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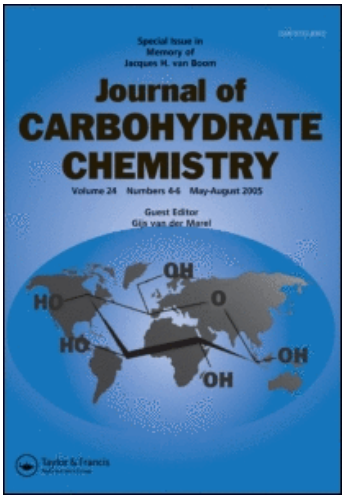

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The Synthesis and Structure of Selected Methyl (3,4-Di-*O*-acetyl-2-deoxy-2-hydroxyimino-d-*arabino*-hexopyranosid)urontes

Zygfryd Smiatacz[a]; Iwona Chrzczanowicz[a]; Henryk Myszka[a]; Paweł Dokurno[a]
[a] Department of Chemistry, University of Gdańsk, Gdańsk, Sobieskiego, Poland

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THE SYNTHESIS AND STRUCTURE OF SELECTED METHYL (3,4-DI-*O*-ACETYL-2-DEOXY-2-HYDROXYIMINO-D-*ARABINO*-HEXOPYRANOSID)URONATES

Zygfryd Smiatacz,* Iwona Chrzczanowicz,
Henryk Myszka and Paweł Dokurno

Department of Chemistry, University of Gdańsk,
80-952 Gdańsk, Sobieskiego 18, Poland

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ABSTRACT

Dimeric methyl (3,4-di-*O*-acetyl-2-deoxy-2-nitroso-α-D-glucopyranosyl chloride)uronate (**1**) reacts with nucleophiles such as: ethanol, pyrazole, methyl *N*-*tert*-butyloxycarbonyl-L-serinate to give corresponding glycosides. The stereospecifity of the glycosidation reaction depends mainly on the employed nucleophile. The configuration and conformation of the obtained glycosides were established on the basis of ^{1}H NMR and polarimetric data, and additionally the structure of 1-(methyl 3,4-di-*O*-acetyl-2-deoxy-2-(*Z*)-hydroxyimino-α-D-*arabino*-hexopyranosyluronate)pyrazole (**6**), was supported by X-ray diffraction data.

INTRODUCTION

D-Glucuronic acid appears to be the most widely distributed hexouronic acid in nature. It has been found in a wide variety of polysaccharides and proteins of microorganisms, plants and animals, where it realizes various functions in the metabolism of many types of organic compounds.[1] It is also

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known that glycosides (*O*-, *N*-, *C*- and *S*-) of D-glucuronic acid play important and complex roles in living organisms.[2]

Previously we have reported on the synthesis of the *N*- and *O*-glycosyl derivatives of pyrazole[3-5] and some hydroxy-L-*α*-amino acids,[6-8] respectively, from *O*-acetyl-2-deoxy-2-nitroso-D-hexopyranosyl chlorides. This nitroso chloride procedure[9,10] gives the corresponding *O*-acetyl-2-deoxy-2-hydroxyimino-D-hexopyranosides, predominantly with an *α* configuration.

Following that route, we now report on the reaction of methyl (3,4-di-*O*-acetyl-2-deoxy-2-nitroso-*α*-D-glucopyranosyl chloride)uronate (**1**) with ethanol, pyrazole and methyl *N*-*tert*-butyloxycarbonyl-L-serinate. This enables us to prepare *O*- and *N*-glycosyl derivatives in which the sugar residue can be modified at C-2 for use in the synthesis of new analogues and derivatives of D-glucuronic acid.

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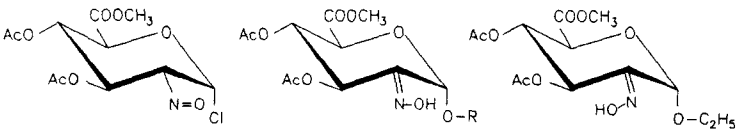
RESULTS AND DISCUSSION

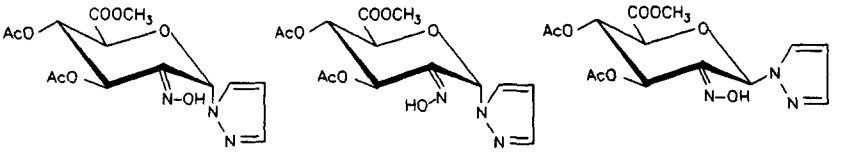
Methyl (3,4-di-*O*-acetyl-2-deoxy-2-nitroso-*α*-D-glucopyranosyl chloride)uronate (**1**) reacted smoothly with nucleophiles such as: ethanol, methyl *N*-*tert*-butyloxycarbonyl-L-serinate (**2**) and pyrazole in *N,N*-dimethylformamide (DMF) to give corresponding methyl 2-deoxy-2-hydroxyimino-D-*arabino*-hexopyranosiduronates (**3**, **4**, **5**, **6**, **7** and **8**). The 2-deoxy-2-hydroxyimino structures of **3**-**8** were established on the basis of the multiplicity of the H-1 (s) and H-3 (d) signals and the intensity of two acetyl methyl group signals in the corresponding ^{1}H NMR spectra, and the appearance of characteristic OH ($\sim$3300 cm^{-1}) and C=N ($\sim$1620 cm^{-1}) frequencies in the IR spectra.

The glycosidation reaction was not stereospecific and provided the *α* or *α* and *β* anomers with *Z* or *E* configuration of the hydroxyimino group. The reaction of **1** with ethanol afforded methyl (ethyl 3,4-di-*O*-acetyl-2-deoxy-2-(*Z*)- (**3**), (53%) and -(*E*)-hydroxyimino-*α*-D-*arabino*-hexopyranosid)uronate (**4**) ($\sim$6%). The *α* configuration at the anomeric carbon atom for both products was established on the basis of the positive optical rotation values, nearly the same for the **3** and **4** (+43° and +41°, respectively). Bearing in mind find-



1 3 R = C_2H_5 4

5 R = $CH_2-CH-COOCH_3$ (NHBoc)



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ings concerning the quantitative effect of the orientation of the hydroxyimino group on the chemical shifts of adjacent protons[10b,11] and the chemical shift values from H-1 and H-3 in **3** (δ 6.15 and 5.95 ppm, respectively) and in **4** (δ 5.55 and 6.17 ppm, respectively) we assume, that the 2-hydroxyimino group has the *Z* orientation in **3** and *E* in **4**.

The coupling constants $J_{3,4}$ = 10 Hz and $J_{4,5}$ = 11 Hz for **3** indicate that the carbohydrate ring adopts a $^4C_1$ conformation. The same conformation was confirmed by crystallographic measurements for structurally similar compounds: 1-(3,4-di-*O*-acetyl-2-deoxy-2-hydroxyimino-α-D-*erythro*-pentopyranosyl)pyrazoles,[5] 1-(3-acetamido-2-acetoxyimino-4-*O*-acetyl-2,3-dideoxy-α-D-*threo*-pentopyranosyl)pyrazole, 1-(3,4-tri-*O*-acetyl-2-deoxy-2-hydroxyimino-α-D-*arabino*-hexopyranosyl)pyrazole,[12] and for 1-(methyl 3,4-di-*O*-acetyl-2-deoxy-2-(*Z*)-hydroxyimino-α-D-*arabino*-hexopyranosyluronate)pyrazole (**6**), the X-ray structure of **6** being described in this paper.

The change of the configuration of the hydroxyimino group in **4** leads to the change of the coupling constant values ($J_{3,4}$ = 6.5 Hz, $J_{4,5}$ = 8 Hz) as compared with **3**. These smaller values point out the deformation of the pyranoid ring. This deformation arises probably from the unfavorable approach of the OH group at C-2 and the acetoxyl group at C-3. The repulsion

between these two groups leads, in consequence, to the deformation of the chair structure.

The reaction of **1** with **2** was stereospecific and gave one product: methyl *N-tert*-butyloxycarbonyl-*O*-(methyl 3,4-di-*O*-acetyl-2-deoxy-2-(*Z*)-hydroxyimino-*α*-D-*arabino*-hexopyranosyluronate)-L-serinate (**5**). The positions of H-1, H-3, H-4 and H-5 signals in **5**, very similar to that observed for **3** as well as the positive value of the optical rotations ($+25^{o}$), indicate that the discussed compound has an *α* anomeric configuration and a *Z* configuration of the hydroxyimino group. The coupling constant values $J_{3,4} = J_{4,5} = 10$ Hz indicate that the sugar ring adopts a $^{4}C_{1}$ conformation. The presence of the aglycon was confirmed from the proton signals of the L-serine moiety. Furthermore signals from the *tert*-butyloxycarbonyl group ($\delta = 1.50$ ppm) and the methyl ester group ($\delta = 3.83$ ppm) of the protected amino acid were observed.

Condensation of **1** with pyrazole provided three products: 1-(methyl 3,4-di-*O*-acetyl-2-deoxy-2-(*Z*)- (**6**), -(*E*)-hydroxyimino-*α*-D-*arabino*-hexopyranosyluronate)pyrazole (**7**), and 1-(methyl-3,4-di-*O*-acetyl-2-deoxy-2-(*Z*)-hydroxyimino-*β*-D-*arabino*-hexopyranosyluronate)pyrazole (**8**). Compounds **6** and **7** were found to be *α* anomers, whereas **8** was a *β* anomer. The *α* anomeric configuration of compounds **6** and **7** were characterized from the high positive values of $[\alpha]_D$ ($+77^{o}$ and $+61^{o}$, respectively) whereas compound **8** had a negative $[\alpha]_D$ value (-44^{o}). The coupling constant values $J_{3,4} = J_{4,5} = 10$ Hz indicate that the carbohydrate ring in **6** adopts a $^{4}C_{1}$ conformation. In turn, the coupling constant values $J_{3,4} = J_{4,5} = 5$ Hz are evidence of the change of the chair conformation in **7** and **8**. The different conformation of the pyranoid ring arises from the change of the configuration of the hydroxyimino group in **7** and of the C-1 in **8** as compared with **6**.

To elucidate the spatial structure of **7** and **8** conformational analyse have been made. The relationship between ^{3}J values and dihedral angles of adjacent C-H bonds is given by the experimental Karplus-Conroy's quotation: $^{3}J = 7 - \cos\varphi + 5\cos 2\varphi$.[13] For $^{3}J = 5$ Hz the dihedral angle can take on

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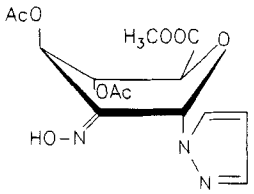
two values ~55° or ~120°. Two structures $^{3,O}B$ and $^{2,5}B$ show good agreement with the assigned dihedral angles. Taking into account nonbonding steric interaction between the substituents in both conformations it seems that the conformation $^{3,O}B$ is much more probable than $^{2,5}B$.



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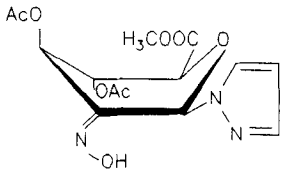

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For **7** (*α* anomer, *E*-configuration of the hydroxyimino group), structure $^{3,O}B$ does not have the unfavorable interaction between the hydroxyimino group at C-2 and the acetoxyl group at C-3, characteristic of the $^{4}C_1$ conformer.

In the case of **8** (*β* anomer, *Z*-configuration of the hydroxyimino group), in the $^{4}C_1$ conformation, two unfavorable effects are observed: a coplanar relationship between the spatial substituents at C-1, C-2 and C-3 as well as a strong electrostatic repulsion between the oxime group and equatorial aglycone. To minimize the described above interactions, substituents at C-1 and C-3 have to be displaced from their equatorial positions. This can be done by change of the $^{4}C_1$ conformation of the pyranoid ring into the $^{3,O}B$ conformation. The results obtained in our laboratory show that the deformation of the $^{4}C_1$ conformation or its change was also observed for other structurally similar compounds: *N*-(protected)-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-(*Z*)-hydroxyimino-*β*-D-*arabino*-hexopyranosyl)-L-serinate and L-threoninate,[6a] *N*-acetyl-*N*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-hydroxyimino-*β*-D-*arabino*-hexopyranosyl)amine and 3,4,6-tri-*O*-acetyl-2-deoxy-2-hydroxyimino-*β*-D-*arabino*-hexopyranosyl)azide.[6b]

It can be concluded that in the case of methyl 2-deoxy-2-hydroxyimino-D-*arabino*-hexopyranosiduronates, as with other 2-deoxy-2-hydroxyimino derivatives of D-*arabino*-hexopyranose,[3,6] *α* anomers with a *Z* configuration of the hydroxyimino group are the main products, and they adopt the $^{4}C_1$

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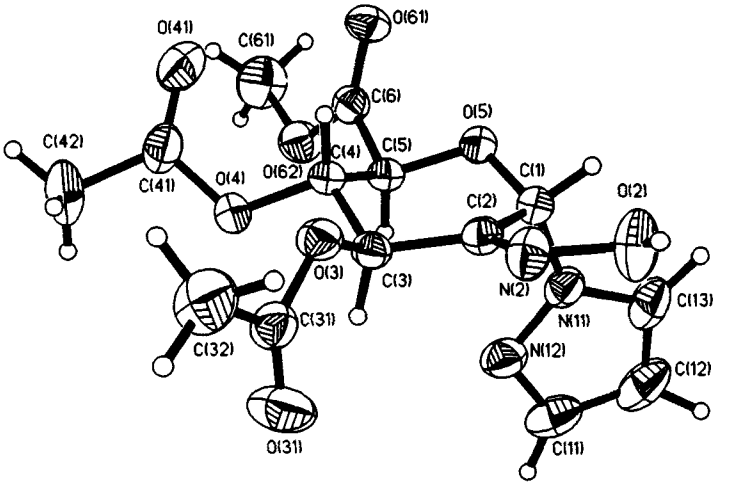

Figure 1. ORTEPII[14] Drawing from the crystal structure of **6**.

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conformation of the pyranoid ring. The change in configuration of the substituents at C-1 or C-2 leads to ring deformation (**4**) or to the change from the $^4C_1$ conformation of the pyranoid ring (**7** and **8**) to a $^{3,O}B$ conformation.

For compound **6**, studied by X-ray diffraction, the view of the molecule is shown in Figure 1.

The methyl group on C(32) is disordered, due to the rotation around the C(31)-C(32) bond. The geometry of the molecule does not deviate from the standard values.[15] The bond lengths are summarized in Table 1, and bond angles and selected torsional angles are given in Table 2.

The pyranoid ring is in a $^4C_1$ chair conformation, flattened by the hydroxyimino group at C-2. The Cremer-Pople[17] parameters characterizing this ring are: Q = 0.506(3) Å, θ = 20.9(4)° and ϕ = -68.1(9)°. The pyrazole ring is planar, with the χ^2 test equal to 3.10. The normal lines to the mean planes of both rings form an angle of 84.3(2)°.

There is one type of rather strong, intermolecular hydrogen bond O(2)-H...O(61)^i (i: -x, -½ +y, -z) with distances: O(2)-H - 0.82(2) Å; H...O(61) - 1.98(2) Å; O(2)...O(61) - 2.774(4) Å and O(2)-H...O(61) angle equal 165(2)°.

Table 1. Bond lengths (Å) with e.s.d.'s in parentheses for compound **6**

C(1)-C(2)	1.504 (5)	C(1)-O(5)	1.405 (4)
C(1)-N(11)	1.430 (5)	C(2)-C(3)	1.486 (4)
C(2)-N(2)	1.259 (4)	C(3)-C(4)	1.506 (5)
C(3)-O(3)	1.411 (4)	C(4)-C(5)	1.516 (5)
C(4)-O(4)	1.425 (3)	C(5)-O(5)	1.412 (3)
C(5)-C(6)	1.495 (5)	C(6)-O(61)	1.194 (4)
C(6)-O(62)	1.303 (3)	N(2)-O(2)	1.388 (4)
O(3)-C(31)	1.336 (4)	C(31)-O(31)	1.181 (5)
C(31)-C(32)	1.479 (7)	O(4)-C(41)	1.349 (5)
C(41)-O(41)	1.177 (5)	C(41)-C(42)	1.473 (6)
O(62)-C(61)	1.443 (6)	N(11)-N(12)	1.346 (4)
N(11)-C(13)	1.345 (5)	N(12)-C(11)	1.312 (6)
C(11)-C(12)	1.393 (8)	C(12)-C(13)	1.333 (6)

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Table 2.[16] Bond angles (°) and selected dihedral ones (°) for compound **6**

C(2)-C(1)-O(5)	111.6(3)	C(2)-C(1)-N(11)	110.3(3)
O(5)-C(1)-N(11)	112.7(2)	C(1)-C(2)-C(3)	118.5(2)
C(1)-C(2)-N(2)	123.3(3)	C(3)-C(2)-N(2)	118.2(3)
C(2)-C(3)-C(4)	111.9(2)	C(2)-C(3)-O(3)	111.5(2)
C(4)-C(3)-O(3)	106.7(3)	C(3)-C(4)-C(5)	109.8(3)
C(3)-C(4)-O(4)	104.5(2)	C(5)-C(4)-O(4)	111.8(2)
C(4)-C(5)-O(5)	108.6(2)	C(4)-C(5)-C(6)	111.7(3)
O(5)-C(5)-C(6)	104.6(2)	C(1)-O(5)-C(5)	115.9(2)
C(5)-C(6)-O(61)	124.5(2)	C(5)-C(6)-O(62)	111.1(3)
O(61)-C(6)-O(62)	124.4(3)	C(2)-N(2)-O(2)	111.0(3)
C(3)-O(3)-C(31)	117.5(3)	O(3)-C(31)-O(31)	123.4(4)
O(3)-C(31)-C(32)	111.1(3)	O(31)-C(31)-C(32)	125.5(4)
C(4)-O(4)-C(41)	117.0(3)	O(4)-C(41)-O(41)	121.8(3)
O(4)-C(41)-C(42)	111.4(4)	O(41)-C(41)-C(42)	126.7(4)
C(6)-O(62)-C(61)	115.6(3)	C(1)-N(11)-N(12)	120.4(3)
C(1)-N(11)-C(13)	127.3(3)	N(12)-N(11)-C(13)	112.2(3)
N(11)-N(12)-C(11)	103.9(3)	N(12)-C(11)-C(12)	111.6(4)
C(11)-C(12)-C(13)	105.6(4)	N(11)-C(13)-C(12)	106.7(4)
C(1)-C(2)-C(3)-C(4)	-36.4(4)	C(1)-C(2)-C(3)-O(3)	-155.9(3)
C(1)-C(2)-N(2)-O(2)	-3.3(5)	C(2)-C(1)-N(11)-N(12)	47.5(4)
C(2)-C(3)-C(4)-C(5)	47.7(4)	C(2)-C(3)-C(4)-O(4)	167.7(3)
C(3)-C(4)-C(5)-C(6)	-175.7(3)	C(2)-C(1)-O(5)-C(5)	-49.9(3)
C(3)-C(2)-C(1)-O(5)	35.5(4)	C(3)-C(4)-C(5)-O(5)	-60.8(3)

These bonds connect molecules into infinite layers and are the only observed intermolecular hydrogen bonds.

EXPERIMENTAL

Melting points are uncorrected. Optical rotations were recorded using a Hilger-Watt polarimeter for solutions in chloroform. TLC was performed on Merck Kieselgel 60 F-254 plates with A, toluene/ethyl acetate (2:1 v/v); B, carbon tetrachloride/acetone (3:2 v/v); C, toluene/ethyl acetate (1:1 v/v). ^{1}H NMR spectra ($CDCl_3$, internal $MeSi_4$) were recorded with a Varian XL-100 (100 MHz) instrument. IR spectra were recorded as Nujol mulls with a Perkin-Elmer 257 spectrophotometer. Field desorption mass spectra (FD-MS) were recorded using a MAT 711 mass spectrometer. Column chromatography was performed on Kieselgel (0.08 mm). Crystal and refinement parameters for **6** are summarized in Table 3; atomic scattering factors were taken from *International Tables for X-ray Crystallography*.[18]

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Dimeric Methyl (3,4-Di-*O*-acetyl-2-deoxy-2-nitroso-α-D-glucopyranosyl chloride)uronate (1), mp 111-112 °C, $[\alpha]_D^{20}$ +159° (*c* 0.63); lit.[19] mp 111-112 °C, $[\alpha]_D^{25}$ +145.9° (*c* 0.95) was prepared according to the literature procedure.[19]

Methyl *N*-*Tert*-butyloxycarbonyl-L-serinate (2) was prepared according to the literature procedure.[20]

General procedure used for the preparation of compounds 3-8. The reaction of **1** with ethanol, **2**, and pyrazole was carried out in dimethylformamide (DMF) at ~20 °C until the starting chloride (**1**) disappeared (TLC, solvent C) and then the mixture was diluted with methylene chloride (100 mL). The solution was then successively washed with saturated sodium hydrogencarbonate (4 × 15 mL) and water (4 × 15 mL) and dried over sodium sulfate. Concentration in vacuo gave a syrup, which was chromatographed to give pure **3-8** respectively.

Methyl (Ethyl 3,4-Di-*O*-acetyl-2-deoxy-2-(*Z*)- and -(*E*)-hydroxyimino-α-D-*arabino*-hexopyranosid)uronate (3 and 4). A solution of **1** (6.47 g, 20 mmol)

Table 3. Crystal and refinement parameters for compound **6**

Crystal data	
Chemical formula	$C_{14}H_{17}N_3O_8$
Formula weight	M_r = 355.3
Crystal system	monoclinic
Space group	$P2_1$
Unit cell dimensions	a = 8.264(2) Å
	b = 9.958(2) Å
	c = 10.831(2) Å
	β = 108.61(3)°
Volume	V = 844.7(3) Å^3
Molecules per unit cell	Z = 2
Density	D_x = 1.397 g/cm^3
Data collection	
Diffractometer used	Kuma KM-4
Radiation	MoKα (λ = 0.71069 Å)
Temperature	293 K
sinθ/λ	0.025 - 0.704
Independent reflections	2591
Reflections observed (F≥4σ(F))	1968
Index ranges	*h:* -11 → 0, *k:* 0 → 14, *l:* -14 → 15
Refinement	
Solution	Direct methods
Refinement method	Full-matrix least-squares
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0020\ F^2$
R	4.66%
wR	5.96%
Goodness of fit	1.04
Largest and mean Δ/σ	0.73, 0.067
Data to parameter ratio	6.6:1
$\Delta\rho_{max}$	0.20 e/Å^3
$\Delta\rho_{min}$	-0.22 e/Å^3

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and ethanol (3.4 mL, 70 mmol) in DMF (20 mL) was stirred for 24 h. The residue was chromatographed (solvent C) to afford, first **3** (53%, syrup): $[\alpha]_D^{20}$ +43° (*c* 0.85); R_F = 0.48 (solvent C); IR 3290 (OH), 1750 (ester CO), 1230 (O-C) cm^{-1}; ^1H NMR δ 1.30 (s, 3H, CH_3CH_2), 2.10, 2.15 (2s, 6H, 2AcO), 3.85 (s, 5H, CO_2Me, CH_3CH_2), 4.57 (d, 1H, $J_{4,5}$ = 11 Hz, H-5), 5.25 (t, 1H, $J_{3,4}$ = 10 Hz, H-4), 5.95 (d, 1H, H-3), 6.15 (s, 1H, H-1), 9.72 (bs, 1H, OH); FD-MS: *m/z* 333 $(M)^+$.

Eluted second was **4** (5.5%, syrup): $[\alpha]_D^{20}$ +40° (*c* 0.39); R_F = 0.38 (solvent C); IR 3280 (OH), 1750 (ester CO), 1225 (O-C) cm^{-1}; ^1H NMR δ 1.32 (s, 3H, CH_3CH_2), 2.10, 2.13 (2s, 6H, 2AcO), 3.90 (s, 5H, CO_2Me, CH_3CH_2), 4.55 (d, 1H, $J_{4,5}$ = 8 Hz, H-5), 5.44 (dd, 1H, $J_{3,4}$ = 6.5 Hz, H-4), 5.55 (s, 1H, H-1), 6.17 (d, 1H, H-3), 6.80 (bs, 1H, OH); FD-MS: *m/z* 333 $(M)^+$.

Methyl *N*-*Tert*-butyloxycarbonyl-*O*-(methyl 3,4-di-*O*-acetyl-2-deoxy-2-(*Z*)-hydroxyimino-α-D-*arabino*-hexopyranosyluronate)-L-serinate (5). A solution of **1** (2.26 g, 7 mmol) and **2** (2.22 g, 10 mmol) in DMF (5 mL) was stirred for 24 h. Column chromatography (solvent E) gave **5** (58%, syrup): $[\alpha]_D^{20}$ +33° (*c* 1.48); R_F = 0.60 (solvent E); IR 3290 (OH), 1760 (ester CO), 1240 (C-O) cm^{-1}; ^1H NMR δ 2.10, 2.15 (2s, 6H, 2AcO), 3.83, 3.86 (2s, 6H, $2CO_2Me$), 4.05 (d, 2H, Ser-H_β), 4.42(m, 1H, Ser-H_α), 4.52 (d, 1H, $J_{4,5}$ = 10 Hz, H-5), 5.32 (t, 1H, $J_{3,4}$ = 10 Hz, H-4), 5.60 (bs, 1H, Ser-NH), 5.82 (d, 1H, H-3), 6.09 (s, 1H, H-1), 9.07 (bs, 1H, OH); FD-MS: *m/z* 506 $(M)^+$.

1-(Methyl 3,4-Di-*O*-acetyl-2-deoxy-2-(*Z*)- (6), -(*E*)-hydroxyimino-α-D-*arabino*-hexopyranosyluronate)pyrazole (7), and 1-(Methyl 3,4-Di-*O*-acetyl-2-deoxy-2-(*Z*)-hydroxyimino-β-D-*arabino*-hexopyranosyluronate)pyrazole (8). The **1** (0.48 g, 1.5 mmol) and pyrazole (0.20 g, 3 mmol) dissolved in DMF (20 mL) was kept for 20 h. Column chromatography (solvent D) gave, first **6** (34%): mp 154-156 °C, $[\alpha]_D^{20}$ +77° (*c* 0.31); R_F = 0.56 (solvent D); IR 3280 (OH), 1740 (ester CO), 1230 (O-C) cm^{-1}; ^1H NMR δ 2.05, 2.08 (2s, 6H, 2AcO), 3.68 (s, 3H, CO_2Me), 4.58 (d, 1H, $J_{4,5}$ = 10 Hz, H-5), 5.40 (t, 1H, $J_{3,5}$ = 10 Hz, H-4), 6.37 (t, 1H, pyrazole), 6.52 (d, 1H, H-3), 7.04 (s, 1H, H-1), 7.65 (dd, 2H, pyrazole), 8.87 (bs, 1H, OH); FD-MS: *m/z* 355 $(M)^+$.

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Table 4. Atomic coordinates ($x10^4$) and equivalent isotropic displacement coefficients ($Å^2x10^3$)

Atom	x/a	y/b	z/c	U_{eq}*
C(1)	652(3)	-889(4)	1460(3)	41(1)
C(2)	1868(3)	-736(3)	691(3)	40(1)
C(3)	3531(3)	-58(3)	1318(3)	37(1)
C(4)	3367(3)	1081(3)	2186(3)	37(1)
C(5)	2365(3)	619(3)	3062(3)	39(1)
O(5)	719(2)	222	2273(2)	43(1)
C(6)	2055(3)	1745(4)	3872(3)	40(1)
N(2)	1569(4)	-1182(4)	-447(3)	51(1)
O(2)	37(3)	-1882(4)	-847(3)	71(1)
O(3)	4202(3)	496(3)	385(2)	44(1)
C(31)	5626(4)	-53(4)	277(3)	50(1)
O(31)	6291(4)	-1007(4)	872(3)	81(1)
C(32)	6254(7)	707(6)	-652(5)	77(2)
O(4)	5083(2)	1417(3)	2914(2)	46(1)
C(41)	5422(4)	2724(4)	3211(4)	55(1)
O(41)	4327(4)	3516(4)	3097(4)	82(1)
C(42)	7274(5)	2982(7)	3688(5)	83(2)
O(61)	947(3)	2560(3)	3495(2)	49(1)
O(62)	3167(3)	1732(3)	5037(2)	56(1)
C(61)	3068(6)	2843(6)	5865(4)	76(2)
N(11)	950(3)	-2133(3)	2155(3)	45(1)
N(12)	2547(4)	-2505(3)	2850(3)	53(1)
C(11)	2346(6)	-3683(4)	3325(4)	65(2)
C(12)	637(8)	-4069(4)	2926(5)	78(2)
C(13)	-215(5)	-3066(4)	2185(4)	62(1)

* $U_{eq} = 1/3 \sum_i \sum_j U_{ij} x(a_i a_i^*) x(a_j a_j^*)$

X-Ray analysis of 6. A crystal of dimensions 0.3 x 0.4 x 0.4 mm, grown from toluene/ethyl acetate (1:1 v/v), was used for measurements on a KUMA KM-4 diffractometer with *Mo Kα* (λ = 0.71069 Å) radiation. The space group and cell parameters were determined on a diffractometer from 25 reflections. Neither absorption nor extinction corrections were applied. 2591 Reflections with $\sin\theta/\lambda \leq 0.704$ $Å^{-1}$ were measured in the range *h*: -11 → 0; *k*: 0 → 14; *l*: -14 → 15, of which 1968 were observed with $F \geq 4\sigma(F)$. The

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structure was solved by direct methods using the *SHELXS86*[21] program with a PC-386 computer. Full-matrix least-squares refinement used anisotropic displacement coefficients for the non-H atoms. The H atoms found from the $\Delta\rho$ map were included into calculations with isotropic displacement coefficients. The hydrogen atoms of a disordered methyl group (rotating around C(31)-C(32) bond) were found in two positions with occupation factors of 0.60 and 0.40, respectively. Calculations converged at R = 4.66% and wR = 5.96%. All calculations were carried out on a PC-386 computer using *SHELX76*[22] and *CSU88*[23] programs. The final coordinates of the non-H atoms are given in Table 4.

Eluted second was **7** (18%, syrup): $[\alpha]_D^{20}$ +61°, (*c* 0.89); R_F = 0.43 (solvent D); IR 3240 (OH), 1745 (ester CO), 1230 (O-C) cm^{-1}; ^1H NMR δ 2.12, 2.20 (s, 6H, 2AcO), 3.83 (s, 3H, CO_2Me), 4.70 (d, 1H, $J_{4,5}$ = 5 Hz, H-5), 5.50 (t, 1H, $J_{3,4}$ = 5 Hz, H-4), 6.42 (t, 1H, pyrazole), 6.48 (s, 1H, H-1), 7.70 (dd, 2H, pyrazole), 9.80 (bs, 1H, OH); FD-MS: *m/z* 355 $(M)^+$.

Eluted third was **8** (18%, syrup): $[\alpha]_D^{20}$ -44° (*c* 0.54), R_F = 0.38 (solvent D); IR 3200 (OH), 1745 (ester CO), 1235 (O-C) cm^{-1}; ^1H NMR δ 2.10 (s, 6H, 2AcO), 3.60 (s, 3H, CO_2Me), 4.28 (d, 1H, $J_{4,5}$ = 5 Hz, H-5), 5.70 (d, 1H, $J_{3,4}$ = 5 Hz, H-3), 5.89 (dd, 1H, H-4), 6.35 (t, 1H, pyrazole), 6.62 (dd, 2H, pyrazole), 6.72 (s, 1H, H-1), 9.92 (bs, 1H, OH); FD-MS: *m/z* 355 $(M)^+$.

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