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THE STRUCTURE AND PROPERTIES OF THE PRODUCTS OF REACTION BETWEEN 3,4,6-TRI-*O*-ACETYL-2-DEOXY-2-NITROSO-α-D-GLUCOPYRANOSYL CHLORIDE AND PYRAZOLE

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ABSTRACT

Dimeric 3,4,6-tri-*O*-acetyl-2-deoxy-2-nitroso-α-D-glucopyranosyl chloride reacts with pyrazole in acetonitrile to give 1-(3,4,6-tri-*O*-acetyl-2-deoxy-2-hydroxyimino-D-hexopyranosyl)pyrazoles. The reaction is not stereospecific and the products have the α- and β-D-*arabino* and α- and β-D-*ribo* structures, with the α-D-*arabino* and β-D-*ribo* isomers being the major products. 1-(3,4,6-Tri-*O*-acetyl-2-deoxy-2-hydroxyimino-α-D-*arabino*- and -β-D-*ribo*-hexopyranosyl)pyrazoles have been modified at C-2 and C-3 to afford the following derivatives: 1-(α-D-gluco-, α-D-manno-, 2-acetamido-2-deoxy-α-D-gluco-, and 2-acetamido-2-deoxy-β-D-altropyranosyl)pyrazole, 1-(3-azido-2,3-dideoxy-2-hydroxyimino-α- and -β-D-*arabino*-, and -α- and -β-D-*ribo*-hexopyranosyl)pyrazole, as well as (*Z*)- and (*E*)-1-(2,3-dideoxy-2-hydroxyimino-α-D-*glycero*-hexopyranosyl)pyrazoles.

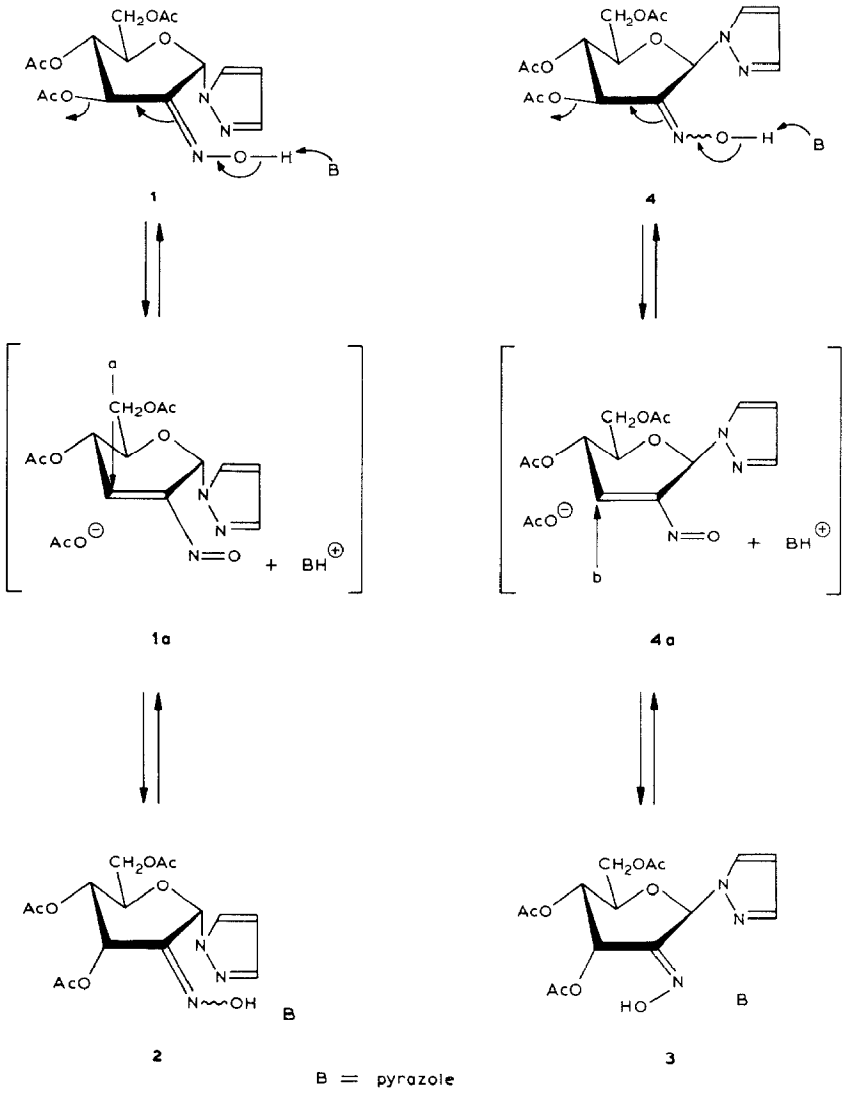
INTRODUCTION

The reaction of 3,4,6-tri-*O*-acetyl-2-deoxy-2-nitroso-α-D-hexopyranosyl chlorides with alcohols and phenols gives the corresponding 3,4,6-tri-*O*-acetyl-2-deoxy-2-hydroxyimino-α-D-hexopyranosides[1,2]. The stereospecificity of the reaction is extremely high even with hindered alcohols[2,3]. The hydroxyimino-α-D-hexopyranosides have been used for the syntheses of glycosides[4] and 2-amino-2-deoxy-α-D-glycosides[5].

We now report an application of this method for the synthesis of *N*-glycosyl derivatives, specifically the reaction of 3,4,6-tri-*O*-acetyl-2-deoxy-2-nitroso-α-D-glucopyranosyl chloride with pyrazole, as a model system for nucleosides.

RESULTS AND DISCUSSION

3,4,6-Tri-*O*-acetyl-2-deoxy-2-nitroso-α-D-glucopyranosyl chloride reacted smoothly with pyrazole in acetonitrile at elevated or ambient temperature to afford 1-[3,4,6-tri-*O*-acetyl-2-deoxy-2-hydroxyimino-α-D-*arabino*- (**1**, 48%), -β-D-*arabino*- (**4**, 4%), -α-D-*ribo*- (**2**, 6%), and -β-D-*ribo*-hexopyranosyl]pyrazole (**3**,



25%). This result was quite different from those of the reactions of the chloride with alcohols and phenols in *N,N*-dimethylformamide, where only the α-D-*arabino* product formed.

The much lower stereospecificity of the *N*-glycosylation reaction, as compared with *O*-glycosylation, may be due to a weaker influence of the anomeric effect. The formation of the products (**2** and **3**) with altered configuration at C-3 may be explained in terms of the findings of Lemieux and co-workers on the properties of AcO-3 in ethyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-hydroxyimino-α-D-*arabino*-hexopyranoside[6], and the reports by Overend and co-workers on the formation and properties of arylazoenopyranosides[7]. Thus, **1** and **4**, the initial prod-

ucts of the reaction of the chloride with pyrazole, rearrange (1,4-elimination) into 2-nitroso-2,3-unsaturated *N*-glycosyl derivatives (**1a** and **4a**) in the presence of pyrazole. Under the reaction conditions, acetate ion, which is a stronger nucleophile than pyrazole, is again added to C-3. With **1a**, for steric reasons, the nucleophile approaches C-3 preferably from the side *trans* to the aglycon (direction a) to form mostly **1** (D-*arabino* structure) and, to a smaller extent, **2** (D-*ribo* isomer). For **4a**, axial addition (along direction b) is more favourable and likewise *trans* to the aglycon residue, this being the reason why the equilibrium of the transformation **4⇄4a⇄3** is shifted toward 3 (*β*-D-*ribo* isomer).

The transformation **4→3** may also be influenced by the configuration of the hydroxyimino group. Studies of *α*-halocyclohexanones[8–10] and oxo sugars[11] have shown that there is a strong electrostatic repulsion between the C=O dipole and the vicinal equatorial substituent. A similar situation probably exists with **4**. If so, then both the *Z* and the *E* configurations of the hydroxyimino group are unfavourable, owing to strong interactions of the dipoles of the almost coplanar-oriented bulky substituents at C-3, C-2, and C-1. The C-3/C-2 interaction is absent from **3** and this is the additional factor affecting the transformation **4→3**. Bearing these interactions in mind, it can be assumed that the hydroxyimino group in **3**, as well as in other *β*-D-*ribo* compounds (**17, 18**), has the *E* configuration.

As has been pointed out[4], the 2-deoxy-2-hydroxyimino derivatives of *α*-D-hexopyranosides exist as the *Z* isomers. Accordingly, it is assumed that 2-deoxy-2-hydroxyimino-*α*-D-hexopyranosylpyrazoles described here possess the same configuration.

The structures of **1–4** are based on ^{1}H-n.m.r. data (Table I). The values of the chemical shifts for the signals of H-1 for **1** and **2** (δ 6.90) as compared with those of H-1 for **3** and **4** (δ 6.50) are due to the equatorial and axial orientation, respectively, of H-1, and the $J_{3,4}$ values for **1** and **4** (9 Hz) and for **2** and **3** (3 Hz) reflect the D-*arabino* and D-*ribo* configurations, respectively. Also, the $[\alpha]_D$ values of **1** and **2** (+80° and +40°, respectively) as well as of **3** and **4** (−6° and +4°, respectively) support *α* and *β* configurations.

The structures of **1** and **3** were also confirmed by carrying out the transformations of =C=N-OH into -NHAc or ⩾C-OAc. Analogous transformations with **2** and **4** could not be carried out due to the small amounts of the compounds available. Hydrogenation of **1** over Pd/C and *N*-acetylation of the product gave **5** having an *α*-D-*gluco* configuration ($J_{1,2}$ ~3, $J_{2,3} = J_{3,4}$ = 9 Hz). The reaction was slow and stereospecific. Deoximation of **1** with acetaldehyde, followed by borohydride reduction of the resulting uloside and acetylation, afforded two 1-(2,3,4,6-tetra-*O*-acetyl-*α*-D-glucopyranosyl)pyrazoles, namely the D-*gluco* isomer (**6**, $J_{1,2}$ ~3, $J_{2,3} = J_{3,4}$ = 9 Hz) and the D-*manno* isomer (**7**, $J_{1,2} \approx J_{2,3} \approx 3$, $J_{3,4}$ ~9 Hz), in the ratio of 5:1. Both the high stereospecificity of the borohydride reduction of the 2-C=O moiety and the preponderance of the D-*gluco* isomer can be explained in terms of findings on the reduction of hexopyranosid-2-uloses[11–14].

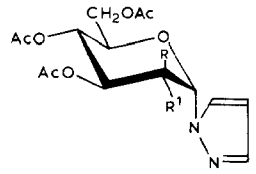
An additional proof in favour of the structure of **6** was obtained by its syn-

TABLE I

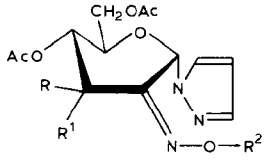
^{1}H-NMR DATA[a] FOR **1–18**

Compound	*H-1*	*H-2*	*H-3*	*H-4*	*H-5*	*H-6*	*N-H*	*Ac*	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$
1	6.87s	—	6.27d	5.25dd	3.90m	4.10m	—	1.90, 9H	—	—	9.0	9.0
2	6.90s	—	5.25d	5.05dd	3.97–4.30m		—	1.87, 9H	—	—	3.0	9.0
3	6.55s	—	5.47d	5.10dd	3.70m	4.10m	—	2.02, 3H 1.97, 3H 1.90, 3H	—	—	2.5	8.5
4	6.47s	—	5.97d	5.07dd	3.75–4.40m		—	2.10, 3H 2.00, 3H 1.90, 3H	—	—	8.5	9.0
5	5.82d	6.05dd	5.18dd	5.12dd				1.93, 12H	3.0	9.0	9.0	9.0
6	6.06d	5.15dd	6.37dd	5.10dd	4.38m	4.00m	—	1.95, 12H	4.0	10.0	10.0	10.0
7	5.70d	5.75	6.07dd	5.25dd	3.77–4.25m		—	2.05, 3H 1.90, 3H 1.87, 3H 1.85, 3H	2.5	2.5	10.0	10.0
9	6.87s	—	5.07d	5.00dd	3.70–4.12m			2.00, 3H 1.87, 3H	—	—	9.0	9.0
10	6.87s	—	—	5.67d	4.35m	4.07m	—	1.87, 3H	—	—	—	2.5
11	6.70s	—	4.82d	4.95dd	3.85–4.20m		—	1.97, 3H	—	—	3.0	9.0
12	6.80s	—	5.85dd	5.13dd	3.85–4.30m		6.50d	2.01, 3H 1.90, 6H 1.87, 3H	—	—	9.0	9.0
13	6.75s	—	5.50dd	5.07dd			8.50d	1.95, 6H 1.90, 6H	—	—	3.0	9.0
14	6.65s	—	3.18m[b]	5.02m	3.87m	4.05m	—	1.97, 3H 1.95, 3H 1.92, 3H	—	—	3.0[c] 9.0[d]	9.0
15	6.77s	—	3.08m[b]	5.00m	3.82m	4.00m	—	1.90, 9H	—	—	3.0[c] 9.0[d]	9.0
16	5.58d	5.02dd	5.17dd	5.12dd	3.88m	4.15m	6.50d	1.96, 6H 1.90, 3H 1.84, 3H	1.5	2.0	3.0	9.0
17	6.67s	—	4.82d	5.72dd	3.87–4.37m			2.07, 3H 1.94, 3H	—	—	3.0	9.0
18	6.65s	—	4.35d	5.12dd	3.75–4.25m			2.01, 3H 1.95, 3H	—	—	9.0	9.0

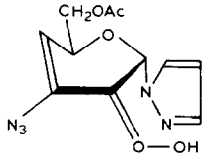
[a]Chemical shifts (δ scale); coupling constants (Hz, ±0.5 Hz) were determined by first-order analysis. [b]H-3*e* and H-3*a*. [c]$J_{3e,4}$. [d]$J_{3a,4}$.



5 R = H, R^1 = NHAc
6 R = H, R^1 = OAc
7 R = OAc, R^1 = H



9 R = N_3, R^1 = H, R^2 = H
11 R = H, R^1 = N_3, R^2 = H
12 R = NHAc, R^1 = H, R^2 = Ac
13 R = H, R^1 = NHAc, R^2 = Ac



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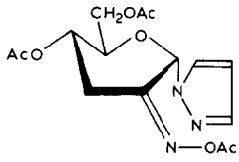

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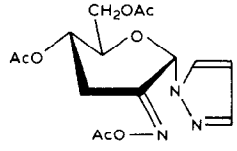

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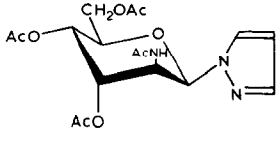

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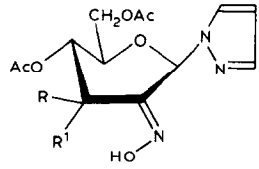

17 R = H, R^1 = N_3
18 R = N_3, R^1 = H

thesis from 3,4,6-tri-*O*-acetyl-β-D-glucopyranosyl chloride (**8**) and pyrazole under Koenigs–Knorr conditions. The structure of **8** (β configuration and HO-2) ensured the formation of the α-product.

The rate of reduction of the hydroxyimino to the amino group in **3** was much lower than in **1** under similar conditions. The reaction was also stereospecific and gave exclusively 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-altropyranoside (**16**, $J_{1,2} = J_{2,3} \approx J_{3,4} \approx 3$ Hz; $[\alpha]_D$ −18°). This high stereospecificity may be rationalised (assuming close similarity of the C=O and C=NOH groups) on the basis of findings on the influence of stereoelectronic interactions on the course of reduction of glycopyranosiduloses[4,13–16].

The properties of AcO-3 as the leaving group were utilised for obtaining derivatives of **1** and **3** modified at C-3. Thus, heating **1** in ethanol in the presence of sodium azide gave **9–11** in the ratios of 11:1:3.5. Compounds **9** and **11** were the expected equatorial (D-*arabino* isomer; $J_{3,4} \approx J_{4,5} \approx 9$ Hz) and axial (D-*ribo* isomer;

$J_{3,4}$ ~3, $J_{4,5}$ ~9 Hz) products, respectively, of the replacement of AcO-3 by N_3. Compound **10** was 1-(6-*O*-acetyl-3-azido-2,3,4-trideoxy-2-hydroxyimino-α-D-*glycero*-hex-3-enopyranosyl)pyrazole. The formation of **10**, most probably from **11** *via* elimination of AcO-4 and H-3, reflects the relatively high mobility of H-3.

Apart from the oxime moiety, the azido groups in **9** and **11** also could be reduced selectively to amino groups, acetylation of which gave **12** and **13**, respectively. Owing to the different ease of hydrogenation of the azido and hydroxyimino groups, **9** and **11** can be precursors of 3-amino or 2,3-diamino *N*-glycosyl derivatives. In turn, the precursors of 2-amino-2,3-dideoxy or 3-deoxy *N*-glycosyl derivatives can be **14** [isomer *E*; δ 6.65 (H-1), 3.26 (H-3)] and **15** [isomer *Z*; δ 6.80 (H-1), 3.10 (H-3)], which were obtained by the reaction of **1** with sodium borohydride in *N,N*-dimethylformamide at ambient temperature, followed by acetylation; **14** and **15** were formed in the ratio 2:1.

Heating of **3** in ethanol in the presence of sodium azide gave two products of substitution of AcO-3 by N_3, having the D-*ribo* (**17**; $J_{3,4}$ 3 Hz) and D-*arabino* configurations (**18**; $J_{3,4}$ 9 Hz), in the ratio of 3:1. The product of axial substitution preponderated, probably for reasons the same as those specified for the formation of **3**.

EXPERIMENTAL

Melting points are uncorrected. Optical rotations were determined (Hilger–Watt instrument) for solutions in chloroform. T.l.c. was performed on Silica Gel G with *A*, carbon tetrachloride–acetone (3:1); *B*, benzene–di-isopropyl ether (1:4); *C*, benzene–ethyl acetate (5:1); *D*, carbon tetrachloride–acetone (1:1); *E*, carbon tetrachloride–acetone (2:1). Column chromatography was performed on Kieselgel (<0.08 mm). ^{1}H-N.m.r. spectra ($CDCl_3$, internal Me_4Si) were recorded with a Tesla-BS 487C (80 MHz) spectrometer. I.r. spectra were recorded for Nujol mulls with a Perkin–Elmer 257 spectrophotometer. Field desorption mass spectra were recorded on a MAT 711 mass spectrometer.

Dimeric 3,4,6-tri-*O*-acetyl-2-deoxy-2-nitroso-α-D-glucopyranosyl chloride, m.p. 127–128°, $[\alpha]_D^{20}$ +151° (*c* 0.5, chloroform) (lit.[17] m.p. 129–130°, $[\alpha]_D^{20}$ +149°), was prepared according to the literature procedure[17].

*1-(3,4,6-Tri-*O*-acetyl-2-deoxy-2-hydroxyimino-α- and -β-*D*-arabino- and -α- and -β-*D*-ribo-hexopyranosyl)pyrazole* (**1** *and* **4**, *and* **2** *and* **3**). — A solution of dimeric 3,4,6-tri-*O*-acetyl-2-deoxy-2-nitroso-α-D-glucopyranosyl chloride (0.02 mol, 13.48 g) and pyrazole (0.084 mol, 5.48 g) in acetonitrile (250 mL) was boiled under reflux until the starting chloride had reacted (35 min; t.l.c., solvent *A*), and then concentrated. A solution of the residue in chloroform (200 mL) was washed with water (2 × 40 mL), dried (Na_2SO_4), and concentrated, and the residue was crystallized from chloroform–hexane to give **1** (40%), m.p. 133–135°, $[\alpha]_D^{20}$ +80°, R_F (solvent *A*) 0.35; ν_{max} 3300 (OH) and 1760 cm^{-1} (ester CO).

Anal. Calc. for $C_{15}H_{19}N_3O_8$: C, 48.78; H, 5.18; N, 11.38. Found: C, 48.68; H, 5.23; N, 11.25.

The mother liquors were concentrated and the resulting syrupy residue was subjected to column chromatography (solvent *A*) to afford, first, **1** (8%).

Eluted second was **2** (syrup, 4%), $[\alpha]_D^{20}$ +40°, R_F (solvent *A*) 0.25; ν_{max} 3350 (OH) and 1750 cm^{-1} (ester CO).

Anal. Found: C, 48.72; H, 5.28; N, 11.33.

Eluted third was **3** (25%), m.p. 116–119°, $[\alpha]_D^{20}$ −6°, R_F (solvent *A*) 0.15; ν_{max} 3340 (OH) and 1750 cm^{-1} (ester CO).

Anal. Found: C, 48.85; H, 5.26; N, 11.45.

Eluted fourth was **4** (syrup, 6%), $[\alpha]_D^{20}$ +4°, R_F (solvent *A*) 0.10; ν_{max} 3345 (OH) and 1755 cm^{-1} (ester CO). Mass spectrum (f.d.): *m/z* 369 (M^+).

Analogous results were obtained when the reaction was carried out at ~20° for 48 h.

*1-(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-*D*-glucopyranosyl)pyrazole* (**5**). — A solution of **1** (1 mmol, 0.369 g) in ethanol (20 mL) was stirred under hydrogen (1 atm) in the presence of 5% Pd/C (250 mg) for 8 days at ~20°. The catalyst was then removed, the filtrate was concentrated to dryness, and the residue was treated with pyridine–acetic anhydride. The resulting oily product was subjected to column chromatography (solvent *A*) to afford **5** as a syrup (25%), $[\alpha]_D^{22}$ +20°, R_F (solvent *A*) 0.13; ν_{max} 3240 (NH), 1755 (ester CO), and 1670 cm^{-1} (amide CO).

Anal. Calc. for $C_{17}H_{23}N_3O_8$: C, 51.38; H, 5.83; N, 10.57. Found: C, 51.69; H, 5.60; N, 10.89.

*1-(2,3,4,6-Tetra-*O*-acetyl-α-*D*-gluco- and -manno-pyranosyl)pyrazole* (**6** *and* **7**). — (*a*) The solution of **1** (2 mmol, 0.792 g), acetaldehyde (6 mmol), and M hydrochloric acid (2 mL) in acetonitrile (20 mL) was stirred at room temperature for 7 days, then cooled to 0°, and treated with sodium borohydride (0.01 mol, 0.378 g) in small portions. The resulting solution was stirred for 5 h at ~20°, then cooled to 0°, neutralised with acetic acid, and concentrated. The residue was treated with acetic anhydride–pyridine, and the product was subjected to column chromatography (solvent *B*) to give, first, **6** (40%), m.p. 108–110°, $[\alpha]_D^{22}$ +98°, R_F (solvent *B*) 0.48; ν_{max} 1750 cm^{-1} (ester CO).

Anal. Calc. for $C_{17}H_{22}N_2O_9$: C, 51.25; H, 5.57; N, 7.03. Found: C, 51.22; H, 5.68; N, 6.95.

Eluted second was **7** (syrup, ~8%), $[\alpha]_D^{21}$ +42°, R_F (solvent *B*) 0.24; ν_{max} 1755 cm^{-1} (ester CO). Mass spectrum (f.d.): *m/z* 398 (M^+).

(*b*) To a solution of 3,4,6-tri-*O*-acetyl-β-D-glucopyranosyl chloride[18] (**8**; 2 mmol, 0.75 g) and pyrazole (4 mmol, 0.272 g) in acetonitrile (20 mL) was added $Hg(CN)_2$ (0.6 g), and the mixture was boiled under reflux for 4 h. T.l.c. (solvent *A*) then showed complete conversion of **8** into one major product. The mixture was filtered, treated with ether, filtered, diluted with chloroform (150 mL), washed with water, dried ($MgSO_4$), and concentrated. Conventional treatment of the residue with acetic anhydride–pyridine and crystallisation of the crude product from ether afforded **6** (55%).

*1-(4,6-Di-*O*-acetyl-3-azido-2,3-dideoxy-2-hydroxyimino-α-*D*-*arabino- *and* α-

D-ribo-*hexopyranosyl)pyrazole* (**9** *and* **11**) *and 1-(6-*O*-acetyl-3-azido-2,3,4-trideoxy-2-hydroxyimino-α-*D*-glycero-hex-3-enopyranosyl)pyrazole* (**10**). — A solution of **1** (3 mmol, 1.107 g) in ethanol (80 mL) was stirred and boiled under reflux with sodium azide (0.03 mol, 1.95 g). T.l.c. (solvent *C*) after 4 h showed complete conversion of **1** into three products. The solution was filtered and concentrated, and the residue was treated with ether, filtered, diluted with chloroform (200 mL), washed with water (2 × 30 mL), dried ($MgSO_4$), and concentrated. Column chromatography (solvent *C*) of the resulting syrup gave, first, **9** (55%), m.p. 100–101°, $[\alpha]_D^{22}$ +85°, R_F (solvent *C*) 0.32; ν_{max} 3260 (OH), 2100 (N_3), and 1750 cm^{-1} (ester CO).

Anal. Calc. for $C_{13}H_{16}N_6O_6$: C, 44.32; H, 4.55; N, 23.86. Found: C, 44.34; H, 4.51; N, 23.81.

Eluted second was **10** as a syrup (~5%), $[\alpha]_D^{20}$ +88°, R_F (solvent *C*) 0.17; ν_{max} 3250 (OH), 2100 (N_3), and 1750 cm^{-1} (ester CO). Mass spectrum (f.d.): *m/z* 292 (M^+).

Eluted third was **11** (syrup, 17%), $[\alpha]_D^{20}$ +113°, R_F (solvent *C*) 0.14; ν_{max} 3250 (OH), 2100 (N_3), and 1755 cm^{-1} (ester CO).

Anal. Calc. for $C_{13}H_{16}N_6O_6$: C, 44.32; H, 4.55; N, 23.86. Found: C, 44.56; H, 4.51; N, 23.84.

*1-(3-Acetamido-2-acetoxyimino-4,6-di-*O*-acetyl-2,3-dideoxy-α-*D*-*arabino- *and* -ribo-*hexopyranosyl)pyrazole* (**12** *and* **13**). — A solution of **9** (1 mmol, 0.352 g) in ethanol (20 mL) was hydrogenated in the presence of 5% Pd/C (200 mg) for 2 h at ~20°, and then processed as described for the preparation of **5**. Column chromatography (solvent *D*) of the crude product of acetylation provided **12** (87%), m.p. 139–142°, $[\alpha]_D^{20}$ +141°, R_F (solvent *C*) 0.53; ν_{max} 3260 (NH), 1760 (ester CO), and 1675 cm^{-1} (amide CO).

Anal. Calc. for $C_{17}H_{22}N_4O_8$: C, 49.76; H, 5.41; N, 13.54. Found: C, 49.86; H, 5.41; N, 13.54.

Likewise, **11** gave **13** as a syrup (90%), $[\alpha]_D^{21}$ +45°; R_F (solvent *D*) 0.51; ν_{max} 3200 (NH), 1735 (ester CO), and 1675 cm^{-1} (amide CO).

1-[(E)*-2-Acetoxyimino-4,6-di-*O*-acetyl-2,3-dideoxy-α-*D*-*erythro-*hexopyranosyl]pyrazole* (**14**) *and its* (Z) *isomer* **15**. — To a solution of **1** (2 mmol, 0.738 g) in *N,N*-dimethylformamide (10 mL) was added sodium borohydride (0.016 mol, 0.030 g) in 3 portions during 1 h. The mixture was stirred for 18 h at 20°, the excess of borohydride was destroyed with methanol (5 mL) with cooling, the solvent was evaporated, and the residue was treated with acetic anhydride in pyridine. Column chromatography (solvent *A*) of the crude product afforded, first, **14** as a syrup (46%), $[\alpha]_D^{20}$ +80°, R_F (solvent *A*) 0.57; ν_{max} 1740 (ester CO).

Anal. Calc. for $C_{15}H_{19}N_3O_7$: C, 50.99; H, 5.38; N, 11.90. Found: C, 50.97; H, 5.35; N, 11.88.

Eluted second was **15** (syrup, 26%), $[\alpha]_D^{22}$ +46°; R_F (solvent *A*) 0.42; ν_{max} 1740 (ester CO).

Anal. Found: C, 50.98; H, 5.40; N, 11.87.

*1-(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-*D*-altropyranosyl)pyrazole* (**16**). — A solution of **3** (1 mmol, 0.352 g) in ethanol (20 mL) was stirred with 5% Pd/C (200 mg) under hydrogen (1 atm) for 14 days at ~20° and then processed as described for the preparation of **5**. Column chromatography (solvent *D*) of the crude product of acetylation gave **16** (syrup, 20%), $[\alpha]_D^{21}$ +17°, R_F (solvent *D*) 0.1; ν_{max} 3200 (NH), 1735 (ester CO), and 1660 cm^{-1} (amide CO).

Anal. Calc. for $C_{17}H_{23}N_3O_8$: C, 51.38; H, 5.83; N, 10.57. Found: C, 51.35; H, 5.77; N, 10.50.

*1-(4,6-Di-*O*-acetyl-3-azido-2,3-dideoxy-2-hydroxyimino-β-*D*-ribo- and -β-*D*-arabino-hexopyranosyl)pyrazole* (**17** *and* **18**). — A solution of **3** (2 mmol, 0.738 g) in ethanol (60 mL) was stirred and boiled under reflux with sodium azide (8 mmol, 0.52 g) for 1.5 h and then processed as described for the preparation of **9** and **11**. Column chromatography (solvent *A*) of the syrupy residue gave, first, **17** (syrup, 45%), $[\alpha]_D^{21}$ −36°, R_F (solvent *A*) 0.46; ν_{max} 2100 (N_3) and 1740 cm^{-1} (ester CO).

Anal. Calc. for $C_{13}H_{16}N_6O_6$: C, 44.32; H, 4.55; N, 23.86. Found: C, 44.32; H, 4.52; N, 23.87.

Eluted second was **18** (syrup, 16%), $[\alpha]_D^{21}$ −14°, R_F (solvent *A*) 0.33; ν_{max} 2100 (N_3) and 1745 cm^{-1} (ester CO).

Anal. Found: C, 44.29; H, 4.50; N, 23.80.

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