_2) (Found: C, 65.44; H, 6.26; N, 7.22. $C_{23}H_{28}N_2O_5$ calc.: C, 65.61; H, 6.29; N, 7.29%).

3(5)-(D-*galacto*-Pentitol-1-yl)-5(3)-phenylpyrazole (**7**; 2.27 g, 77%) [from D-galactose hydrazone[19] (**3**, 1.94 g) and β-nitrostyrene[18] (1.49 g)], m.p. 179–181°, $[\alpha]_D^{25}$ +28° (*c* 1, pyridine); λ_{max}^{MeOH} 251 nm (ε 10 000); ν_{max}^{KBr} 3300 (OH), 1585 (phenyl), 1565 (pyrazole C=N), 1490 (phenyl), 920 cm^{-1} (pyrazole ring bending). N.m.r. data: ^{1}H [$(CD_3)_2SO$ + D_2O], δ 7.9–7.4 (m, 5 H, Ph), 6.70 (s, 1 H, H-4), 5.07 (d, $J_{1',2'}$ 1.4 Hz, H-1'), 3.86 (m, 1 H, H-4'), 3.76 (m, 1 H, H-2'), 3.66 (dd, 1 H, $J_{2',3'}$ 7.6, $J_{3',4'}$ 1.0 Hz, H-3'), 3.54 (m, 2 H, H-5'a,5'b); ^{13}C [$(CD_3)_2SO$], δ 150.2 (s, C-3), 147.8 (s, C-5), 132.9 (s, *ipso*-C of Ph), 129.2, 127.9 (2 d, *o*-, *m*-, and *p*-C of Ph), 100.4 (d, C-4), 73.1, 70.2, 69.5, 66.0 (4 d, C-1',4'), 63.3 (t, C-5') (Found: C, 57.08; H, 6.20; N, 9.49. $C_{14}H_{18}N_2O_5$ calc.: C, 57.13; H, 6.17; N, 9.52%).

3-(α-D-Lyxofuranosyl)-1,4,5-trimethylpyrazole (**10**). — A solution of **5** (0.50 g, 1.92 mmol) in trifluoroacetic acid (1.5 mL, 19.5 mmol) was kept at room temperature for 24 h. The acid was then evaporated *in vacuo* and the residual traces were removed by repeated distillation of ethanol from the residue, which was then crystallised from methanol to give a product (0.34 g, 73%), m.p. 174–176°, that was recrystallised from methanol to afford **10** (63%), m.p. 175–176°, $[\alpha]_D^{25}$ +63° (*c* 1, pyridine); ν_{max}^{KBr} 3430, 3380 (OH), 1570 (pyrazole C=N), 900 cm^{-1} (pyrazole ring bending). For the n.m.r. data, see Tables I and II. Mass spectrum: *m/z* 139 (100%, $[B + 30]^+$), 153 (49, $[B + 44]^+$), 123 (18, $[B + 14]^+$), 224 (15, $[M - 18]^+$), 111 (8, $[B + 2]^+$), 109 (6, B^+), 242 (5, M^+). Periodate consumption, 1.10 mol. (Found: C, 54.41; H, 7.46; N, 11.32. $C_{11}H_{18}N_2O_4$ calc.: C, 54.33; H, 7.49; N, 11.56%).

*3-(α-D-Lyxofuranosyl)-1,4-dimethyl-5-(*p*-tolyl)pyrazole* (**11**). — A solution of 1,4-dimethyl-3-(D-*galacto*-pentitol-1-yl)-5-(*p*-tolyl)pyrazole[2] (**8**; 0.50 g, 1.49 mmol) in trifluoroacetic acid (1.0 mL, 13.0 mmol) was kept at room temperature for 24 h, then worked-up as described for **10**. Column chromatography on Silica Gel 60 (Merck, 63–200 μm) (15:1 dichloromethane–methanol) gave **11** (0.33 g, 69%), m.p. 167–168°, $[\alpha]_D^{25}$ +63° (*c* 1, pyridine); ν_{max}^{KBr} 3350 (OH), 1615 (phenyl), 1510 (pyrazole C=N), 915 cm^{-1} (pyrazole ring bending). For the n.m.r. data, see Tables I and II. Mass spectrum: *m/z* 215 (100%, $[B + 30]^+$), 229 (60, $[B+44]^+$), 199 (43, $[B+14]^+$), 185 (14, B^+), 300 (9, $[M-18]^+$), 187 (7, $[B+2]^+$), 318 (5, M^+). Periodate consumption, 0.94 mol. (Found: C, 63.93; H, 7.00; N, 8.56. $C_{17}H_{22}N_2O_4$ calc.: C, 64.13; H, 6.97; N, 8.80%).

3-(α-D-Lyxofuranosyl- (**12**) *and β-D-lyxofuranosyl)-1-methyl-5-*(p-*tolyl)pyrazole* (**13**). — A solution of 1-methyl-3-(D-*galacto*-pentitol-1-yl)-5-(*p*-tolyl)pyrazole[2] (**9**; 0.50 g, 1.64 mmol) in trifluoroacetic acid (1.0 mL, 13.0 mmol) was kept at room temperature for 24 h, then worked-up as described for **10**. T.l.c. (6:1 dichloromethane–methanol) of the residue revealed products with R_F 0.59 and 0.62, that were isolated by preparative t.l.c. (4:1 dichloromethane–methanol).

Compound **12** (0.205 g, 41%), R_F 0.62, had m.p. 139–140°, $[\alpha]_D^{25}$ +64° (*c* 1, pyridine); ν_{max}^{KBr} 3420, 3280 (OH), 1550 (pyrazole C=N), 1515 (phenyl), 960 cm^{-1} (pyrazole ring bending). For the n.m.r. data, see Tables I and II. Mass spectrum: *m/z* 201 (100%, $[B + 30]^+$), 215 (58, $[B + 44]^+$), 185 (18, $[B + 14]^+$), 286 (14, $[M - 18]^+$), 173 (7, $[B + 2]^+$), 171 (5, B^+), 304 (5, M^+). Periodate consumption, 0.91 mol. (Found: C, 62.97; H, 6.65; N, 9.11. $C_{16}H_{20}N_2O_4$ calc.: C, 63.14; H, 6.62; N, 9.21%).

Compound **13** (0.069 g, 14%), R_F 0.59, was a colourless syrup, $[\alpha]_D^{25}$ +6.7° (*c* 1, pyridine); ν_{max}^{KBr} 3380 (OH), 1610 (phenyl), 1510 (pyrazole C=N), 940 cm^{-1} (pyrazole ring bending). For the n.m.r. data, see Tables I and II. Mass spectrum: *m/z*: 201 (100%, $[B + 30]^+$), 215 (43, $[B + 44]^+$), 185 (31, $[B + 14]^+$), 286 (6, $[M - 18]^+$), 173 (6, $[B + 2]^+$), 304 (4, M^+). Periodate consumption, 1.06 mol. Mass spectrum: *m/z*: 304.1431; calc. for $C_{16}H_{20}N_2O_4$: 304.1424.

*1,4-Dimethyl-5-(*p*-tolyl)-3-(2,3,5-tri-*O*-acetyl-α-D-lyxofuranosyl)pyrazole* (**14**). — Conventional treatment of **11** (0.050 g, 0.16 mmol) with pyridine (0.5 mL) and acetic anhydride (0.5 mL) at 0° for 48 h, with preparative t.l.c. (4:1 ether–hexane) of the product, gave **14** (0.058 g, 83%) as colourless oil, $[\alpha]_D^{25}$ +50° (*c* 1, chloroform); ν_{max} 1745

(ester C=O), 1510 cm^{-1} (pyrazole C=N). For the n.m.r. data, see Tables I and II. Mass spectrum: *m/z* 444.1952 (calc. for $C_{23}H_{28}N_2O_7$: 444.1897), 265 (100%, [M − 2 HOAc − OAc]$^+$), 215 (29, [B + 30]$^+$), 325 (16, [M − HOAc − OAc]$^+$).

3-(2,3-O-Isopropylidene-α-D-lyxofuranosyl)-1,4-dimethyl-5-(p-tolyl)pyrazole (**15**). — A mixture of **11** (0.050 g, 0.16 mmol), acetone (7 mL), and *p*-toluenesulphonic acid monohydrate (0.070 g) was kept at room temperature for 24 h. T.l.c. showed that **11** had reacted completely. The mixture was poured into aqueous sodium hydrogen carbonate (75 mL) at 0°, most of the acetone was allowed to evaporate, and the crystalline product was collected, washed thoroughly with water, and recrystallised from methanol to give **15** (0.054 g, 96%), m.p. 108–109°, $[\alpha]_D^{25}$ +25° (*c* 1, chloroform); ν_{max}^{KBr} 3330 (OH), 1620 (phenyl), 1515 (pyrazole C=N), 930 cm^{-1} (pyrazole ring bending). For the n.m.r. data, see Tables I and II. Mass spectrum: *m/z* 215 (100%, [B + 30]$^+$), 185 (31, B$^+$), 199 (27, [B + 14]$^+$), 340 (7, [M − 18]$^+$), 358 (3, M$^+$) (Found: C, 67.06; H, 7.30; N, 7.35. $C_{20}H_{26}N_2O_4$ calc.: C, 67.02; H, 7.31; N, 7.82%).

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