Carbohydrate Research, 163 (1987) 132–135
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

Synthesis of glycofuranoimidazolidin-2-ones from 2-amino-2-deoxyaldoses

Juan A. Galbis Pérez, Francisca Zamora Mata, and Pilar Turmo Fernandez
Department of Organic Chemistry, Faculty of Pharmacy, University of Seville, 41071 Seville (Spain)

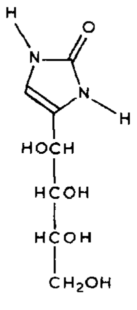
(Received October 31st, 1986; accepted for publication, December 19th, 1986)

In seeking to prepare 4-(D-*arabino*-tetritol-1-yl)-imidazolin-2-one (**1**) by reaction[1] of 2-amino-2-deoxy-D-glucose with silver cyanate, 1,2-dideoxy-α-D-glucofurano[1,2-*d*]imidazolidin-2-one (**2**) was obtained. This type of product has not been obtained hitherto from 2-amino sugars, although the 2-thione analogues are well known[2].

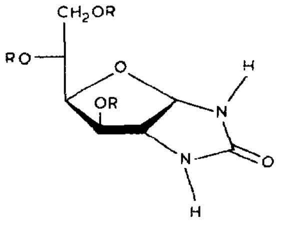
The structure of **2** is supported by its chemical and spectroscopic data. The u.v. spectrum of **2** contained no absorption band above 200 nm, and the ^{1}H- and ^{13}C-n.m.r. spectra of **2** and its triacetate **3** (see Tables I and II) accord only with the bicyclic structures **2** and **3**. We believe that the product obtained by Pauly and Ludwig[1] was really an impure sample of **2**.

An attempt to obtain **1** by acid-catalysed isomerisation of **2**, as described for some glycofuranoimidazolidines[3], gave a complex mixture of products that could not be identified. In the absence of acid, **2** did not react.

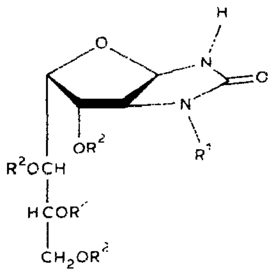
In a similar manner, 2-amino-2-deoxy-D-*glycero*-L-*gluco*-heptose[4] reacted with silver cyanate to afford 1,2-dideoxy-β-D-*glycero*-L-*gluco*-heptofurano[1,2-*d*]imidazolidin-2-one (**4**), characterised as the tetra-acetate **5**, the structures of which were indicated by their ^{1}H- and ^{13}C-n.m.r. spectra. Likewise, the epimeric



1



2 R = H
3 R = Ac



4 $R^1 = R^2 = H$
5 $R^1 = H, R^2 = Ac$
6 $R^1 = Et, R^2 = H$

TABLE I

^{1}H-N.M.R. DATA FOR **2–6**

Compound	Solvent	Chemical shifts (δ)										
		H-1'	H-2'	H-3'	H-4'	H-5'	H-6'	H-6"	H-7'	H-7"	NH	OAc
2	D_2O	5.75 d	←4.26–4.18 m→		←3.90–3.50 m→							
	$(CD_3)_2SO$	5.47 dd	←3.90–3.20 m→								7.18 s[a] 6.64 s[a]	
3	$CDCl_3$	5.78 dd	4.17 m	5.20 d	4.32 dd	5.26 dq	4.53 dd	4.11 dd			6.33 s[a] 6.23 s[a]	2.07 s (6 H) 2.02 s (3 H)
	$CDCl_3 + D_2O$	5.78 d	4.17 d	5.19 d	4.32 dd	5.26 dq	4.56 dd	4.11 dd				2.07 s (6 H) 2.02 s (3H)
4	$(CD_3)_2SO$	5.46 dd	←4.00–3.00 m→								7.17 s 6.65 s	
5	$CDCl_3$	5.75 dd	4.16 dd	5.13 d	4.25dd	←5.55–5.28 m→			4.33 dd	3.94 dd	5.70 d 5.55 d	2.10 s (3 H) 2.07 s (3 H) 2.04 s (3 H) 2.03 s (3 H)
	$CDCl_3 + D_2O$	5.75 d	4.14 d	5.12 d	4.24 dd	←5.75–5.28 m→			4.33 dd	3.94 dd		2.11 s (3 H) 2.08 s (3 H) 2.05 s (3 H) 2.03 s (3 H)
6	D_2O	5.66 d	4.20 d	4.34 d	←4.00–3.50 m→							

Compound	Solvent	J values (Hz)											
		$J_{1',2'}$	$J_{2',3'}$	$J_{3',4'}$	$J_{4',5'}$	$J_{5',6'}$	$J_{5',6''}$	$J_{6',6''}$	$J_{6',7'}$	$J_{6',7''}$	$J_{7',7''}$	$J_{2',NH}$	$J_{1',NH}$
2	D_2O	6.3	~0										
	$(CD_3)_2SO$	6.0	~0										1.4
3	$CDCl_3$	6.2	~0	2.9	8.9	2.5	5.6	−12.3					1.1
	$CDCl_3 + D_2O$	6.3	~0	2.9	9.3	2.4	5.7	−12.3					
4	$(CD_3)_2SO$	6.1	~0										1.3
5	$CDCl_3$	6.0	~0	2.8							−11.6	2.2	1.6
	$CDCl_3 + D_2O$	6.3	~0	2.8	8.8				4.8	7.0	−11.6		
6	D_2O	6.5	~0	1.7									

[a] Broadening due to ^{14}N-quadrupole relaxation.

TABLE II

^{13}C-N.M.R. DATA FOR **2–6**

Compound	*Solvent*	*Chemical shifts (p.p.m.)*							
		C-1'	*C-2'*	*C-3'*	*C-4'*	*C-5'*	*C-6'*	*C-7'*	*C=O*
2	D_2O	87.8	64.9	75.6	79.7	69.8	64.8		164.6
3	$CDCl_3$	86.9	62.5	76.0	76.0	68.0	63.4		161.3
4	$(CD_3)_2SO$	86.6	64.2	75.0	78.8	67.6[a]	71.6[a]	63.3	162.5
5	$CDCl_3$	86.7	62.4	75.8	75.8	67.7[a]	70.0[a]	62.4	160.7
6	D_2O	85.5	68.4	73.3	79.2	68.8[a]	72.5[a]	64.0	167.8

[a] These assignments may be interchanged.

mixture of 2-deoxy-2-ethylamino-D-*glycero*-L-*gluco*- and -D-*glycero*-L-*manno*-heptose[5] gave a product (**6**) having the β-D-*glycero*-L-*gluco* configuration, for which the $J_{2,3}$ value of ~0 Hz accorded[2] with a *trans* arrangement of H-2,3. The α-D-*glycero*-L-*manno* isomer was detected spectroscopically and chromatographically, but could not be isolated.

EXPERIMENTAL

General methods. — Solutions were concentrated *in vacuo* at <40°. Melting points are uncorrected. Optical rotations were measured at 20 ±2°, using a 10-cm cell. T.l.c. was performed on Silica Gel GF_{254} (Merck) with ether–hexane (3:1 or 1:1), and detection with u.v. light or iodine vapour. P.c. (ascending and descending) was performed on Whatman No. 1 paper, using 1-butanol–pyridine–water (1:1:1) and 1-butanol–acetic acid–water (4:1:5), and detection with silver nitrate–sodium hydroxide and iodine vapour. I.r. spectra were recorded for KBr discs. ^{1}H- (80.13 MHz) and ^{13}C-n.m.r. (20.15 MHz) spectra were recorded with a Bruker WP-80-SY spectrometer.

*1,2-Dideoxy-α-D-glucofurano[1,2-*d*]imidazolidin-2-one* (**2**). — A suspension of 2-amino-2-deoxy-D-glucose hydrochloride (1 g, 4.7 mmol) and silver cyanate (0.8 g, 5.3 mmol) in water (8 mL) was kept at ~45° until the chloride test was negative, then filtered, and concentrated to dryness. To a solution of the residue in methanol was added ethanol to incipient turbidity. The mixture was stored at 0° for 3 days, to give **2** (0.63 g, 70%), m.p. 156–158° (from methanol), $[\alpha]_D$ −70° (*c* 1, water); ν_{max} 3600–3000 (NH,OH), 1690 and 1660 cm^{-1} (urea).

Anal. Calc. for $C_7H_{12}N_2O_5$: C, 41.17; H, 5.92; N, 13.72. Found: C, 41.22; H, 6.01; N, 13.78.

Conventional treatment of **2** with pyridine–acetic anhydride gave the triacetate **3** (31%), m.p. 166–168° (from aqueous 96% ethanol), $[\alpha]_D$ +22° (*c* 1, chloroform); ν_{max} 3500–3000 (NH), 1750, 1740 and 1710 (ester), 1765 and 1665 cm^{-1} (urea).

Anal. Calc. for $C_{13}H_{18}N_2O_8$: C, 47.27; H, 5.49; N, 8.48. Found: C, 46.95; H, 5.20; N, 8.19.

*1,2-Dideoxy-α-*D-glycero-L-gluco-*heptofurano[1,2-*d]*imidazolidin-2-one* (**4**). — Treatment of 2-amino-2-deoxy-D-*glycero*-L-*gluco*-heptose hydrochloride (1 g, 4 mmol) and silver cyanate (0.7 g, 4.6 mmol), as described for **2**, gave **4** (0.37 g, 40%), m.p. 182–184° (from methanol–water), $[\alpha]_D$ +52° (*c* 1, water); ν_{max} 3600–3000 (NH,OH), 1690 and 1660 cm^{-1} (urea).

Anal. Calc. for $C_8H_{14}N_2O_6$: C, 41.02; H, 6.02; N, 11.96. Found: C, 41.02; H, 6.08; N, 11.94.

The tetra-acetate (**5**) of **4** had m.p. 168–170° (from ethanol), $[\alpha]_D$ +28° (*c* 1, chloroform); ν_{max} 3500–3000 (NH), 1740 and 1720 (ester), 1690 and 1670 cm^{-1} (urea).

Anal. Calc. for $C_6H_{22}N_2O_{10}$: C, 47.76; H, 5.51; N, 6.96. Found: C, 47.52; H, 5.20; N, 6.81.

*3-Ethyl-(1,2-dideoxy-β-*D-glycero-L-gluco-*heptofurano)[1,2-*d]*imidazolidin-2-one* (**6**). — A suspension of the epimeric mixture of 2-deoxy-2-ethylamino-D-*glycero*-L-*gluco*- and -D-*glycero*-L-*manno*-heptose hydrochloride (3.4 g, 12.4 mmol) and silver cyanate in water (20 mL) was processed as for **2**, to yield a 3:2 mixture (^{1}H-n.m.r. data) of **6** and the α-D-*glycero*-L-*manno* isomer. Crystallisation of this amorphous mixture from methanol–ethanol gave **6** (2 g, 55%), m.p. 157–159°, $[\alpha]_D$ +74° (*c* 1, water); ν_{max} 3600–3100 (NH,OH), 1670 and 1650 cm^{-1} (urea).

Anal. Calc. for $C_{10}H_{18}N_2O_6$: C, 45.79; H, 6.90; N, 10.68. Found: C, 45.54; H, 6.88; N, 10.76.

REFERENCES

1 H. PAULY AND E. LUDWIG, *Hoppe-Seyler's Z. Physiol. Chem.*, 121 (1922) 170–176.
2 J. A. GALBIS PEREZ, J. C. PALACIOS ALBARRAN, J. L. JIMENEZ REQUEJO, M. AVALOS GONZALEZ, AND J. M. FERNANDEZ-BOLAÑOS, *Carbohydr. Res.*, 131 (1984) 71–82, and references therein.
3 J. FUENTES MOTA, P. ARECES BRAVO, F. REBOLLEDO VICENTE, J. F. FERNANDEZ GARCIA-HIERRO, AND J. A. GALBIS PEREZ, *J. Nucleos. Nucleot.*, 3 (1984) 115–121.
4 J. A. GALBIS PEREZ, R. M. PINTO CORRALIZA, E. ROMAN GALAN, AND M. GOMEZ GUILLEN, *An. Quím.*, 75 (1979) 387–391.
5 J. A. GALBIS PEREZ, J. L. JIMENEZ REQUEJO, J. C. PALACIOS ALBARRAN, M. AVALOS GONZALEZ, AND J. FERNANDEZ-BOLAÑOS, *An. Quím., Ser. C*, 82 (1986) 11–17.