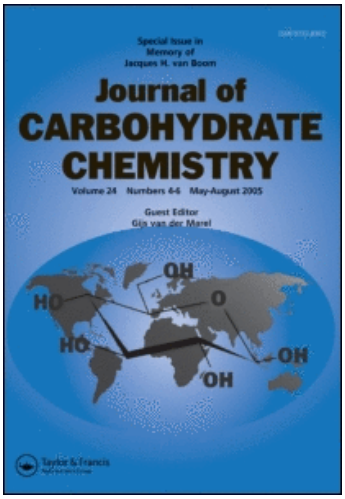

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SYNTHESIS AND PROPERTIES OF 1-(3,4-DI-*O*-ACETYL-2-DEOXY-2-HYDROXYIMINO-D-*THREO*-PENTOPYRANOSYL)PYRAZOLES†

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ABSTRACT

3,4-Di-*O*-acetyl-2-deoxy-2-nitroso-α-D-*xylo*-pentopyranosyl chloride (**2**) reacts with pyrazole to afford 1-[3,4-di-*O*-acetyl-2-deoxy-2-(*Z*)-hydroxyimino-α- (**3**) and β-D-*threo*-pentopyranosyl]pyrazole (**4**). The products of condensation were modified at C-2 or C-3 to give pyrazole derivatives with 3-azido-2,3-dideoxy-2-hydroxyimino-pentopyranosyl (**5**,**7**,**8**,**9**,**10**), 2-acetoxyimino-2,3-dideoxy-β-D-*glycero*-pentopyranosyl (**12**,**13**), β-D-*lyxo*- (**14**), β-D-xylopentopyranosyl (**15**) structures and 2,3-dihydro-2-pyrazol-1-yl-6H-pyran-3-one oximes (**6**,**11**). The conformation of the sugar residue and configuration at the anomeric centre and of the hydroxyimino group were established on the basis of ^{1}H NMR and polarimetric data.

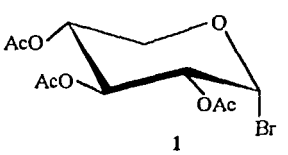
INTRODUCTION

We have reported previously on the reaction products of *O*-acetyl-2-deoxy-2-nitroso-α-D-gluco-,[1] -α-D-galacto-,[2] -β-D-arabinopyranosyl chloride[3] and methyl (3,4-di-*O*-acetyl-2-deoxy-2-nitroso-α-D-glucopyranosyl chloride)uronate[4] with pyrazole. A number of 2-deoxy-2-hydroxyimino *N*-glycosyl pyrazoles modified at C-2 and C-3, have been prepared as model systems for nucleosides.[5,6] In this paper a similar route was followed to prepare *N*-glycosides of pyrazole with 2-deoxy-2-hydroxyimino-D-*threo* structure, also modified at C-2 and C-3.

† This paper is dedicated to the memory of Professor R. U. Lemieux.

RESULTS AND DISCUSSION

Condensation of 3,4-di-*O*-acetyl-2-deoxy-2-nitroso-α-D-xylopyranosyl chloride (**2**) with 2 equiv of pyrazole in acetonitrile for 48 h at room temperature gave 1-[3,4-di-*O*-acetyl-2-deoxy-2-(*Z*)-hydroxyimino-α-D- (**3**) and β-D-*threo*-pentopyranosyl)pyrazole (**4**) in ~70% combined yield and in the ratio ~1:1.



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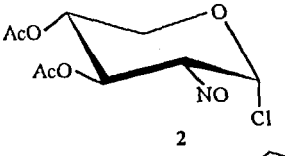

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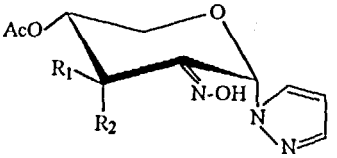
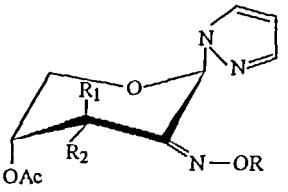
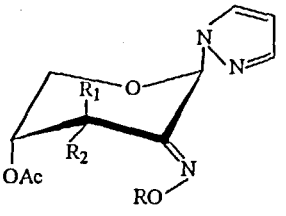


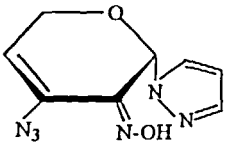
3 $R_1 = OAc$, $R_2 = H$
5 $R_1 = N_3$, $R_2 = H$
7 $R_1 = H$, $R_2 = N_3$



4 $R = H$, $R_1 = OAc$, $R_2 = H$
8 $R = H$, $R_1 = H$, $R_2 = N_3$
9 $R = H$, $R_1 = N_3$, $R_2 = H$
12 $R = Ac$, $R_1 = R_2 = H$



10 $R = H$, $R_1 = N_3$, $R_2 = H$
13 $R = Ac$, $R_1 = R_2 = H$



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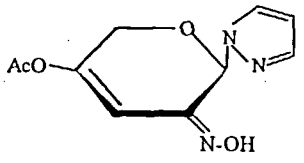

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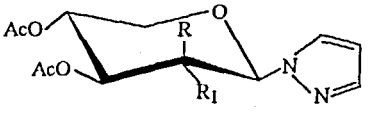


14 $R = OAc$, $R_1 = H$
15 $R = H$, $R_1 = OAc$

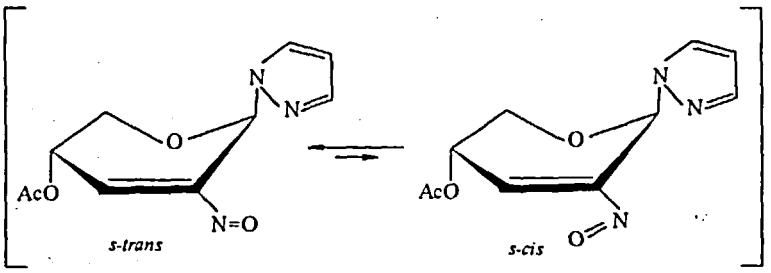
The α-D-*threo*-$^4C_1$ and β-D-*threo*-$^1C_4$ structures, respectively, of **3** and **4** in solution were established as follows. The H-1 chemical shifts of **3** and **4** (both at δ 6.85) indicate that both are equatorial protons. Lack of difference in their chemical shifts can be attributed to different conformations of the sugar ring. For the same conformation but

different spatial orientation of the aglycon, a difference of ~ 0.55 ppm would be expected.[7] The $^3J_{H,H}$ values indicate that both H-3 and H-4 are axial in **3** ($J_{3,4}$ = 10 Hz), and equatorial in **4** ($J_{3,4}$ = 2.5 Hz). It is interesting to note that, despite its axial orientation, H-3 in **3** is much more deshielded ($\Delta\delta$ 0.7 ppm) than equatorial H-3 in **4**. This is due to the effect of the axial substituent at C-1. As was previously reported, β anomers of 2-deoxy-2-hydroxyimino glycosides in the $^4C_1$ conformation are destabilised owing to the strong steric and electrostatic repulsion of the nearly coplanar oriented dipoles of the C_1-aglycon, C_2=N-OH and C_3-OAc bonds.[3,4,8] These unfavourable interactions as well as an anomeric effect caused adoption of the $^1C_4$ form for pentopyranoside **4**. The $[\alpha]_D$ values of **3** (+53°) and **4** (-243°) confirm the α and β configurations, respectively.

The 2-deoxy-2-hydroxyimino structures of **3** and **4** were consistent with the splitting of ^{1}H NMR signals for H-1 (s) and H-3 (d), the presence of OH signals (δ 9.60 and 10.70, respectively), and the IR absorptions for OH (3200 cm^{-1}) and C=N (1660 cm^{-1}) groups. Bearing in mind data concerning the influence of the orientation of the oxime hydroxyl group on chemical shifts in ^{1}H NMR spectra,[9,10] chemical shifts for H-1 and H-3 for **3** (δ 6.85 and 6.30, respectively) and **4** (δ 6.85 and 5.60, respectively) are indicative of the *Z* configuration for the oxime group in both glycosides.

Compounds **3** and **4** were treated with sodium azide in boiling ethanol. Reaction between **3** and NaN_3 afforded **5-7** with overall yield ~65% in the ratio 11.5:1:4. The α-D-*threo*-$^4C_1$ derivative **5** ($J_{3,4}$ = 8, $J_{4,5a}$ = 7 Hz, $J_{5e,4}$ = 2 Hz) was formed by equatorial displacement of the 3-OAc with azide ion, whereas the α-D-*erythro*-$^4C_1$ derivative **7** ($J_{3,4}$ = 3, $J_{4,5a}$ = 7, $J_{5e,4}$ = 2 Hz) was the product of axial substitution. Compound **6** was identified as (2*S*)-4-azido-2,3-dihydro-2-pyrazol-1-yl-6*H*-pyran-3-one oxime, formed probably from **7** *via trans*-elimination of 4-OAc and H-3. A comparison of the H-1 chemical shifts value of starting **3** (δ 6.85) with those of products **5** (δ 6.85), **6** (δ 7.0) and **7** (δ 6.75) implied that the 2-hydroxyimino group has a *Z* configuration in **5-7**.

Reaction of **4** with NaN_3 gave **8-11** with 50% overall yield, in the ratio 7:2:1:2.5. The β-D-*erythro*-$^1C_4$ product **8** ($J_{3,4}$ = 4, $J_{4,5}$ = 3.5 Hz) has an equatorial azido group at C-3, whereas the β-D-*threo*-$^1C_4$ derivatives **9** ($J_{3,4}$ = 2, $J_{5e,4}$ = 1, $J_{4,5a}$ = 3 Hz) and **10** ($J_{3,4}$ = 2, $J_{5e,4}$ = 1, $J_{4,5a}$ = 2 Hz) have an axial azido group at C-3. Compound **11** was identified as (2*R*)-5-acetoxy-2,3-dihydro-2-pyrazol-1-yl-6*H*-pyran-3-one oxime, formed probably



Scheme

from 1-(4-*O*-acetyl-2,3-dideoxy-2-nitroso-β-D-*glycero*-pent-2-enopyranosyl)pyrazole (Scheme), the intermediate product of reaction of **4** with NaN_3 as suggested elsewhere.[11,12,13] Nucleophilic addition of azide ion to this intermediate resulted in formation of **8-10**. However, azide ion may also behave as a base and abstract the proton at C-4 to afford **11**.[11] Taking into account the δ values of the H-1 and H-3 signals in **8** (δ 6.95, 4.90, respectively), **9** (δ 6.80, 4.45, respectively), **10** (δ 6.30, 5.40, respectively) and of H-1 in **11** (δ 7.00), we postulate that the oxime group has the *Z* configuration in **8**,**9**,**11** and *E* configuration in **10**.

Treatment of **4** with sodium borohydride in *N*,*N*-dimethylformamide at ambient temperature followed by acetylation resulted in **12** and **13** with 50% overall yield in the ratio 1:1. The vicinal coupling constant $J_{3a,4}$ = 4 Hz calls for a $^1C_4$ conformation for **12** and **13**. Chemical shifts values of H-1, H-3_a and H-3_e indicate that compound **12** (δ 6.75, 3.40, 2.95, respectively) is the *Z* isomer, and **13** (δ 6.60, 3.85, respectively) is the *E* isomer. This conclusion is supported by the fact that there is no difference in the optical rotation for **12** and **13**. Again, the axial H-3 proton in **12** is much more deshielded (Δδ 0.45 ppm) than the equatorial H-3 owing to the influence of the 1,3-diaxial oriented aglycone and axial 4-OAc group. In the case of **13** both H-3 protons resonate at lower field than H-3 in **12** in accord with the *E* configuration of the oxime.

Compound **4** was modified at C-2 *via* the reaction sequence: >C=N-OH → >C=O → >CH-OH → >CH-OAc. The deoximation of the hydroxyimino group in **4** was accomplished with acetaldehyde in the presence of hydrochloric acid.[14] The resulting ketone was reduced with sodium borohydride[15] and then acetylated to afford **14** and **15** in

a 2:1 ratio and 30% overall yield. The coupling constants values indicate β-D-lyxo-$^4C_1$ ($J_{1,2}$ = 4, $J_{5a,4}$ = 9, $J_{5e,4}$ = 4 Hz) and β-D-xylo-$^4C_1$ ($J_{1,2}$ = $J_{5a,4}$ = 10, $J_{5e,4}$ = 5 Hz) structures of **14** and **15**, respectively. It is noteworthy that from starting **4** conversion of the 2-deoxy-2-hydroxyimino group into 2-OAc gave β glycosides **14** and **15** with a $^4C_1$ rather than $^1C_4$ conformation. The structure of **15** was additionally confirmed by synthesis. Compound **15** was independently prepared by reaction of 2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl bromide (**1**) with pyrazole according to the Koenigs-Knorr method.

EXPERIMENTAL

General methods. Melting points were uncorrected. Optical rotations were recorded using a Hilger-Watt polarimeter for solutions in $CHCl_3$ at 20 °C. TLC was run on the Merck Kieselgel 60 F-254 plates with: A, CCl_4-acetone (3:1); B, CCl_4-acetone (4:1); C, $CHCl_3$-Et_2O (3:1). Column chromatography was performed on MN Kieselgel 60 (< 0.08 mm). The ^1H NMR spectra ($CDCl_3$, internal Me_4Si) were recorded with a Varian XL-100 (100 MHz) instrument. The IR spectra were determined as Nujol mulls with a Bruker IFS 66 spectrophotometer. Field desorption mass spectra (FD-MS) were conducted using a Varian Mat 711 mass spectrometer.

2,3,4-Tri-*O*-acetyl-α-D-xylopyranosyl Bromide (1). Prepared according to the literature procedure: mp 98-101 °C; lit.[16] mp 100-102 °C.

Dimeric 3,4-Di-*O*-acetyl-2-deoxy-2-nitroso-α-D-xylopyranosyl Chloride (2). Prepared according to the literature procedure: $[\alpha]_D$ + 152° (*c* 0.41); lit.[17] $[\alpha]_D^{23}$ + 164° (*c* 3, $CHCl_3$). The structure and purity of **2** were confirmed from ^1H NMR data.

1-[3,4-Di-*O*-acetyl-2-deoxy-2-(*Z*)-hydroxyimino-α- (3) and -β-D-*threo*-pentopyranosyl]pyrazole (4). A solution of **2** (1.5 g, 5.6 mmol) and pyrazole (0.75 g, 11 mmol) in acetonitrile (15 mL) was stirred for 3 h at ~20 °C until the starting chloride **2** disappeared (TLC, solvent A). The solution was then concentrated, diluted with $CHCl_3$ (100 mL), washed with water (3 x 20 mL), and dried (Na_2SO_4). Concentration *in vacuo* gave a syrup which was chromatographed (solvent A) to afford, first **3** (31%, syrup): $[\alpha]_D$ + 53° (*c* 0.57); R_F = 0.47 (solvent A); IR ν 3200 (OH), 1745 (C=O), 1660 (C=N), 1300 (C-N), 1240 and 1100 (C-O) cm^{-1}; ^1H NMR δ 2.00, 2.05 (2s, 6H, 2AcO), 3.65 (t, 1H, $J_{5a,5e}$ = 11 Hz, H-5_a), 3.85 (dd, 1H, $J_{5e,4}$ = 5.5 Hz, H-5_e), 5.20 (m, 1H, $J_{4,5a}$ = 10 Hz,

H-4), 6.30 (d, 1H, $J_{3,4}$ = 10 Hz, H-3), 6.85 (s, 1H, H-1), 6.30, 7.60 (2m, 3H, pyrazole), 9.60 (bs, 1H, OH); FD-MS: *m/z* 298 $(M+1)^+$.

Eluted second was **4** (39%): mp 131-133 °C (crystallization from CCl_4 – acetone); $[\alpha]_D$ - 243° (*c* 0.53); R_F = 0.34 (solvent A); IR ν 3200 (OH), 1745 (C=O), 1660 (C=N), 1300 (C-N), 1245 and 1100 (C-O) cm^{-1}; ^1H NMR δ 2.00, 2.10 (2s, 6H, 2AcO), 3.75 (dd, 1H, $J_{5e,4}$ = 2.5 Hz, H-5_e), 4.00 (dd, 1H, $J_{5a,5e}$ = 14 Hz, H-5_a), 4.90 (m, 1H, $J_{4,5a}$ = 4 Hz, H-4), 5.60 (d, 1H, $J_{3,4}$ = 3 Hz, H-3), 6.85 (s, 1H, H-1), 6.30, 7.60 (2m, 3H, pyrazole), 10.80 (s, 1H, OH); FD-MS: *m/z* 297 $(M)^+$.

1-[4-*O*-Acetyl-3-azido-2,3-dideoxy-2-(*Z*)-hydroxyimino-α-D-*threo*- (5), -α-D-*erythro*-pentopyranosyl]pyrazole (7), and (2*S*)-4-Azido-2,3-dihydro-2-pyrazol-1-yl-6*H*-pyran-3-one oxime (6). A suspension of NaN_3 (0.416 g, 6.4 mmol) in a solution of **3** (0.476 g, 1.6 mmol) in EtOH (80 mL) was stirred and refluxed. TLC (solvent A) after 2 h showed complete conversion of **3** into three products. The solution was filtered and concentrated, and the residue was extracted with ether. The extract was filtered, diluted with CH_2Cl_2 (300 mL), washed with water (3 x 50 mL), dried (Na_2SO_4), and concentrated. Column chromatography of the resulting syrup (solvent B) gave first, **5** (46%, syrup): $[\alpha]_D$ +60° (*c* 0.56); R_F = 0.76 (solvent A); IR ν 3200 (OH), 2100 (N_3), 1740 (C=O), 1660 (C=N), 1245 (C-O) cm^{-1}; ^1H NMR δ 2.05 (s, 3H, AcO), 3.40-3.90 (m, 2H, $J_{5e,4}$ = 2 Hz, 2H-5), 5.05 (m, 2H, $J_{3,4}$ = 8, $J_{4,5a}$ = 7 Hz, H-3, H-4), 6.85 (s, 1H, H-1), 6.35, 7.60 (m, 2H, pyrazole), 9.8 (bs, 1H, OH); FD-MS: *m/z* 281 $(M+1)^+$.

Eluted second was **6** (4%, syrup): $[\alpha]_D$ +153° (*c* 0.5); R_F = 0.70 (solvent A); IR ν 3250 (OH), 2110 (N_3), 1640 (C=N) cm^{-1}; ^1H NMR δ 4.25 (d, 2H, 2H-5), 5.90 (t, 1H, $J_{4,5}$ = 4 Hz, H-4), 7.00 (s, 1H, H-1), 6.40, 7.70 (2m, 3H, pyrazole); FD-MS: *m/z* 220 $(M)^+$.

Eluted third was **7** (15%, syrup): $[\alpha]_D$ +168° (*c* 0.56); R_F = 0.62 (solvent A); IR ν 3100 (OH), 2110 (N_3), 1745 (C=O), 1660 (C=N), 1250 (C-O) cm^{-1}; ^1H NMR δ 2.05 (s, 3H, AcO), 3.70 (dd, 1H, $J_{5a,5e}$ = 8 Hz, H-5_a), 4.00 (m, 1H, $J_{5e,4}$ = 2 Hz, H-5_e), 4.85 (m, 1H, $J_{4,5a}$ = 7 Hz, H-4), 5.40 (d, 1H, $J_{3,4}$ = 3 Hz, H-3), 6.75 (s, 1H, H-1), 6.30, 7.65 (2m, 3H, pyrazole); FD-MS: *m/z* 281 $(M+1)^+$.

1-[4-*O*-Acetyl-3-azido-2,3-dideoxy-2-(*Z*)-hydroxyimino-β-D-*erythro*- (8), -β-D-*threo*- (9), -2-(*E*)-hydroxyimino-β-D-*threo*-pentopyranosyl]pyrazole (10), and (2*R*)-5-Acetoxy-2,3-dihydro-2-pyrazol-1-yl-6*H*-pyran-3-one oxime (11). A solution of **4** (0.402 g, 1.35 mmol) in EtOH (70 mL) was stirred and refluxed with NaN_3 (0.351 g, 5.4

mmol). TLC (solvent A) after 2 h showed complete conversion of **4** into several products. The solution was filtered and concentrated, and the residue was treated with ethyl ether. The suspension was filtered again, diluted with CH_2Cl_2 (300 mL), washed with water (3 x 50 mL), dried (Na_2SO_4), and concentrated. Column chromatography of the crude residue (solvent B) gave, first, **8** (29%, syrup): $[\alpha]_D$ -154° (*c* 0.47); R_F = 0.46 (solvent B); IR ν 3200 (OH), 2095 (N_3), 1735 (C=O), 1660 (C=N), 1240 (C-O) cm^{-1}; ^1H NMR δ 2.10 (s, 3H, AcO), 3.90 (d, 2H, 2H-5), 4.90 (d, 1H, $J_{3,4}$ = 4 Hz, H-3), 5.30 (t, 1H, $J_{4,5}$ = 3.5 Hz, H-4), 6.95 (s, 1H, H-1), 6.30, 7.50, 7.60 (3m, 3H, pyrazole), 9.8 (bs, 1H, OH); FD-MS: *m/z* 281 $(M+1)^+$.

Eluted second was **9** (7%, syrup): $[\alpha]_D$ -226° (*c* 0.33); R_F = 0.32 (solvent B); IR ν 3100 (OH), 2090 (N_3), 1735 (C=O), 1640 (C=N), 1240 (C-O) cm^{-1}; ^1H NMR δ 2.10 (s, 3H, AcO), 3.65 (dd, 1H, $J_{5a,5e}$ = 12 Hz, H-5_a), 4.05 (dd, 1H, $J_{5e,4}$ = 1 Hz, H-5_e), 4.45 (d, 1H, $J_{3,4}$ = 2 Hz, H-3), 4.80 (m, 1H, $J_{4,5a}$ = 3 Hz, H-4), 6.80 (s, 1H, H-1), 6.30, 7.60 (2m, 3H, pyrazole); FD-MS: *m/z* 281 $(M+1)^+$.

Eluted third was **10** (4%, syrup): R_F = 0.26 (solvent B); IR ν 3100 (OH), 2080 (N_3), 1735 (C=O), 1650 (C=N), 1240 (C-O) cm^{-1}; ^1H NMR δ 2.10 (s, 3H, AcO), 3.95 (d, 2H, $J_{5e,4}$ = 1 Hz, 2H-5), 4.85 (m, 1H, $J_{4,5a}$ = 2 Hz, H-4), 5.40 (d, 1H, $J_{3,4}$ = 2 Hz, H-3), 6.30 (s, 1H, H-1), 6.45, 7.50, 7.75 (3m, 3H, pyrazole); FD-MS: *m/z* 281 $(M+1)^+$.

Eluted fourth was **11** (10%, syrup): $[\alpha]_D$ -114° (*c* 0.5); R_F = 0.21 (solvent B); IR ν 3100 (OH), 1730 (C=O), 1640 cm^{-1} (C=N), 1240 (C-O) cm^{-1}; ^1H NMR δ 2.10 (s, 3H, AcO), 3.90 (d, 2H, 2H-5), 4.95 (s, 1H, H-4), 7.00 (s, 1H, H-1), 6.30, 7.60, 7.85 (3m, 3H, pyrazole).

1-[(*Z*)- (12) and -(*E*)-2-Acetoxyimino-4-*O*-acetyl-2,3-dideoxy-β-D-*glycero*-pentopyranosyl]pyrazole (13). A solution of **4** (0.3 g, 1.01 mmol) in DMF (5 mL) was stirred with $NaBH_4$ for 18 h at room temperature until the starting **4** disappeared (TLC, solvent A). The excess of borohydride was destroyed with methanol, the solution was concentrated, and the residue was acetylated conventionally with Ac_2O-pyridine. Column chromatography (solvent A) of the crude product gave, first, **12** (23%, syrup): $[\alpha]_D$ -72° (*c* 0.48); R_F = 0.59 (solvent A); IR ν 1740 (C=O), 1660 cm^{-1} (C=N), 1245 (C-O) cm^{-1}; ^1H NMR δ 2.05, 2.10 (2s, 6H, 2AcO), 2.95 (dd, 1H, $J_{3e,4}$ = 2 Hz, H-3_e), 3.40 (dd, 1H, $J_{3a,4}$ = 4 Hz, H-3_a), 3.75 (m, 2H, 2H-5), 5,15 (m, 1H, H-4), 6.75 (s, 1H, H-1), 6.35, 7.60 (2m, 3H, pyrazole). FD-MS: *m/z* 239 $(M+1\text{-}Ac)^+$, 223 $(M+1\text{-}OAc)^+$.

Eluted second was **13** (27%, syrup): $[\alpha]_D$ -72° (*c* 0.43); R_F = 0.48 (solvent A); IR ν 1740 (C=O), 1650 cm^{-1} (C=N), 1250 (C-O) cm^{-1}; ^1H NMR δ 2.00, 2.05 (2s, 6H, 2AcO), 3.85 (m, 2H, 2H-3), 4.20 (m, 2H, 2H-5), 5,10 (m, 1H, H-4), 6.60 (s, 1H, H-1), 6.30, 7.55 (2m, 3H, pyrazole). FD-MS: *m/z* 280 $(M-1)^+$.

1-(2,3,4-Tri-*O*-acetyl-β-D-*lyxo*- (14) and -β-D-*xylo*-pentopyranosyl)pyrazole (15). a) A solution of **4** (0.366 g, 1.23 mmol), acetaldehyde (0.158 g, 3.6 mmol), and 1 M HCl (1.2 mL) in acetonitrile (7 mL) was stirred for 17 days at room temperature until the starting **4** disappeared (TLC, solvent A). Then the mixture was cooled to 0 °C and $NaBH_4$ (0.234 g, 6.2 mmol) was added in small portions. The resulting solution was stirred for 3 h, cooled to 0 °C, neutralised with CH_3COOH, and concentrated. The residue was treated conventionally with Ac_2O-pyridine. Column chromatography (solvent A) of the crude product gave, first, **14** (19%, syrup): $[\alpha]_D$ -26° (*c* 0.56); R_F = 0.51 (solvent A); IR ν 1745 (C=O), 1240 (C-O) cm^{-1}; ^1H NMR δ 1,85, 2.00 (2s, 9H, 3AcO), 3.50 (dd, 1H, $J_{5a,5e}$ = 11, $J_{5a,4}$ = 9 Hz, H-5_a), 4.20 (dd, 1H, $J_{5e,4}$ = 4 Hz, H-5_e), 5.20-5.80 (m, 3H, H-2, H-3, H-4), 5.70 (d, 1H, $J_{1,2}$ = 4 Hz, H-1), 6.25, 7.55 (2m, 3H, pyrazole); FD-MS: *m/z* 326 $(M)^+$.

Eluted second was **15** (10%, syrup): $[\alpha]_D$ -28° (*c* 0.46); R_F = 0.43 (solvent A); IR ν 1750 (C=O), 1250 (C-O) cm^{-1}; ^1H NMR δ 1,90, 2.05 (2s, 9H, 3AcO), 3.55 (dd, 1H, $J_{5a,5e}$ = 12, $J_{5a,4}$ = 10 Hz, H-5_a), 4.30 (dd, 1H, $J_{5e,4}$ = 5 Hz, H-5_e), 5.10-5.60 (m, 3H, H-2, H-3, H-4), 5.50 (d, 1H, $J_{1,2}$ = 10 Hz, H-1), 6.35, 7.65 (2m, 3H, pyrazole); FD-MS: *m/z* 327 $(M+1)^+$.

b) A mixture of **1** (1.017 g, 3 mmol), pyrazole (0.224 g, 3.3 mmol) and $Hg(CN)_2$ (0.757 g, 3 mmol) in benzene (17 mL) and nitromethane (17 mL) was stirred for 24 h at room temperature until the starting **1** disappeared (TLC, solvent A). Then the mixture was concentrated, diluted with $CHCl_3$ (200 mL), filtered, washed with a 30% solution of KI (3 x 50 mL), and water (50 mL), dried ($MgSO_4$) and concentrated again. Column chromatography of the crude residue (solvent C) gave **15** (32%): mp 134-135 °C (crystallisation from CCl_4 – acetone); $[\alpha]_D$ - 27° (*c* 0.52); R_F = 0.38 (solvent C), 0.43 (solvent A).

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