www.elsevier.nl/locate/carres
Carbohydrate Research 332 (2001) 351–361
CARBOHYDRATE RESEARCH

Synthesis and structure determination of some sugar amino acids related to alanine and 6-deoxymannojirimycin

Miroslav Koóš,[a,*] Bohumil Steiner,[a] Júlia Mičová,[a] Vratislav Langer,[b] Marián Ďurík,[c] Dalma Gyepesová[c]

[a]*Institute of Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, SK-84238 Bratislava, Slovak Republic*
[b]*Department of Inorganic Environmental Chemistry, Chalmers University of Technology, SE-41296 Gothenburg, Sweden*
[c]*Institute of Inorganic Chemistry, Slovak Academy of Sciences, SK-84236 Bratislava, Slovak Republic*

Received 18 January 2001; accepted 19 April 2001

Dedicated to Professor Dr Peter Köll on the occasion of his 60th birthday

Abstract

(5′*R*)-5′-Methyl-5′-[methyl (4*S*)-2,3-*O*-isopropylidene-β-L-erythrofuranosid-4-*C*-yl]-imidazolidin-2′,4′-dione was synthesised starting from methyl 6-deoxy-2,3-*O*-isopropylidene-α-D-*lyxo*-hexofuranosid-5-ulose applying the Bucherer–Bergs reaction. Its 5′-*R* configuration was confirmed by X-ray crystallography. Corresponding α-amino acid–methyl (5*R*)-5-amino-5-*C*-carboxy-5,6-dideoxy-α-D-*lyxo*-hexofuranoside (alternative name: 2-[methyl (4*S*)-2,3-*O*-isopropylidene-β-L-erythrofuranosid-4-*C*-yl]-D-alanine) was obtained from the above hydantoin by acid hydrolysis of the isopropylidene group followed by basic hydrolysis of the hydantoin ring. Total deprotection afforded 5-*C*-carboxy-6-deoxymannojirimycin. Analogously, methyl (5*S*)-5-amino-5-*C*-carboxy-5,6-dideoxy-α-L-*lyxo*-hexofuranoside and 5-*C*-carboxy-6-deoxy-L-mannojirimycin were prepared from the corresponding (5′*S*)-5′-methyl-5′-[methyl (4*R*)-2,3-*O*-isopropylidene-β-D-erythrofuranosid-4-*C*-yl]-imidazolidin-2′,4′-dione starting from methyl 6-deoxy-2,3-*O*-isopropylidene-α-L-*lyxo*-hexofuranosid-5-ulose. © 2001 Published by Elsevier Science Ltd.

Keywords: Sugar amino acids; Hydantoins, Alanine; 6-Deoxymannojirimycin; Methyl 2,3-*O*-isopropylidene-hexofuranosid-5-uloses; X-ray analysis

1. Introduction

Glycoconjugates of lipids and proteins represent a very important group of organic compounds, especially with respect to their biological activity. Some α-amino acids derived from carbohydrates are naturally occurring.[1–5] Due to their responsibility for recognition in biological events,[4] there is growing interest in the use of synthetic glycopeptides as model compounds. In this respect, many O- and N-linked glycoproteins have been synthesised and studied intensively.[6–26] Besides these mostly anomerically linked carbohydrate–amino acid conjugates, some analogs linked through C–C bonds have also been described.[1,3,27–35]

* Corresponding author. Fax: +421-7-59410222.
E-mail address: chemmiro@savba.sk (M. Koóš).

0008-6215/01/$ - see front matter © 2001 Published by Elsevier Science Ltd.
PII: S0008-6215(01)00109-4

In this paper, we present the synthesis and structure determination of some model compounds having C-2-linked amino acid attached to a hexose backbone in the C-5 position. Alanine derivatives branched at the C-2 atom are obtained from suitably O-protected 6-deoxy-hexofuranos-5-ulose. Further studies on analogous hexofuranos-5-uloses, 6-deoxy-6-isopropyl-hexofuranos-5-uloses and 6-deoxy-6-phenyl-hexofuranos-5-uloses affording glycoconjugates of serine, leucine and phenylalanine, respectively, are in progress.

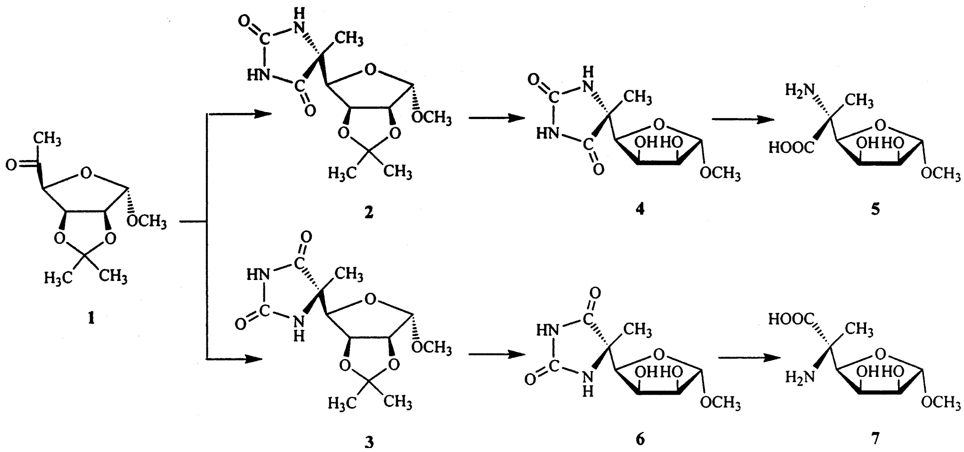
2. Results and discussion

Although a lot of sugar hydantoins (either as a final compound or precursor of the final amino acid) have been prepared,[24,28–31,36–39] the Bucherer–Bergs reaction has been applied only several times to a carbohydrate derivative.[28,29,36]

Recently, we have described[40] the synthesis of two sugar amino acids via corresponding hydantoin derivatives starting from methyl 6-deoxy-2,3-*O*-isopropylidene-α-L-*lyxo*-hexopyranosid-4-ulose. Application of the Bucherer–Bergs reaction to methyl 6-deoxy-2,3-*O*-isopropylidene-α-D-*lyxo*-hexofuranosid-5-ulose (**1**)[41] (prepared from methyl 2,3-*O*-isopropylidene-α-D-*lyxo*-pentodialdo-1,4-furanoside[42,43] by the Grignard reaction with methylmagnesium iodide and subsequent oxidation of the reaction product with pyridinium dichromate) led to the formation of the corresponding hydantoin derivative **2** (Scheme 1). The stereoselectivity of this reaction is about 85% (based on the analysis of NMR spectra) in favour of the hydantoin (**2**) having *R* configuration at C-5 and the isolation and purification of the isomer with *S* configuration at C-5 (**3**) is rather difficult. In fact, we were able to isolate only ca. 4% of pure **3**. Acid hydrolysis of the 2,3-*O*-isopropylidene group (to increase the solubility of the product **4** in water) and subsequent basic hydrolysis of the hydantoin afforded the desired amino acid **5**. The C-5 and C-6 atoms of a saccharide moiety represent in this case the α- and β-carbon atoms of alanine, as well.

Because of the obvious difficulties in unambiguous establishing the configuration at C-5 (*R* versus *S*) by NMR methods, suitable crystals of compound **2** were subjected to X-ray analysis. This confirmed 5-*R* configuration of **2**. There are two independent molecules (A and B) of the compound **2** and four water molecules in the asymmetric unit, which is equal in this case to the unit cell. Fig. 1 shows molecule A of compound **2** and the numbering scheme adopted for both molecules A and B. The H-positions (with the exception for water molecules) have been put at calculated positions and were, during refinement, riding on their respective pivot atoms. The relevant crystallographic data for **2** are given in Table 1. The bond lengths and bond angles are listed in Table 2. A list of selected torsion angles is given in Table 3. The final positional parameters for compound **2** are summarised in Table 4.

The presence of a 1,3-dioxolane ring fused to a furanose ring at the 2,3-position and the α-glycosidic methyl group imposes some con-



Scheme 1.

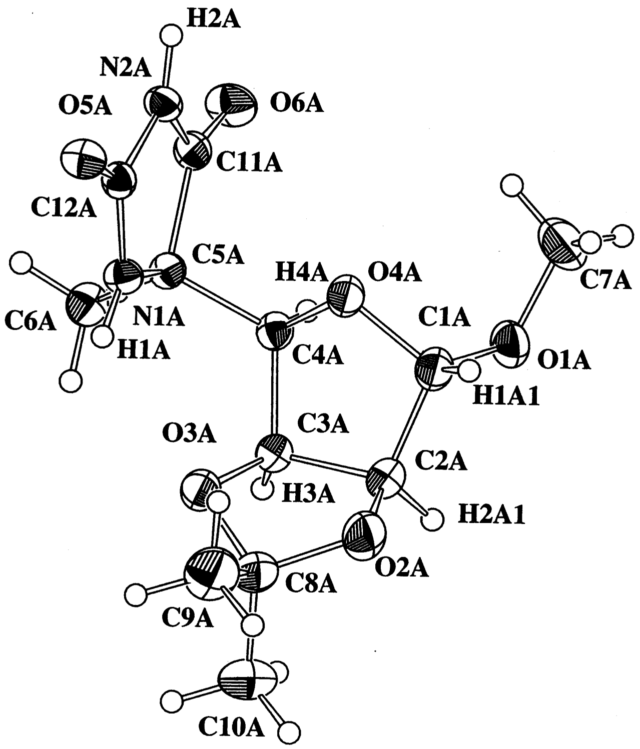


Fig. 1. ZORTEP plot and atomic numbering of molecule A of (5′*R*)-5′-methyl-5′-[methyl (4*S*)-2,3-*O*-isopropylidene-β-L-erythrofuranosid-4-*C*-yl]-imidazolidin-2′,4′-dione (**2**).

formational rigidity on **2**. The values of relevant torsion angles [C-1–C-2–C-3–C-4 = 6.9(2)°, O-4–C-1–C-2–C-3 = 16.6(2)°, C-2–C-3–C-4–O-4 = −28.0(2)° for molecule A and C-1–C-2–C-3–C-4 = 3.6(2)°, O-4–C-1–C-2–C-3 = 21.6(2)°, C-2–C-3–C-4–O-4 = −27.5(1)° for molecule B] and puckering parameters [$Q = 0.359(2)$ Å, $\varphi = 348.7(3)°$ for molecule A and $Q = 0.390(2)$ Å, $\varphi = 354.5(2)°$ for molecule B] indicate slightly deformed ^5E conformation of the furanoside ring where C-1, C-2, C-3, C-4 atoms lie almost in a plane. Analogously, the puckering parameters $Q = 0.314(2)$ Å, $\varphi = 134.3(3)°$ for molecule A and $Q = 0.328(2)$ Å, $\varphi = 139.9(3)°$ for molecule B and the relevant torsion angles O-2–C-2–C-3–O-3, C-2–C-3–O-3–C-8, C-8–O-2–C-2–C-3 of 5.5(2), −24.8(2), 16.1(2)° for molecule A and 2.4(2), −23.4(1), 19.6(2)° for molecule B, respectively, are indicative of E_3 form for five-membered 1,3-dioxolane ring with O-2, C-2, C-3, O-3 atoms approximately in a plane. The five-membered hydantoin rings are almost planar as all relevant torsion angles are close to zero.

Analysis of the molecular packing in the unit cell revealed several hydrogen bonds. In addition to weak intramolecular hydrogen bonds between N-1–H and O-3 (in both independent molecules A and B), there are two strong hydrogen bonds, each one involving the N-1–H of one of the two independent molecules and the O-5 of the carbonyl group at C-2 (C-12 in the ZORTEP plot) of the hydantoin ring of the other molecule. Four molecules of water present in the cell unit take

Table 1
Crystallographic and experimental data for compound **2** [a]

Empirical formula	$C_{12}H_{18}N_2O_6 \cdot 2\ H_2O$
Formula weight	322.32
Temperature, T (K)	183(2)
Wavelength, λ (Å)	0.71073
Crystal system	triclinic
Space group	$P1$
Unit cell dimensions	
a (Å)	8.04030 (10)
b (Å)	9.10680 (10)
c (Å)	11.5856 (2)
α (°)	92.7080(10)
β (°)	108.8510(10)
γ (°)	92.2050 (10)
Unit-cell volume V (Å^3)	800.618 (19)
Formula units per unit cell, Z	2
D_{calcd} (g/cm^3)	1.337
Radiation	Mo K_α
Absorption coefficient, μ (mm^{-1})	0.113
F(000)	344
Crystal size (mm)	0.70 (max) 0.10 (min)
Diffractometer	Siemens SMART CCD
θ Range (°)	1.86–32.72
Range of h	$-12 \rightarrow 11$
Range of k	$-13 \rightarrow 13$
Range of l	$-16 \rightarrow 17$
Scan mode	ω
Reflections	14106
Independent reflections	10353 ($R_{int} = 0.0179$)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	10353/15/473
Goodness-of-fit (all)	1.010
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0447$, $wR_2 = 0.1128$
R indices (all data)	$R_1 = 0.0536$, $wR_2 = 0.1204$
Largest difference peak and hole (e/Å^3)	0.237 and −0.445

[a] Standard deviations in parentheses.

Table 2
Bond lengths (Å) and bond angles (°) for compound **2** [a]

Bond lengths (Å)			
O-1A–C-1A	1.401(2)	O-1B–C-1B	1.416(2)
O-1A–C-7A	1.435(3)	O-1B–C-7B	1.435(2)
O-2A–C-2A	1.420(2)	O-2B–C-2B	1.4259(19)
O-2A–C-8A	1.431(2)	O-2B–C-8B	1.433(2)
O-3A–C-3A	1.424(2)	O-3B–C-3B	1.4297(18)
O-3A–C-8A	1.444(2)	O-3B–C-8B	1.4371(18)
O-4A–C-1A	1.4301(19)	O-4B–C-1B	1.4197(18)
O-4A–C-4A	1.4348(19)	O-4B–C-4B	1.4362(18)
O-5A–C-12A	1.2287(18)	O-5B–C-12B	1.2315(19)
O-6A–C-11A	1.224(2)	O-6B–C-11B	1.2230(19)
N-1A–C-12A	1.3410(19)	N-1B–C-12B	1.3406(19)
N-1A–C-5A	1.4581(19)	N-1B–C-5B	1.4554(18)
N-2A–C-11A	1.361(2)	N-2B–C-11B	1.356(2)
N-2A–C-12A	1.4014(19)	N-2B–C-12B	1.4018(19)
C-1A–C-2A	1.532(2)	C-1B–C-2B	1.536(2)
C-2A–C-3A	1.553(2)	C-2B–C-3B	1.559(2)
C-3A–C-4A	1.530(2)	C-3B–C-4B	1.527(2)
C-4A–C-5A	1.538(2)	C-4B–C-5B	1.5314(19)
C-5A–C-6A	1.531(2)	C-5B–C-6B	1.533(2)
C-5A–C-11A	1.536(2)	C-5B–C-11B	1.538(2)
C-8A–C-9A	1.509(3)	C-8B–C-9B	1.503(3)
C-8A–C-10A	1.522(3)	C-8B–C-10B	1.530(3)
Bond angles (°)			
C-1A–O-1A–C-7A	112.65(15)	C-1B–O-1B–C-7B	112.54(14)
C-2A–O-2A–C-8A	108.35(14)	C-2B–O-2B–C-8B	107.56(12)
C-3A–O-3A–C-8A	107.27(12)	C-3B–O-3B–C-8B	106.73(11)
C-1A–O-4A–C-4A	106.42(11)	C-1B–O-4B–C-4B	105.18(11)
C-12A–N-1A–C-5A	112.56(12)	C-12B–N-1B–C-5B	112.33(12)
C-11A–N-2A–C-12A	110.99(13)	C-11B–N-2B–C-12B	110.92(13)
O-1A–C-1A–O-4A	112.11(14)	O-1B–C-1B–O-4B	110.99(13)
O-1A–C-1A–C-2A	107.45(14)	O-1B–C-1B–C-2B	107.22(13)
O-4A–C-1A–C-2A	105.66(12)	O-4B–C-1B–C-2B	105.12(12)
O-2A–C-2A–C-1A	109.69(15)	O-2B–C-2B–C-1B	109.58(13)
O-2A–C-2A–C-3A	104.90(13)	O-2B–C-2B–C-3B	104.31(12)
C-1A–C-2A–C-3A	104.72(13)	C-1B–C-2B–C-3B	103.97(12)
O-3A–C-3A–C-4A	111.95(12)	O-3B–C-3B–C-4B	111.14(12)
O-3A–C-3A–C-2A	103.82(13)	O-3B–C-3B–C-2B	104.23(11)
C-4A–C-3A–C-2A	103.03(13)	C-4B–C-3B–C-2B	102.75(12)
O-4A–C-4A–C-3A	104.95(12)	O-4B–C-4B–C-3B	104.88(11)
O-4A–C-4A–C-5A	108.41(11)	O-4B–C-4B–C-5B	107.43(11)
C-3A–C-4A–C-5A	118.46(12)	C-3B–C-4B–C-5B	119.73(12)
N-1A–C-5A–C-6A	112.60(12)	N-1B–C-5B–C-4B	113.56(11)
N-1A–C-5A–C-4A	113.27(12)	N-1B–C-5B–C-6B	112.68(13)
C-6A–C-5A–C-4A	111.67(12)	C-4B–C-5B–C-6B	111.94(12)
N-1A–C-5A–C-11A	100.79(12)	N-1B–C-5B–C-11B	100.92(12)
C-6A–C-5A–C-11A	110.67(13)	C-4B–C-5B–C-11B	105.85(12)
C-4A–C-5A–C-11A	107.17(12)	C-6B–C-5B–C-11B	111.12(12)
O-2A–C-8A–O-3A	103.79(13)	O-3B–C-8B–O-2B	104.14(12)
O-2A–C-8A–C-9A	108.57(18)	O-3B–C-8B–C-9B	109.33(13)
O-3A–C-8A–C-9A	109.27(15)	O-2B–C-8B–C-9B	108.76(15)
O-2A–C-8A–C-10A	110.38(17)	O-3B–C-8B–C-10B	109.95(15)
O-3A–C-8A–C-10A	110.35(18)	O-2B–C-8B–C-10B	110.86(14)
C-9A–C-8A–C-10A	113.97(18)	C-9B–C-8B–C-10B	113.39(16)
O-6A–C-11A–N-2A	127.02(15)	O-6B–C-11B–N-2B	127.23(15)
O-6A–C-11A–C-5A	125.53(15)	O-6B–C-11B–C-5B	125.33(15)
N-2A–C-11A–C-5A	107.45(12)	N-2B–C-11B–C-5B	107.43(12)
O-5A–C-12A–N-1A	127.74(14)	O-5B–C-12B–N-1B	127.76(14)
O-5A–C-12A–N-2A	124.11(14)	O-5B–C-12B–N-2B	123.90(14)
N-1A–C-12A–N-2A	108.14(12)	N-1B–C-12B–N-2B	108.34(13)

[a] Standard deviations in parentheses.

part in additional hydrogen bonds, gluing thus the dimers of **2** into an infinite 2-dimensional array (see Table 5 and Fig. 2), approximately in the mean plane of both hydantoin rings (dihedral angle between the mean planes defined by the hydantoin rings is 21.55(9)°).

Identically to compounds **4** and **5** prepared from **2**, the derivatives **6** and **7** with 5*S* configuration were also prepared from hydantoin **3**.

The same reaction steps as in the case of preparation of **5** were also applied to methyl 6-deoxy-2,3-*O*-isopropylidene-α-L-*lyxo*-hexofuranosid-5-ulose (**8**)[44,45] (prepared by oxidation of methyl 6-deoxy-2,3-*O*-isopropylidene-α-L-mannofuranoside[46]) giving the major (5*S*)-amino acid **12** and minor (5*R*)-amino acid **14** as final products (Scheme 2). The configuration at C-5 in this series (compounds **9**, **11** and **12**) was determined on the basis of following facts: (a) configuration at C-1, C-2, C-3 and C-4 is known (α-L-*lyxo*) and did not change; (b) identical ^{1}H and ^{13}C NMR spectral data with those given for compounds **2**, **4** and **5**; (c) the same values but reverse signs of the specific rotation as those observed for **2**, **4** and **5**. These facts clearly indicate that configuration at C-5 in **9**, **11** and **12** must be *S*. The same relationship was observed in the series of compounds **10**, **13** and **14** in comparison with **3**, **6** and **7**.

Table 3
Selected torsion angles (°) for compound **2** [a]

Torsion angle	Molecule A	Molecule B
C-1–C-2–C-3–C-4	6.9(2)	3.6(2)
O-4–C-1–C-2–C-3	16.6(2)	21.6(2)
C-2–C-3–C-4–O-4	−28.0(2)	−27.5(1)
C-3–C-4–O-4–C-1	40.4(2)	43.1(1)
C-4–O-4–C-1–C-2	−35.6(2)	−40.4(1)
O-2–C-2–C-3–O-3	5.5(2)	2.4(2)
C-2–C-3–O-3–C-8	−24.8(2)	−23.4(1)
C-3–O-3–C-8–O-2	35.1(2)	36.0(2)
O-3–C-8–O-2–C-2	−31.4(2)	−34.6(2)
C-8–O-2–C-2–C-3	16.1(2)	19.6(2)
C-11–C-5–N-1–C-12	1.6(2)	0.4(2)
C-5–N-1–C-12–N-2	−2.6(2)	−1.8(2)
N-1–C-12–N-2–C-11	2.7(2)	2.6(2)
C-12–N-2–C-11–C-5	−1.7(2)	−2.3(2)
N-2–C-11–C-5–N-1	0.1(2)	1.2(2)

[a] Standard deviations in parentheses.

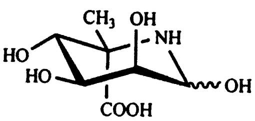
Table 4
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for compound **2** [a]

Atom	X	y	z	U_{eq}
O-1A	10881.1(18)	3668.2(15)	11240.2(11)	33.2(3)
O-2A	8685.6(19)	622.8(17)	9282.6(14)	39.1(3)
O-3A	10747.2(16)	328.4(14)	8358.6(11)	29.3(2)
O-4A	10833.3(16)	3531.4(13)	9200.3(11)	27.2(2)
O-5A	10311.0(15)	4108.3(12)	5453.6(10)	26.3(2)
O-6A	14631.2(18)	5240.1(15)	9124.4(12)	34.3(3)
N-1A	11618.2(17)	2692.4(14)	7067.5(11)	22.5(2)
H-1A	11029	1848	6773	44(7)
N-2A	12454.6(18)	5067.5(14)	7234.0(12)	23.2(2)
H-2A	12475	5993	7051	55(8)
C-1A	10023(2)	3043.8(19)	10057.5(15)	28.1(3)
H-1A1	8749	3260	9785	23(5)
C-2A	10232(2)	1380.1(19)	10089.8(16)	29.5(3)
H-2A1	10549	1039	10938	46(7)
C-3A	11680(2)	1097.0(17)	9498.6(14)	25.0(3)
H-3A	12647	524	10020	30(5)
C-4A	12320(2)	2652.7(17)	9333.4(14)	22.8(3)
H-4A	13271	3010	10104	29(5)
C-5A	12996.8(19)	2892.1(16)	8253.3(13)	21.1(2)
C-6A	14582(2)	1979(2)	8323.1(15)	28.4(3)
H-6A1	14233	930	8277	26(5)
H-6A2	15524	2238	9097	29(5)
H-6A3	15005	2186	7640	40(6)
C-7A	10729(4)	5231(2)	11334(2)	47.6(5)
H-7A1	11416	5716	10885	74(11)
H-7A2	11177	5589	12196	72(10)
H-7A3	9490	5455	10987	60(9)
C-8A	9190(3)	−389(2)	8488.9(18)	34.1(4)
C-9A	7753(3)	−527(3)	7265(2)	45.8(5)
H-9A1	6666	−939	7362	64(9)
H-9A2	8107	−1179	6699	55(8)
H-9A3	7553	448	6937	44(7)
C-10A	9627(4)	−1846(2)	9077(3)	51.3(6)
H-10A	10572	−1674	9863	71(10)
H-10B	10012	−2514	8537	67(9)
H-10C	8579	−2289	9210	92(13)
C-11A	13494(2)	4543.3(17)	8291.6(14)	23.9(3)
C-12A	11347.3(19)	3936.8(16)	6475.2(13)	21.2(3)
O-1B	1765.8(16)	500.4(13)	3249.0(12)	28.5(2)
O-2B	4169.5(16)	3420.8(14)	5372.2(11)	29.0(2)
O-3B	6123.7(14)	3825.5(12)	4370.8(10)	24.6(2)
O-4B	4836.9(14)	629.8(12)	4059.5(10)	24.7(2)
O-5B	10302.3(15)	54.0(13)	5532.3(11)	27.4(2)
O-6B	5965.7(19)	−1109.7(15)	1877.5(12)	35.8(3)
N-1B	8312.7(16)	1481.9(14)	4220.6(11)	21.8(2)
H-1B	8632	2340	4632	35(6)
N-2B	8194.2(17)	−921.9(14)	3740.8(12)	23.9(2)
H-2B	8433	−1855	3813	32(6)
C-1B	3252(2)	1071.1(18)	4228.0(15)	25.2(3)
H-1B1	3176	775	5031	30(5)
C-2B	3319(2)	2753.4(17)	4176.2(14)	24.8(3)
H-2B1	2136	3139	3773	33(6)
C-3B	4640.5(19)	3069.3(16)	3474.2(13)	22.1(3)
H-3B	4130	3652	2745	46(7)
C-4B	5079.0(19)	1526.0(16)	3132.7(13)	20.5(2)

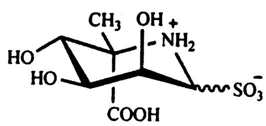
Table 4 (*Continued*)

Atom	*X*	*y*	*z*	U_{eq}
H-4B	4185	1175	2334	25(5)
C-5B	6909.1(19)	1266.2(16)	3050.8(13)	20.5(2)
C-6B	7285(2)	2132(2)	2051.0(16)	29.2(3)
H-6B1	7152	3182	2201	43(7)
H-6B2	6453	1783	1252	41(6)
H-6B3	8490	1984	2060	69(10)
C-7B	1753(3)	−1067(2)	3045(2)	38.5(4)
H-7B1	2716	−1312	2737	41(7)
H-7B2	627	−1426	2444	30(6)
H-7B3	1908	−1534	3815	45(7)
C-8B	5490(2)	4476.4(18)	5292.1(15)	27.1(3)
C-9B	6958(3)	4618(2)	6495.0(18)	37.8(4)
H-9B1	7440	3653	6688	76(11)
H-9B2	6503	4979	7139	55(8)
H-9B3	7887	5313	644	41(7)
C-10B	4690(3)	5941(2)	4888(2)	40.9(4)
H-10D	5588	6613	4761	45(7)
H-10E	4264	6379	5522	63(9)
H-10F	3706	5769	4123	41(7)
C-11B	6935(2)	−401.2(17)	2784.2(14)	23.6(3)
C-12B	9063.3(19)	224.8(16)	4599.6(14)	21.5(3)
Ow-1	14751(4)	8363(3)	9222(2)	90.9(10)
Hw-11	15420(60)	8730(50)	10080(30)	95(13)
Hw-12	14900(60)	7280(40)	9290(40)	99(14)
Ow-2	5669(3)	−4267.7(19)	1752.3(15)	60.8(6)
Hw-21	5520(50)	−3240(30)	1630(30)	77(11)
Hw-22	5550(50)	−4550(40)	1000(30)	61(9)
Ow-3	12555(2)	8025.4(17)	6845.9(15)	46.8(4)
Hw-31	13080(50)	8340(40)	7600(30)	69(10)
Hw-32	11790(40)	8570(40)	6500(30)	67(10)
Ow-4	8911(2)	−3836.6(15)	3731.7(15)	41.5(3)
Hw-41	7990(40)	−4120(40)	3300(30)	73(11)
Hw-42	9180(40)	−4400(30)	4290(30)	55(8)

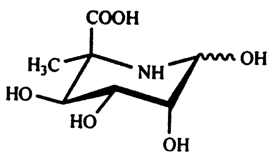
[a] Standard deviations in parentheses.



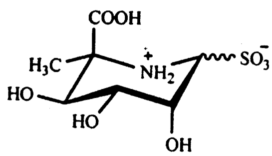
15



16



17



18

Finally, total deprotection of **5** afforded 5-*C*-carboxy-6-deoxymannojirimycin (**15**) which was isolated as corresponding hydrogensulfite adduct **16**. Analogously, 5-*C*-carboxy-6-deoxy-L-mannojirimycin (**17**) and its hydrogensulfite adduct **18** were obtained from amino acid **12**.

3. Experimental

General methods.—^{1}H and ^{13}C NMR spectra (in $CDCl_3$ unless specified other, internal standard Me_4Si) were recorded on a Bruker Avance DPX 300 instrument operating at 300.13 and 75.46 MHz working frequencies, respectively. For the assignments of signals, 1D NOESY and C–H heterocorrelated experiments were used. The quaternary carbon atoms were identified on the basis of a semislective INEPT experiment and a 1D INADEQUATE pulse sequence technique. The EI and CI (using pyridine as a reactive gas) mass spectra (70 eV) were obtained on a Finnigan MAT SSQ 710 instrument. Specific rotations were determined on a Perkin–Elmer 241 polarimeter (10-cm cell). Microanalyses were performed on a Fisons EA 1108 analyser. Melting points were determined with a Boetius PHMK 05 microscope. All reactions were monitored by TLC on Silica Gel plates (E. Merck) using the following solvents: 3:2 EtOAc–hexane (eluent A), 5:1 $CHCl_3$–MeOH (eluent B), 1:3 $CHCl_3$–MeOH (eluent C). Visualisation was affected with iodine vapour or H_2SO_4. Column chromatography was performed as flash chromatography on Silica Gel 60 (E. Merck, 230–400 mesh) with the same eluents.

X-ray techniques.—Crystal and experimental data for compound **2** are listed in Table 1. The structure was solved by direct methods and refined by a full-matrix least-squares technique. The crystallographic computations were performed with Bruker SHELXTL.[47] The ZORTEP program[48] was used for the molecular graphics drawing.

(5′R)-5′-Methyl-5′-[methyl (4S)-2,3-O-isopropylidene-β-L-erythrofuranosid-4-C-yl]-imidazolidin-2′,4′-dione (**2**).—To a solution of 5-ulose **1** (6.49 g, 30 mmol) in 50% aq EtOH (50 mL), was added NaCN (2.94 g, 60 mmol) and $(NH_4)_2CO_3$ (13.45 g, 140 mmol) and the mixture was stirred at 60 °C for 6 h. Ethanol was then evaporated and after cooling to rt, the first portion (3.24 g) of **2** crystallised from the aqueous solution. This was filtered off, and

Table 5
Hydrogen bond geometry in compound **2** [a]

X–H···Y	Symmetry code	X–H (Å)	H···Y (Å)	X···Y (Å)	X–H···Y (°)
N-1A–H-1A···O-3A		0.8803	2.4137	2.8684(18)	112.51
N-1A–H-1A···O-5B		0.8803	2.0588	2.8706(17)	152.91
N-1B–H-1B···O-3B		0.8798	2.4173	2.8522(17)	110.90
N-1B–H-1B···O-5A		0.8798	2.0443	2.8707(17)	156.07
N-2A–H-2A···Ow-3		0.8796	1.8785	2.754(2)	173.56
N-2B–H-2B···Ow-4		0.8802	1.8638	2.7380(19)	171.85
Ow-1–Hw-11···O-6B	$1+x$, $1+y$, $1+z$	1.00(3)	1.98(3)	2.921(3)	156(4)
Ow-1–Hw-12···O-6A		1.00(4)	1.86(4)	2.838(3)	166(4)
Ow-2–Hw-21···O-6B		0.96(3)	1.95(3)	2.870(2)	160(3)
Ow-2–Hw-22···O-6A	$-1+x$, $-1+y$, $-1+z$	0.87(3)	2.05(3)	2.893(2)	162(4)
Ow-3–Hw-31···Ow-1		0.87(3)	1.92(3)	2.744(3)	157(4)
Ow-3–Hw-32···O-5B	x, $1+y$, z	0.82(3)	1.98(4)	2.784(2)	168(3)
Ow-4–Hw-41···Ow-2		0.77(3)	2.12(3)	2.860(3)	159(3)
Ow-4–Hw-42···O-5A	x, $-1+y$, z	0.82(3)	1.99(3)	2.7952(19)	165(3)

[a] Standard deviations in parentheses.

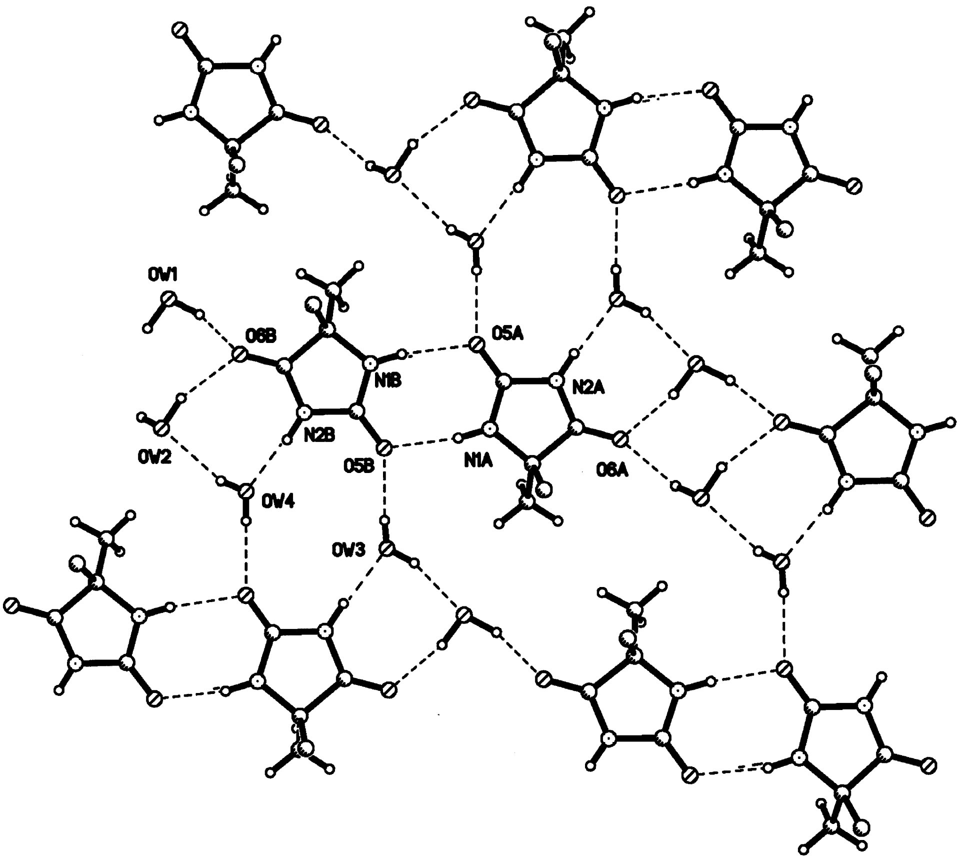
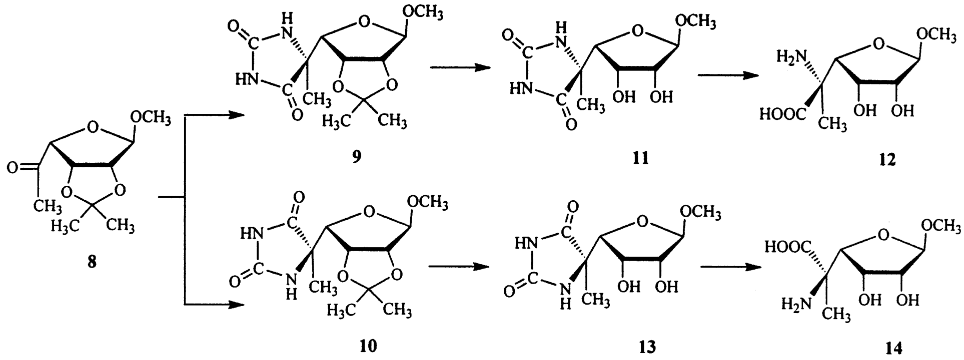


Fig. 2. Crystal packing and hydrogen bonds of compound **2**.

the aqueous solution concentrated under diminished pressure and the residue chromatographed on a column of silica gel with eluent A. The fractions having R_f 0.35 were collected and evaporated to give a further portion (2.14 g) of **2**. The combined portions of **2** were recrystallised from EtOAc–hexane affording white crystals (5.23 g, 61%) with mp 179–180 °C. Recrystallisation from water afforded **2** as a dihydrate having mp 205–



Scheme 2.

207 °C; $[\alpha]_D$ + 151° (*c* 1, $CHCl_3$), + 145° (*c* 1, MeOH); NMR: ^1H (300 MHz, $CDCl_3$): δ 9.03 (bs, 1 H, NH), 6.02 (bs, 1 H, NH), 4.91 (s, 1 H, H-1), 4.84 (dd, 1 H, $J_{2,3}$ 5.8, $J_{3,4}$ 3.4 Hz, H-3), 4.57 (d, 1 H, H-2), 4.12 (d, 1 H, H-4), 3.25 (s, 3 H, OCH_3), 1.53 and 1.31 (2 s, each 3 H, Me_2C), 1.52 (s, 3 H, H-6); ^{13}C (75.5 MHz, $CDCl_3$): δ 176.0 (CO at C-4 of hydantoin), 156.8 (CO at C-2 of hydantoin), 113.1 (CMe_2), 106.6 (C-1), 84.6 (C-2), 79.5 (C-4), 79.1 (C-3), 63.4 (C-5), 54.6 (OCH_3), 25.7 and 24.1 [$(CH_3)_2C$], 20.2 (C-6); EIMS (70 eV): *m*/*z* 271 $[M-Me]^+$, 255, 211, 197, 173 (100%), 168, 125, 115, 113, 96, 87, 85, 71, 59, 43, 42. CIMS: *m*/*z* 366 $[M+80]^+$. Anal. Calcd for $C_{12}H_{18}N_2O_6 \cdot 2\,H_2O$: C, 44.70; H, 6.88; N, 8.69. Found: C, 44.59; H, 6.93, N, 8.62.

(5′S)-5′-Methyl-5′-[methyl (4S)-2,3-O-isopropylidene-β-L-erythrofuranosid-4-C-yl]-imidazolidin-2′,4′-dione (**3**).—The fractions having R_f 0.30 from the above column chromatography were collected and evaporated. Fractional crystallisation of the product from EtOAc–hexane gave pure **3** (343 mg, 4% yield); mp 156–158 °C; $[\alpha]_D$ + 6° (*c* 1, $CHCl_3$); NMR: ^1H (300 MHz, $CDCl_3$): δ 9.04 (bs, 1 H, NH), 6.16 (bs, 1 H, NH), 4.99 (s, 1 H, H-1), 4.75 (dd, 1 H, $J_{2,3}$ 5.9, $J_{3,4}$ 3.8 Hz, H-3), 4.56 (d, 1 H, H-2), 4.00 (d, 1 H, H-4), 3.34 (s, 3 H, OCH_3), 1.62 and 1.24 (2 s, each 3 H, Me_2C), 1.43 (s, 3 H, H-6); ^{13}C (75.5 MHz, $CDCl_3$): δ 176.0 (CO at C-4 of hydantoin), 157.1 (CO at C-2 of hydantoin), 113.1 (CMe_2), 106.3 (C-1), 84.7 (C-2), 79.7 (C-4), 79.3 (C-3), 62.6 (C-5), 54.7 (OCH_3), 24.3 and 24.0 [$(CH_3)_2C$], 25.3 (C-6); EIMS (70 eV): *m*/*z* 271 $[M-Me]^+$, 255, 211, 197, 173 (100%), 168, 125, 115, 113, 96, 87, 85, 71, 59, 43, 42. CIMS: *m*/*z* 366 $[M+80]^+$. Anal. Calcd for $C_{12}H_{18}N_2O_6$: C, 50.30; H, 6.34; N, 9.79. Found: 50.22; H, 6.39; N, 9.72.

(5′R)-5′-Methyl-5′-[methyl (4S)-β-L-erythrofuranosid-4-C-yl]-imidazolidin-2′,4′-dione (**4**).—A suspension of hydantoin **2** (2.86 g, 10 mmol, R_f 0.87 in solvent B) in diluted AcOH (70%, 50 mL) was heated at 80 °C for 75 min. The reaction mixture became clear during the first 15 min. The solvent was evaporated to dryness under diminished pressure and co-evaporated twice with toluene. The residual white solid was dissolved in EtOAc (30 mL), treated with charcoal, filtered and the solvent was evaporated. Recrystallisation from EtOAc–hexane afforded pure **4** (R_f 0.50, solvent B) as white crystals (1.57 g, 64%); mp 188–190 °C; $[\alpha]_D$ + 150° (*c* 1, water), + 179° (*c* 1, MeOH); NMR: ^1H (300 MHz, D_2O): δ 5.04 (d, 1 H, $J_{1,2}$ 4.6 Hz, H-1), 4.53 (dd, 1 H, $J_{2,3}$ 4.6, $J_{3,4}$ 3.7 Hz, H-3), 4.41 (d, 1 H, H-4), 4.16 (t, 1 H, H-2), 3.48 (s, 3 H, OCH_3), 1.56 (s, 3 H, H-6); ^{13}C (75.5 MHz, D_2O): δ 180.5 (CO at C-4 of hydantoin), 159.6 (CO at C-2 of hydantoin), 109.2 (C-1), 81.5 (C-4), 76.5 (C-2), 71.4 (C-3), 65.3 (C-5), 57.2 (OCH_3), 19.4 (C-6); EIMS (70 eV): *m*/*z* 247 $[M+1]^+$, 215, 133, 114 (100%), 113, 87, 73, 45, 42. Anal. Calcd for $C_9H_{14}N_2O_6$: C, 43.90; H, 5.73; N, 11.40. Found: C, 43.84; H, 5.78; N, 11.31.

*Methyl (5R)-5-amino-5-C-carboxy-5,6-dideoxy-α-D-*lyxo*-hexofuranoside* (**5**).—A mixture of hydantoin **4** (1.23 g, 5 mmol), barium hydroxide octahydrate (4.73 g, 15 mmol) and water (50 mL) was heated under reflux for 6 h. Carbon dioxide gas was then passed into the hot mixture. The separated barium carbonate was removed by filtration and washed with hot water. Carbon dioxide gas was again passed into the hot solution and after cooling to rt, another portion of barium carbonate separated. Filtration and decolourising with charcoal gave a clear solution. Water was evaporated under diminished pressure and the residual solid was purified on a short column of silica gel (eluent C). Fractions with R_f 0.39 (eluent C) were collected and evaporated to afford **5** (420 mg, 38%). Analytical sample (white needles) was obtained by recrystallisation from water–methanol; mp (dec) 190 °C; $[\alpha]_D$ +93° (*c* 1, water); NMR: ^{1}H (300 MHz, D_2O): δ 4.99 (d, 1 H, $J_{1,2}$ 4.5 Hz, H-1), 4.51 (d, 1 H, $J_{3,4}$ 3.3 Hz, H-4), 4.49 (dd, 1 H, $J_{2,3}$ 4.5 Hz, H-3), 4.14 (t, 1 H, H-2), 3.41 (s, 3 H, OCH_3), 1.54 (s, 3 H, H-6); ^{13}C (75.5 MHz, D_2O): δ 175.7 (CO), 108.9 (C-1), 80.6 (C-4), 77.1 (C-2), 72.1 (C-3), 62.8 (C-5), 56.9 (OCH_3), 18.8 (C-6); EIMS (70 eV): *m*/*z* 176 $[M-COOH]^+$, 144, 116, 102, 87, 86 (100%), 74, 73, 57, 44, 43, 42. Anal. Calcd for $C_8H_{15}NO_6$: C, 43.40; H, 6.83; N, 6.33. Found: C, 43.47; H, 6.88; N, 6.37.

(5′S)-5′-Methyl-5′-[methyl (4S)-β-L-erythrofuranosid-4-C-yl]-imidazolidin-2′,4′-dione (**6**).—Starting from **3** (572 mg, 2 mmol), and application of the same reaction procedure as described for the preparation of **4** afforded **6** (335 mg, 68%); mp 238–239 °C; $[\alpha]_D$ +19° (*c* 1, MeOH); NMR: ^{1}H (300 MHz, D_2O): δ 4.82 (s, 1 H, H-1), 4.33 (dd, 1 H, $J_{2,3}$ 4.6, $J_{3,4}$ 7.6 Hz, H-3), 4.16 (d, 1 H, H-4), 4.01 (t, 1 H, H-2), 3.29 (s, 3 H, OCH_3), 1.46 (s, 3 H, H-6); ^{13}C (75.5 MHz, D_2O): δ 180.4 (CO at C-4 of hydantoin), 159.8 (CO at C-2 of hydantoin), 108.4 (C-1), 83.9 (C-4), 75.2 (C-2), 71.7 (C-3), 66.1 (C-5), 55.8 (OCH_3), 18.2 (C-6); EIMS (70 eV): *m*/*z* 247 $[M+1]^+$, 215, 133, 114 (100%), 113, 87, 73, 45, 42. Anal. Calcd for $C_9H_{14}N_2O_6$: C, 43.90; H, 5.73; N, 11.40. Found: C, 43.80; H, 5.79; N, 11.35.

*Methyl (5S)-5-amino-5-C-carboxy-5,6-dideoxy-α-D-*lyxo*-hexofuranoside* (**7**).—Starting from **6** (246 mg, 1 mmol), and application of the same reaction procedure as described for the preparation of **5** afforded **7** (91 mg, 41%); mp (dec) 196 °C; $[\alpha]_D$ +12° (*c* 1, water); NMR: ^{1}H (300 MHz, D_2O): δ 4.88 (s, 1 H, H-1), 4.24 (dd, 1 H, $J_{2,3}$ 4.6, $J_{3,4}$ 7.7 Hz, H-3), 4.10 (d, 1 H, H-4), 3.98 (t, 1 H, H-2), 3.25 (s, 3 H, OCH_3), 1.38 (s, 3 H, H-6); ^{13}C (75.5 MHz, D_2O): δ 176.1 (CO), 108.0 (C-1), 82.8 (C-4), 77.3 (C-2), 70.7 (C-3), 66.6 (C-5), 56.2 (OCH_3), 18.9 (C-6); EIMS (70 eV): *m*/*z* 176 $[M-COOH]^+$, 144, 116, 102, 87, 86 (100%), 74, 73, 57, 44, 43, 42. Anal. Calcd for $C_8H_{15}NO_6$: C, 43.40; H, 6.83; N, 6.33. Found: C, 43.44; H, 6.90; N, 6.37.

(5′S)-5′-Methyl-5′-[methyl (4R)-2,3-O-isopropylidene-β-D-erythrofuranosid-4-C-yl]-imidazolidin-2′,4′-dione (**9**).—Starting from **8** (6.49 g, 30 mmol), and application of the same reaction procedure as described for the preparation of **2** afforded **9** (5.06 g, 59%); mp 208–209 °C; $[\alpha]_D$ −151° (*c* 1, $CHCl_3$), −145° (*c* 1, MeOH); NMR and mass spectra were identical with those reported for compound **2**. Anal. Calcd for $C_{12}H_{18}N_2O_6$: C, 50.30; H, 6.34; N, 9.79. Found: 50.19; H, 6.40; N, 9.73.

(5′R)-5′-Methyl-5′-[methyl (4R)-2,3-O-isopropylidene-β-D-erythrofuranosid-4-C-yl]-imidazolidin-2′,4′-dione (**10**).—Fractional crystallisation (from EtOAc–hexane) of the product, obtained from column chromatography (R_f 0.30, eluent A) of the crude product from the mother liquor (after exhaustive recovery of **9**) from above preparation of **9**, afforded pure **10** (377 mg, 4.4% yield); mp 158–160 °C; $[\alpha]_D$ −6° (*c* 1, $CHCl_3$); NMR and mass spectra were identical with those reported for compound **3**. Anal. Calcd for $C_{12}H_{18}N_2O_6$: C, 50.30; H, 6.34; N, 9.79. Found: 50.23; H, 6.38; N, 9.84.

(5′S)-5′-Methyl-5′-[methyl (4R)-β-D-erythrofuranosid-4-C-yl]-imidazolidin-2′,4′-dione (**11**).—Starting from **9** (2.86 g, 10 mmol), and application of the same reaction procedure as described for the preparation of **4** afforded **11** (1.62 g, 66%); mp 184–186 °C; $[\alpha]_D$ −150° (*c* 1, water), −179° (*c* 1, MeOH); NMR and mass spectra were identical with those reported for compound **4**. Anal. Calcd for $C_9H_{14}N_2O_6$: C, 43.90; H, 5.73; N, 11.40. Found: C, 43.98; H, 5.78; N, 11.32.

*Methyl (5S)-5-amino-5-C-carboxy-5,6-dideoxy-α-L-*lyxo*-hexofuranoside* (**12**).—Starting from **11** (1.23 g, 5 mmol), and application of the same reaction procedure as described for the preparation of **5** afforded **12** (442 mg, 40%); mp (dec) 193 °C; $[\alpha]_D$ −93° (*c* 1, water); NMR and mass spectra were identical with those reported for compound **5**. Anal.

Calcd for $C_8H_{15}NO_6$: C, 43.40; H, 6.83; N, 6.33. Found: C, 43.42; H, 6.86; N, 6.31.

*(5′*R*)-5′-Methyl-5′-[methyl (4*R*)-β-*D*-erythrofuranosid-4-*C*-yl]-imidazolidin-2′,4′-dione* (**13**).—Starting from **10** (572 mg, 2 mmol), and application of the same reaction procedure as described for the preparation of **4** afforded **13** (320 mg, 65%); mp 240–241 °C; $[\alpha]_D$ −19° (*c* 1, MeOH). NMR and mass spectra were identical with those reported for compound **6**. Anal. Calcd for $C_9H_{14}N_2O_6$: C, 43.90; H, 5.73; N, 11.40. Found: C, 43.82; H, 5.79; N, 11.38.

*Methyl (5*R*)-5-amino-5-*C*-carboxy-5,6-dideoxy-α-*L*-*lyxo*-hexofuranoside* (**14**).—Starting from **13** (246 mg, 1 mmol), and application of the same reaction procedure as described for the preparation of **5** afforded **14** (97 mg, 44%); mp (dec) 191 °C; $[\alpha]_D$ −11° (*c* 1, water). NMR and mass spectra were identical with those reported for compound **7**. Anal. Calcd for $C_8H_{15}NO_6$: C, 43.40; H, 6.83; N, 6.33. Found: C, 43.45; H, 6.87; N, 6.30.

*5-*C*-Carboxy-6-deoxymannojirimycin hydrogensulfite adduct* (**16**).—A solution of **5** (221 mg, 1 mmol) in water (5 mL) saturated with SO_2 at 0 °C was stored at 40 °C in a sealed vessel for 72 h, and then cooled and filtered to give **16** (206 mg, 76%); mp (dec) 168 °C; Anal. Calcd for $C_7H_{13}NO_8S$: C, 31.00; H, 4.83; N, 5.16; S, 11.80. Found: C, 31.12; H, 4.89; N, 5.10; S, 11.71.

*5-*C*-Carboxy-6-deoxy-*L*-mannojirimycin hydrogensulfite adduct* (**18**).—Treatment of **12** (221 mg, 1 mmol) with SO_2 solution as described for **16** afforded **18** (198 mg, 73%); mp (dec) 166 °C; Anal. Calcd for $C_7H_{13}NO_8S$: C, 31.00; H, 4.83; N, 5.16; S, 11.80. Found: C, 30.86; H, 4.87; N, 5.20; S, 11.90.

4. Supplementary material

Crystallographic data for the structural analysis for compound **2** has been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 154357. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

The authors thank K. Paule, G. Košický, A. Karovičová, A. Kanská, and Dr V. Pätoprstý (Institute of Chemistry) for microanalyses, optical rotation, NMR, and mass spectral measurements. Financial support of this work by the Scientific Grant Agency (VEGA, Slovak Academy of Sciences, Grant No. 2/7144/20) is gratefully appreciated.

References

1. Isono, K.; Asahi, K.; Suzuki, S. *J. Am. Chem. Soc.* **1969**, *91*, 7490–7505.
2. Hamill, R. L.; Hoehn, M. M. *J. Antibiot.* **1973**, *26*, 463–465.
3. Banfi, L.; Beretta, M. G.; Colombo, L.; Gennari, C.; Scolastico, C. *J. Chem. Soc., Perkin Trans. 1* **1983**, 1613–1619.
4. Varki, A. *Glycobiology* **1993**, *3*, 97–130.
5. Suzuki, T.; Kitajima, K.; Inoue, K.; Inoue, S. *Glycoconjugate J.* **1995**, *12*, 183–193.
6. Pochet, S.; Allard, P.; Tam, H. D.; Igolen, J. *J. Carbohydr. Chem.* **1983**, *1*, 277–288.
7. Kunz, H. *Angew. Chem.* **1987**, *99*, 297–311.
8. Rademacher, T. W.; Parekh, R. B.; Dwek, R. A. *Ann. Rev. Biochem.* **1988**, *57*, 785–787.
9. Horvat, Š.; Horvat, J.; Kantoci, D.; Varga, L. *Tetrahedron* **1989**, *45*, 4579–4584.
10. Maguire, M. P.; Feldman, P. L.; Rapoport, H. *J. Org. Chem.* **1990**, *55*, 948–955.
11. Allen, H. J.; Kisailus, E. C. *Glycoconjugates: Composition, Structure and Function*; Marcel Dekker: New York, 1992.
12. Kobata, A. *Eur. J. Biochem.* **1992**, *209*, 483–501.
13. Kunz, H. *Pure Appl. Chem.* **1993**, *65*, 1223–1232.
14. Schultz, M.; Kunz, H. *Tetrahedron: Asymm.* **1993**, *4*, 1205–1220.
15. Jurczak, J. *Synlett* **1993**, 241–245.
16. Sosnovsky, G.; Baysal, M.; Erciyas, E. *J. Pharm. Sci.* **1994**, *83*, 999–1005.
17. Meldal, M. In *Neoglycoconjugates: Preparation and Application*; Lee, Y. C.; Lee, R. T., Eds.; Academic Press: San Diego, 1994; pp. 145–198.
18. Kunz, H. *Pure Appl. Chem.* **1995**, *67*, 1627–1635.
19. Peters, S.; Meldal, M.; Bock, K. In *Modern Methods in Carbohydrate Synthesis*; Khan, S. H.; O'Neill, R. A., Eds.; Harwood: Amsterdam, 1996; pp. 352–377.
20. Montreuil, J.; Vliegenthart, J. F. G.; Schachter, S. *Glycoproteins, New Comprehensive Biochemistry*; Elsevier: Amsterdam, 1996; Vol. 298.
21. Roy, R. In *Modern Methods in Carbohydrate Synthesis*; Khan, S. H.; O'Neill, R. A., Eds.; Harwood: Amsterdam, 1996; pp. 378–402.
22. Graf von Roedern, E.; Lohof, E.; Hessler, G.; Hoffmann, M.; Kessler, H. *J. Am. Chem. Soc.* **1996**, *118*, 10156–10167.
23. Čudić, M.; Kojić-Prodić, B.; Milinković, V.; Horvat, J.; Horvat, Š.; Elofsson, M.; Kihlberg, J. *Carbohydr. Res.* **1996**, *287*, 1–19.

24. Estevez, J. C.; Smith, M. D.; Lane, A. L.; Crook, S.; Watkin, D. J.; Besra, G. S.; Brennan, P. J.; Nash, R. J.; Fleet, G. W. J. *Tetrahedron: Asymm*. **1996**, *7*, 387–390.
25. Heidelberg, T.; Thiem, J. *Carbohydr. Res*. **1997**, *301*, 145–153.
26. Jiaang, W. T.; Chang, M. Y.; Tseng, P. H.; Chen, S. T. *Tetrahedron Lett*. **2000**, *41*, 3127–3130.
27. Petruš, L.; BeMiller, J. N. *Carbohydr. Res*. **1992**, *230*, 197–200.
28. Yanagisawa, H.; Kinoshita, M.; Nakada, S.; Umezawa, S. *Bull. Chem. Soc. Jpn*. **1970**, *43*, 246–252.
29. Rosenthal, A.; Dodd, R. R. *J. Carbohydr. Nucleos. Nucleot*. **1979**, *6*, 467–476.
30. Estevez, J. C.; Estevez, R. J.; Ardron, H.; Wormald, M. R.; Brown, D.; Fleet, G. W. J. *Tetrahedron Lett*. **1994**, *35*, 8885–8888.
31. Estevez, J. C.; Ardron, H.; Wormald, M. R.; Brown, D.; Fleet, G. W. J. *Tetrahedron Lett*. **1994**, *35*, 8885–8888.
32. Gurjar, M. K.; Mainkar, A. S.; Syamala, M. *Tetrahedron: Asymm*. **1993**, *4*, 2343–2346.
33. Estevez, J. C.; Burton, J. W.; Estevez, R. J.; Ardron, H.; Wormald, M. R.; Dwek, R. A.; Brown, D.; Fleet, G. W. J. *Tetrahedron: Asymm*. **1998**, *9*, 2137–2154.
34. Robins, M. J.; Parker, J. M. R. *Can. J. Chem*. **1983**, *61*, 312–316.
35. Westermann, B.; Walter, A.; Diedrics, N. *Angew. Chem. (Int. Ed. Engl.)* **1999**, *38*, 3384–3386.
36. Kuszmann, J.; Márton-Merész, M.; Jerkovich, G. *Carbohydr. Res*. **1988**, *175*, 249–264.
37. Mio, S.; Kumagawa, Y.; Sugai, S. *Tetrahedron* **1991**, *47*, 2133–2144.
38. Burton, J. W.; Son, J. C.; Fairbanks, A. J.; Choi, S. S.; Taylor, H.; Watkin, D. J.; Winchester, B. G.; Fleet, G. W. J. *Tetrahedron Lett*. **1993**, *34*, 6119–6122.
39. Nakajima, N.; Matsumoto, M.; Kirihara, M.; Hashimoto, M.; Katoh, T.; Terashima, S. *Tetrahedron* **1996**, *52*, 1177–1194.
40. Koóš, M.; Steiner, B.; Langer, V.; Gyepesová, D.; Ďurík, M. *Carbohydr. Res*. **2000**, *328*, 115–126.
41. Gourlain, T.; Wadouachi, A.; Beaupère, D. *Carbohydr. Res*. **2000**, *324*, 66–73.
42. Krajewski, J. W.; Gluziński, P.; Pakulski, Z.; Zamojski, A.; Mishnev, A.; Kemme, A. *Carbohydr. Res*. **1994**, *252*, 97–105.
43. Barton, D. H. R.; Stephane, D.; Quiclet-Sire, B.; Samadi, M. *Tetrahedron: Asymm*. **1994**, *5*, 2123–2136.
44. Klemer, A.; Waldmann, M. *Liebigs Ann. Chem*. **1986**, *2*, 221–225.
45. Anisuzzaman, A. K. M.; Whistler, R. L. *Carbohydr. Res*. **1977**, *55*, 205–214.
46. Lerner, L. M. *Carbohydr. Res*. **1974**, *36*, 392–397.
47. Bruker AXS Inc., SHELXTL Version 5.10; Madison, WI, USA, 1997.
48. Zsolnai, L.; Huttner, G. Program ZORTEP; University of Heidelberg: Germany, 1994.